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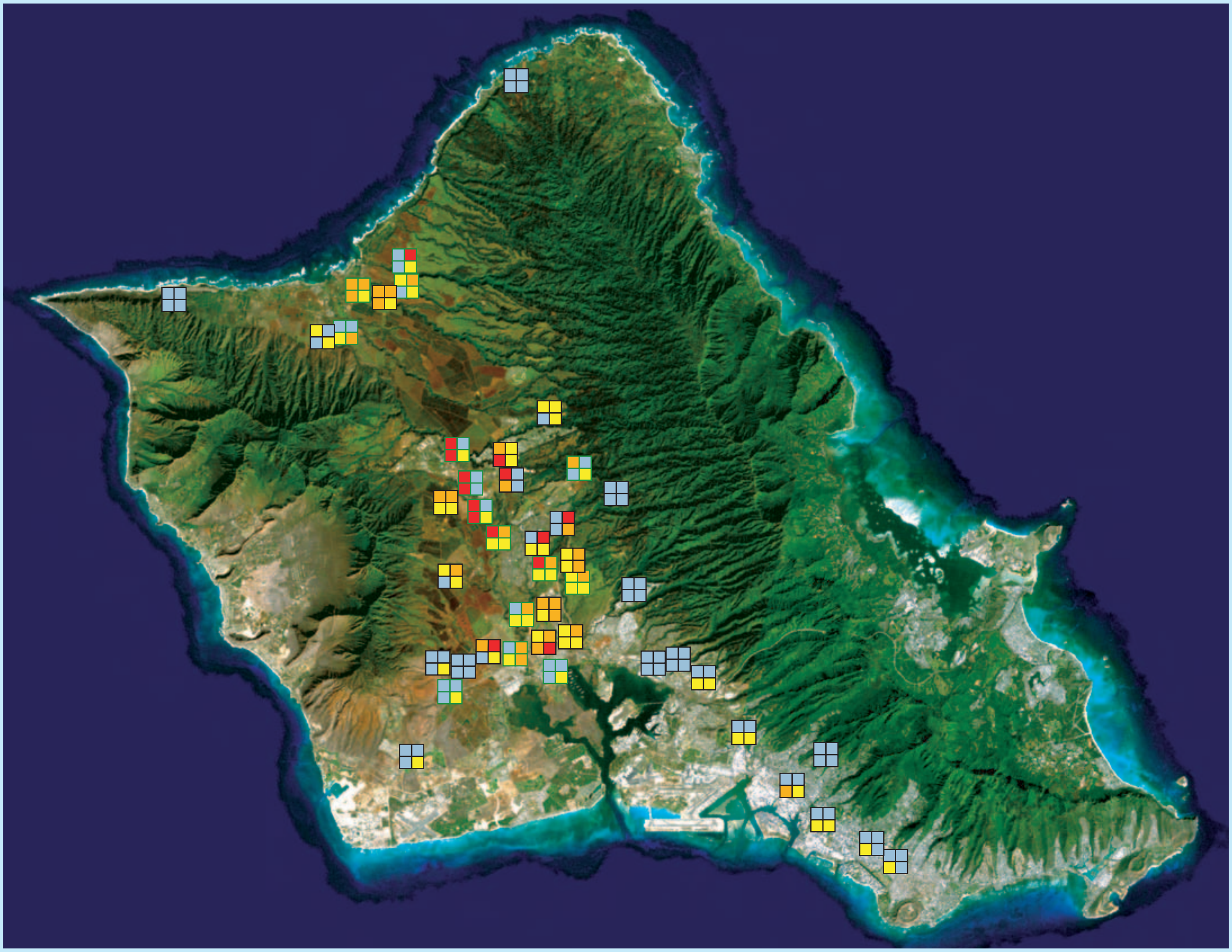
Ground-Water Quality and its Relation to Land Use on Oahu, Hawaii, 2000–01

U.S. Department of the Interior
U.S. Geological Survey

Water-Resources Investigations Report 03-4305



Distribution of volatile organic compound mixtures in ground water.

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NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

Front cover: Island of Oahu as seen by Landsat satellite (cloud-free mosaic by the Pacific Disaster Center) and showing distribution of volatile organic compound mixtures in sampled public-supply and monitoring wells, as seen in figure number 32.

Ground-Water Quality and its Relation to Land Use on Oahu, Hawaii, 2000–01

By Charles D. Hunt, Jr.

U.S. GEOLOGICAL SURVEY

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NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

Honolulu, Hawaii
2004

U.S. DEPARTMENT OF THE INTERIOR
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U.S. GEOLOGICAL SURVEY
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FOREWORD

The U.S. Geological Survey (USGS) is committed to providing the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (http://www.usgs.gov/). Information on the quality of the Nation's water resources is critical to assuring the long-term availability of water that is safe for drinking and recreation and suitable for industry, irrigation, and habitat for fish and wildlife. Population growth and increasing demands for multiple water uses make water availability, now measured in terms of quantity *and* quality, even more essential to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program in 1991 to support national, regional, and local information needs and decisions related to water-quality management and policy (http://water.usgs.gov/nawqa). Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities.

From 1991-2001, the NAWQA Program completed interdisciplinary assessments in 51 of the Nation's major river basins and aquifer systems, referred to as Study Units (http://water.usgs.gov/nawqa/studyu.html). Baseline conditions were established for comparison to future assessments, and long-term monitoring was initiated in many of the basins. During the next decade, 42 of the 51 Study Units will be reassessed so that 10 years of comparable monitoring data will be available to determine trends at many of the Nation's streams and aquifers. The next 10 years of study also will fill in critical gaps in characterizing water-quality conditions, enhance understanding of factors that affect water quality, and establish links between *sources* of contaminants, the *transport* of those contaminants through the hydrologic system, and the potential *effects* of contaminants on humans and aquatic ecosystems.

The USGS aims to disseminate credible, timely, and relevant science information to inform practical and effective water-resource management and strategies that protect and restore water quality. We hope this NAWQA publication will provide you with insights and information to meet your needs, and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

The USGS recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for cost-effective management, regulation, and conservation of our Nation's water resources. The NAWQA Program, therefore, depends on advice and information from other agencies—Federal, State, interstate, Tribal, and local—as well as nongovernmental organizations, industry, academia, and other stakeholder groups. Your assistance and suggestions are greatly appreciated.

Robert M. Hirsch

Robert M. Hirsch
Associate Director for Water

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Water-Quality Data, Provided in Excel Format

Conversion factors, abbreviations, and datums

Multiply	By	To obtain
foot (ft)	0.3048	meter
foot per mile (ft/mi)	0.1894	meter per kilometer
foot per day (ft/d)	0.3048	meter per day
square foot per day (ft^2/d)	0.09290	square meter per day
foot per day per foot (ft/d)/ft	1	meter per day per meter
cubic foot (ft^3)	0.02832	cubic meter
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
gallon (gal)	0.003785	cubic meter
gallon per day (gal/d)	3.785	liter per day
million gallons (Mgal)	3,785	cubic meter
million gallons per day (Mgal/d)	0.04381	cubic meter per second
mile (mi)	1.609	kilometer
square mile (mi^2)	2.590	square kilometer
inch (in.)	25.4	millimeter
inch per year (in/yr)	2.54	centimeter per year

Water temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by using the equation:

$$°F = 1.8 \times °C + 32$$

Abbreviations used in water-quality descriptions:

kg, kilograms
mg/L, milligrams per liter
µg/L, micrograms per liter
µS/cm, microsiemens per centimeter at 25° Celsius
pCi/L, picoCuries per liter
TU, tritium units

Datums

Vertical coordinate information is referenced relative to mean sea level.
Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Ground-Water Quality and its Relation to Land Use on Oahu, Hawaii, 2000–01

By Charles D. Hunt, Jr.

ABSTRACT

Water quality in the main drinking-water source aquifers of Oahu was assessed by a one-time sampling of untreated ground water from 30 public-supply wells and 15 monitoring wells. The 384 square-mile study area, which includes urban Honolulu and large tracts of forested, agricultural, and suburban residential lands in central Oahu, accounts for 93 percent of the island's ground-water withdrawals.

Organic compounds were detected in 73 percent of public-supply wells, but mostly at low concentrations below minimum reporting levels. Concentrations exceeded drinking-water standards in just a few cases: the solvent trichloroethene and the radionuclide radon-222 exceeded Federal standards in one public-supply well each, and the fumigants 1,2-dibromo-3-chloropropane (DBCP) and 1,2,3-trichloropropane (TCP) exceeded State standards in three public-supply wells each. Solvents, fumigants, trihalomethanes, and herbicides were prevalent (detected in more than 30 percent of samples) but gasoline components and insecticides were detected in few wells. Most water samples contained complex mixtures of organic compounds: multiple solvents, fumigants, or herbicides, and in some cases compounds from two or all three of these classes.

Characteristic suites of chemicals were associated with particular land uses and geographic locales. Solvents were associated with central Oahu urban-military lands whereas fumigants, herbicides, and fertilizer nutrients were associated with central Oahu agricultural lands. Somewhat unexpectedly, little contamination was detected in Honolulu where urban density is highest, most likely as a consequence of sound land-use planning, favorable aquifer structure, and less intensive application of chemicals (or of less mobile chemicals) over recharge zones in comparison to agricultural areas.

For the most part, organic and nutrient contamination appear to reflect decades-old releases and former land use. Most ground-water ages were decades old, with recharge dates ranging from pre-1940 to the present, and with most dates falling within the 1950s to 1980s time span. Several widely detected compounds were discontinued as long ago as the 1970s but have yet to be flushed from the ground-water system. Although large tracts of land in central Oahu have been converted from agriculture to residential urban use since the 1950s, water quality in the converted areas still more closely reflects the former agricultural land. It appears to be too early to detect a distinct water-quality signature characteristic of the newer urban use, although several urban turfgrass herbicides in use for just 10 years or so were detected in monitoring wells and may represent early arrivals of urban contaminants at the water table.

INTRODUCTION

The USGS National Water-Quality Assessment (NAWQA) is designed to assess the status of and trends in the quality of the Nation's water resources and to develop an understanding of the natural and human factors that affect water quality. A key element of the program is the application of standardized methods that allow valid comparisons of results from various NAWQA Study Units located around the United States.

In Hawaii, NAWQA efforts are represented by the Oahu Study Unit. Coordinated studies of streams (surface water), stream ecology, and ground water on the island of Oahu were begun in 1997. The studies seek to describe the occurrence and distribution of inorganic elements, nutrients, organic compounds, radionuclides, and species abundance in Oahu's streams or ground water. Ground water is especially important on Oahu because it is the primary source of fresh drinking water. Even minute quantities of certain contaminants can render ground water unsuitable for drinking and require costly water treatment for purification.

A fundamental tenet of the NAWQA program is that chemical measures of water quality are commonly closely tied to surrounding land use, which largely governs the types and amounts of point and nonpoint chemical releases to the environment. Of particular local interest is an ongoing change in land use that is taking place in much of the Oahu Study Unit. It entails replacement of former large-scale sugarcane plantations that were stable through the 1950s with urban development and diversified-crop agriculture. Oahu NAWQA studies seek to discern the effect of these land-use changes on water quality and stream ecology.

Objectives of the Oahu NAWQA Ground-Water Study

Investigations by the various NAWQA Study Units are intended to contribute to the nationwide water-quality assessment as well as to provide water-quality information that is relevant to the local community in formulating land- and water-related policies. The Oahu ground-water study was designed to meet the following objectives:

(1) Describe the occurrence and distribution of inorganic elements and organic compounds in Oahu ground water.

(2) Evaluate relationships between ground-water quality and land use.

(3) Determine whether land-use changes have caused changes in ground-water quality.

(4) Describe how the chemical composition of ground water is influenced by flow-system factors such as depth below the water table, proximity to recharge areas, and presence or absence of confining units.

A principal objective of the NAWQA program is to assess the quality of drinking-water resources. This role complements Federal and State programs that administer drinking-water regulations and testing at the tap but does not duplicate those efforts. NAWQA ground-water studies sample ambient ground water within the aquifer, either directly from the open interval of a well using a downhole sampling pump or from the well head in the case of a high-capacity supply well. Samples are collected prior to any water treatment or conditioning that may be applied to make the water suitable for distribution and consumption. Although the aquifer may provide source water for drinking, NAWQA samples are not identical to samples of "finished" water taken at the tap for drinking-water compliance monitoring.

NAWQA ground-water studies have ecological relevance where ground water discharges to streams, lakes, or marine waters. Ground water can carry excess nutrients that promote nuisance plant or algal growth (eutrophication), and can carry other chemical loads that may affect the health of stream biota. Ground water also may have beneficial effects, for example by supplying a base component of flow that keeps a stream from going dry or by ensuring a steadier stream temperature.

Results of NAWQA studies can be used by policy makers to evaluate whether existing zoning, land-use, chemical-handling, and crop-management practices adequately protect ground water and surface water. An important limitation is that most NAWQA studies are "occurrence and distribution" studies, and results can be used to make only the most general inferences regarding specific sources and pathways of chemicals unless these aspects were specific elements of a particular study. Many chemicals have multiple uses, and there may be several potential sources of a given chemical within a Study Unit.

Study Area and Land Use

The study area for Oahu NAWQA ground-water investigations encompasses 384 mi^2 of central Oahu between the Waianae and Koolau mountain ranges (figs. 1 and 2). The study area coincides with the central Oahu ground-water flow system as defined in Hunt (1996). It includes the bulk of ground-water development on Oahu, having accounted for 93 percent of Oahu pumpage in the decade 1971–80, or 336 Mgal/d (Nichols and others, 1996).

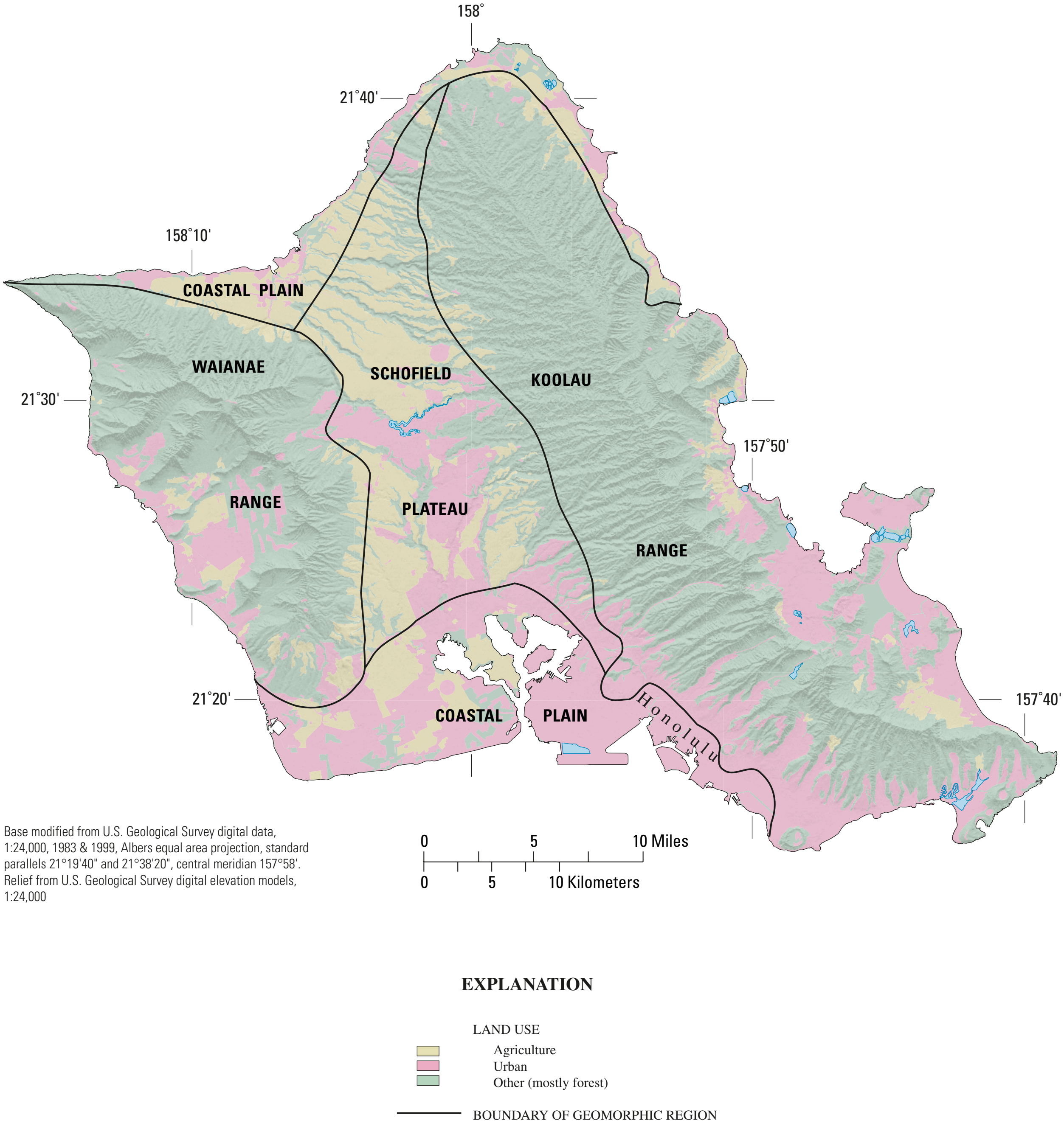

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Figure 1. Geomorphic provinces and land use, Oahu, Hawaii (modified from Visher and Mink, 1964; Klasner and Mikami, 2003).

Land use was mapped as part of the Oahu NAWQA study (Klasner and Mikami, 2003) and portrays conditions in about 1998. Only the broadest categories of land use are shown here (fig. 1): urban, agriculture, and "other" (which is mostly forested and referred to simply as "forested"). Superimposed on the present land-use classification are several additional use categories that may have affected water quality (fig. 2):

1. United States military installations (fig. 2A).
2. former pineapple fields (fig. 2B); and
3. present and former sugarcane fields (fig. 2C).

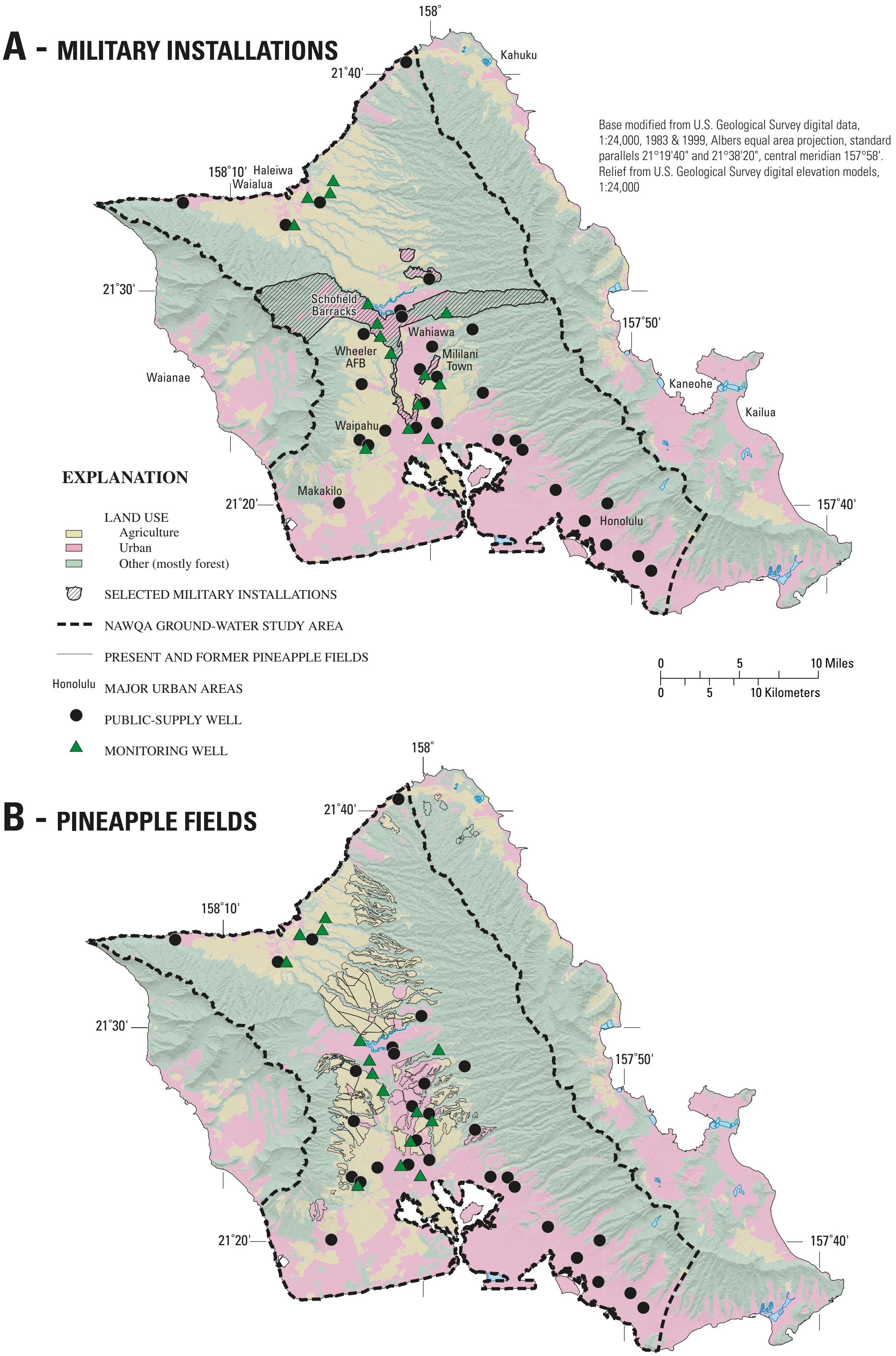

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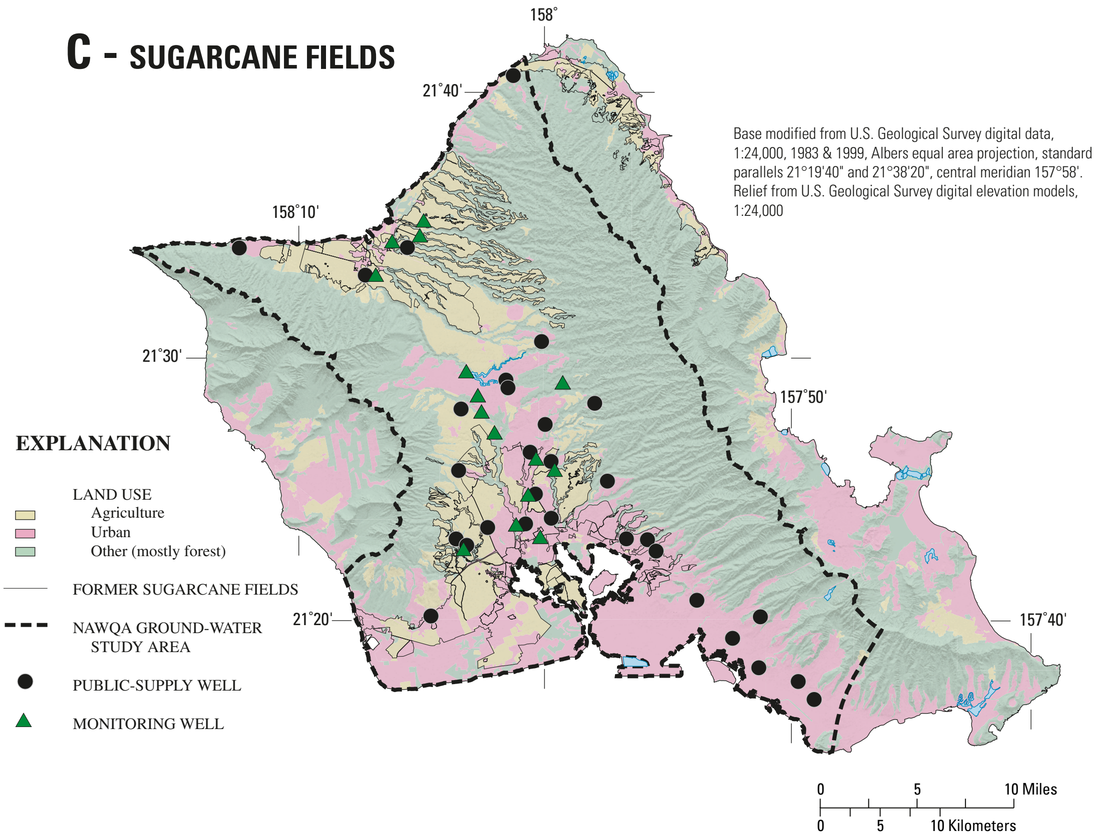
Figure 2. NAWQA ground-water study area, land use, and sampled wells, Oahu, Hawaii: (A) military installations; (B) present and former pineapple fields; (C) former sugarcane fields; (D) land converted from agricultural to urban use, 1950–2000, and mean annual rainfall. Land use is from about 1998 and is modified from Klasner and Mikami (2003). Pineapple and sugarcane fields are modified from Oki and Brasher (2003). Rainfall is from Giambelluca and others (1986).

C - SUGARCANE FIELDS



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D - RAINFALL AND RECENT URBANIZATION

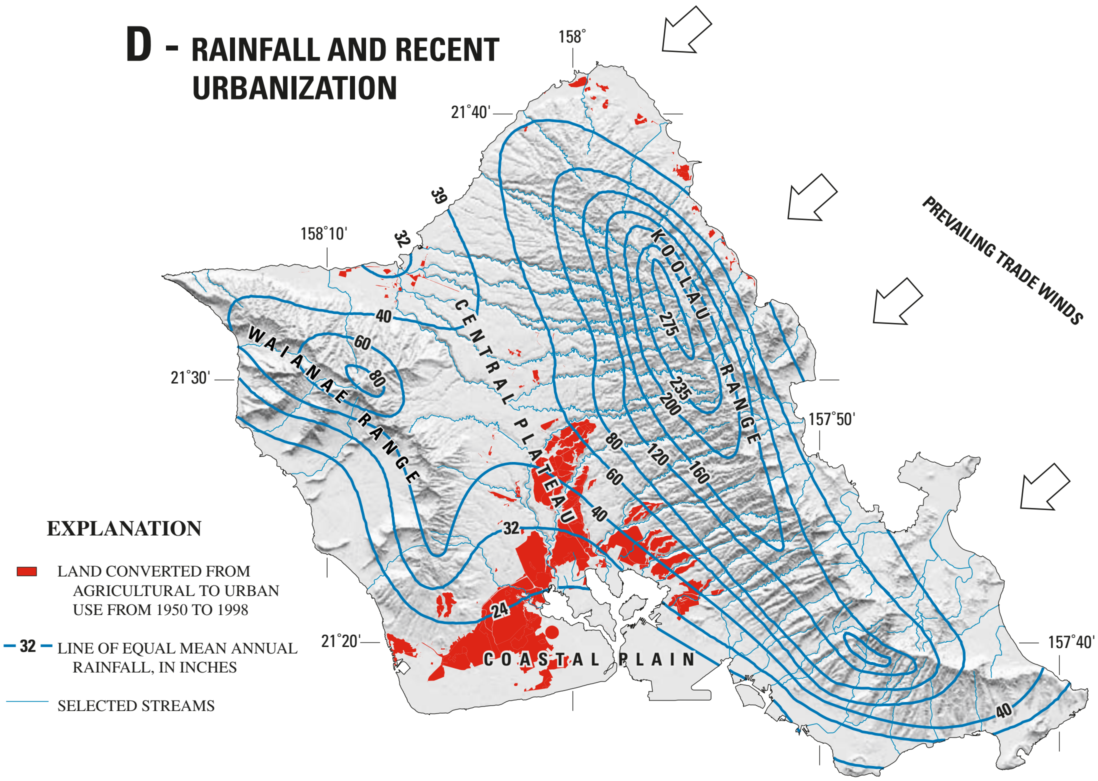


Figure 2. NAWQA ground-water study area, land use, and sampled wells, Oahu, Hawaii: (A) military installations; (B) present and former pineapple fields; (C) former sugarcane fields; (D) land converted from agricultural to urban use, 1950–2000, and mean annual rainfall. Land use is from about 1998 and is modified from Klasner and Mikami (2003). Pineapple and sugarcane fields are modified from Oki and Brasher (2003). Rainfall is from Giambelluca and others (1986).--*Continued*

The pineapple and sugarcane boundaries encompass areas used for those purposes at any time during the period 1940–2000 (modified from Oki and Brasher, 2003).

The southeastern part of the study area is occupied by the city of Honolulu. The western part of the study area includes large tracts of agricultural land that cover much of central Oahu. Urbanization has increasingly expanded from the Honolulu urban core to occupy former agricultural lands in central Oahu. The largest change has been in the southern part of central Oahu (fig. 2D), where suburban residential development has supplanted former agricultural land, mostly since the 1960s. In contrast, northern Oahu has remained largely in agriculture. Conversion to urban use accelerated in the 1980s as sugarcane cultivation was reduced and ultimately abandoned in the mid-1990s. Former sugarcane fields not converted to urban use are presently used for pineapple, diversified-crop agriculture, or are fallow. Pineapple is still cultivated widely on Oahu, although some former pineapple land has been converted to urban use. Areas of military installations have been mostly stable since the mid-1900s World War II era.

Chemical Use and Application

Past use of agricultural and industrial chemicals in the study area has provided opportunities for subsequent migration of chemicals to ground water. Some chemicals were released as nonpoint-source agricultural applications of fertilizers, soil fumigants, and pesticides. Other chemicals such as fuels and solvents likely were released as point-source spills or leaks. Recent decades have brought much greater awareness of the need for proper handling and disposal, whereas in the mid-1900s it was a more common practice to dispose fuels, solvents, and other chemicals on the ground or into drains and sumps that leached to the ground. The use and application of pesticides on Oahu has been summarized as part of the Oahu NAWQA study by Oki and Brasher (2003).

Fuels and solvents have been used intensively by the United States military dating back to at least the 1940s. Solvent compounds also are in many household and industrial products in the civilian urban environment, for example degreasers, paint thinners, and paint strippers. Gas stations, automotive repair shops, and dry cleaners—all sources of fuels or solvents—are scattered throughout the urban environment. Petroleum refining has been restricted to the southwest coast of Oahu but several large fuel-storage facilities over inland recharge areas have been operated by the military in the mid-1900s.

Fertilizers and pesticides have been applied widely for agriculture in central Oahu, with fertilizer use dating back to 1900 or earlier and pesticide use dating back to the 1950s. A study of pesticide use for 1977 (Takahashi, 1982) cited the following Statewide totals:

4,200,000 kg of pesticides, consisting of:

2,000,000 kg of nematicide fumigants (48 percent);

1,300,000 kg of herbicides (32 percent);

238,000 kg of insecticides (6 percent);

119,000 kg of fungicides (3 percent); and

449,000 kg of wood preservatives (11 percent).

Agricultural use accounted for the largest share of 1977 pesticide use: 82 percent of pesticides overall, 100 percent of nematicide fumigants, 92 percent of herbicides, and 32 percent of insecticides. Nematicide fumigants (the largest pesticide class) were applied in pineapple cultivation since the 1940s to control nematode rootworms. Herbicides have been applied variously, but most heavily on sugarcane (72 percent sugarcane, 15 percent diversified agriculture, 7 percent government, 5 percent pineapple, and 1 percent home and garden; all 1977 figures from Takahashi, 1982). Herbicide use on Hawaiian sugarcane and pineapple crops has been particularly intensive, with annual application rates as much as five times those of major temperate-region field crops (Green and others, 1977). In addition to nonpoint application of agricultural chemicals, point-source releases may also have occurred at pesticide mixing and storage sites or at disposal sites.

Urban insecticide application in 1977 was 68 percent greater than that for agriculture. Most insecticides applied were termiticides that are hydrophobic and have limited leaching potential. Urban herbicide use (weed and brush control by Federal and local governments, utilities, and commercial and residential property owners) tends to rely more on post-emergence herbicides having much less leaching potential than the pre-emergence herbicides used for agriculture. Fertilizers have been applied in the urban environment to maintain lawns and gardens, although treated acreage is less than in agricultural areas because large percentages of urban land are taken up by buildings and paved surfaces.

Previous Water-Quality Studies

Water-quality studies on Oahu progressed through several topical themes during the 20th century. Early studies dating back to the early 1900s focused on the problem of saltwater intrusion. These studies reported on salt content and other inorganic chemical elements, and were conducted mainly by the Honolulu Board of Water Supply (Wentworth, 1951 provides a comprehensive summary). The potential for introduced contaminants from agricultural and industrial applications became a focus of study in the mid-1900s. Notable reports that touched on this topic in addition to saltwater intrusion include those by Visher and Mink (1964), Swain (1973), and Takasaki (1977).

Agricultural effects on water quality were studied increasingly in the late 1900s. The topic of irrigation-return recharge received much attention, with most studies focusing on nutrients and inorganic elements (for example, Tenorio and others, 1969). The use of isotopic tracers for tracing and dating ground water was also introduced, culminating in a comprehensive report by Hufen and others (1980).

Agricultural fumigants were detected in Oahu ground water in 1980. Their presence and migration were investigated using soil sampling, laboratory analyses, and numerical simulation; notable summaries include Lau (1987) and Oki and Giambelluca (1987). The other main topic of study from about 1980 to the present involved fuels, solvents, and metals. These contaminants were investigated by the U.S. military and by owners of private facilities under the regulatory umbrella of the U.S. Environmental Protection Agency Resource Conservation and Recovery Act (USEPA/RCRA). Results of these investigations are contained in numerous reports by environmental consultants and military agencies.

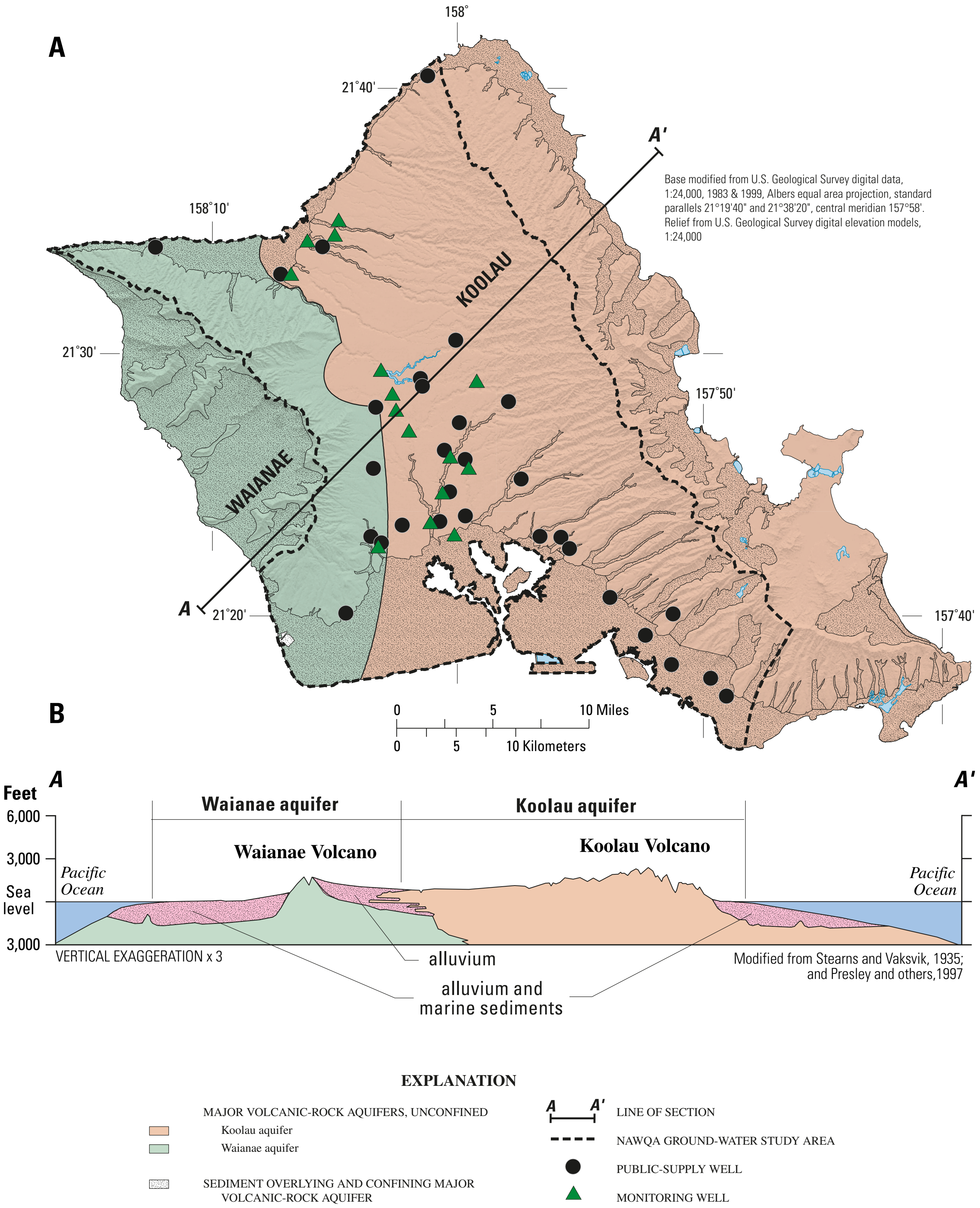
Geohydrologic Setting

The island of Oahu consists of two volcanic mountain ranges, the Waianae Range and the Koolau Range (fig. 1), an intervening saddle between the ranges called the Schofield Plateau, and lowland coastal plains underlain by sediments. The mountain ranges are the eroded remnants of two former shield volcanoes built by successive outpourings of basaltic lava flows. Subsequent weathering and erosion have left a landscape of deep valleys and steep interfluvial ridges, with gentler slopes in the central plateau, along the floors of the larger valleys, and on the coastal plain. Maximum elevations in the Waianae and Koolau mountains are 4,025 and 3,150 ft above sea level, respectively, and the top of the central plateau is at about 900 ft above sea level.

The target of sampling in this study was ground water in the volcanic-rock aquifers of central Oahu (fig. 3). The Waianae and Koolau aquifers consist of highly permeable, fractured and rubbly basaltic lavas of the Waianae Volcanics and the Koolau Basalt. The aquifers overlap in the western part of the study area (fig. 3B) to form a layered, multi-aquifer system with an intervening, leaky confining unit of clay-rich soil and saprolite (weathered rock) at the top of the Waianae Volcanics. Although most NAWQA studies restrict sampling to a single aquifer, both aquifers were included in this study because their lithologies are similar and both are sources of public drinking-water supplies.

Fresh ground-water flow through the volcanic-rock aquifers is driven by topography and rainfall (fig. 4 and fig. 2D). Rainfall is greatest in the mountains, with average annual maxima of 80 and 275 in/yr in the Waianae and Koolau Ranges, respectively (Giambelluca and others, 1986). Annual rainfall averages about 60 in/yr in the central plateau and tapers to 30 in/yr or less in the coastal lowlands. Ground water flows inward from both mountain ranges to the central plateau and then north and south to the coast. This interior drainage of ground water from the Koolau and Waianae Ranges has been termed the central Oahu ground-water flow system (Hunt, 1996). The central flow system encompassed 68 percent of natural, predevelopment recharge on Oahu (521 Mgal/d; Nichols and others, 1996), most of it originating in the wetter Koolau Range.

Ground-water levels in the volcanic-rock aquifers (fig. 5) are smoothly continuous over large areas but show abrupt changes at identifiable subsurface barriers such as volcanic dikes and weathered valley fills (Visher and Mink, 1964; Dale and Takasaki, 1976; Hunt, 1996). Ground-water levels are about 280 ft



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Modified from Stearns and Vaksvik, 1935; and Presley and others,1997

Figure 3. Waianae and Koolau volcanic-rock aquifers, Oahu, Hawaii: (A) areal extent of aquifers within depths tapped by wells (modified from Hunt, 1996); (B) aquifers in cross section (modified from Stearns and Vaksvik, 1935; Oki and others, 1997; and Presley and others, 1997). Sampled wells are shown for reference.

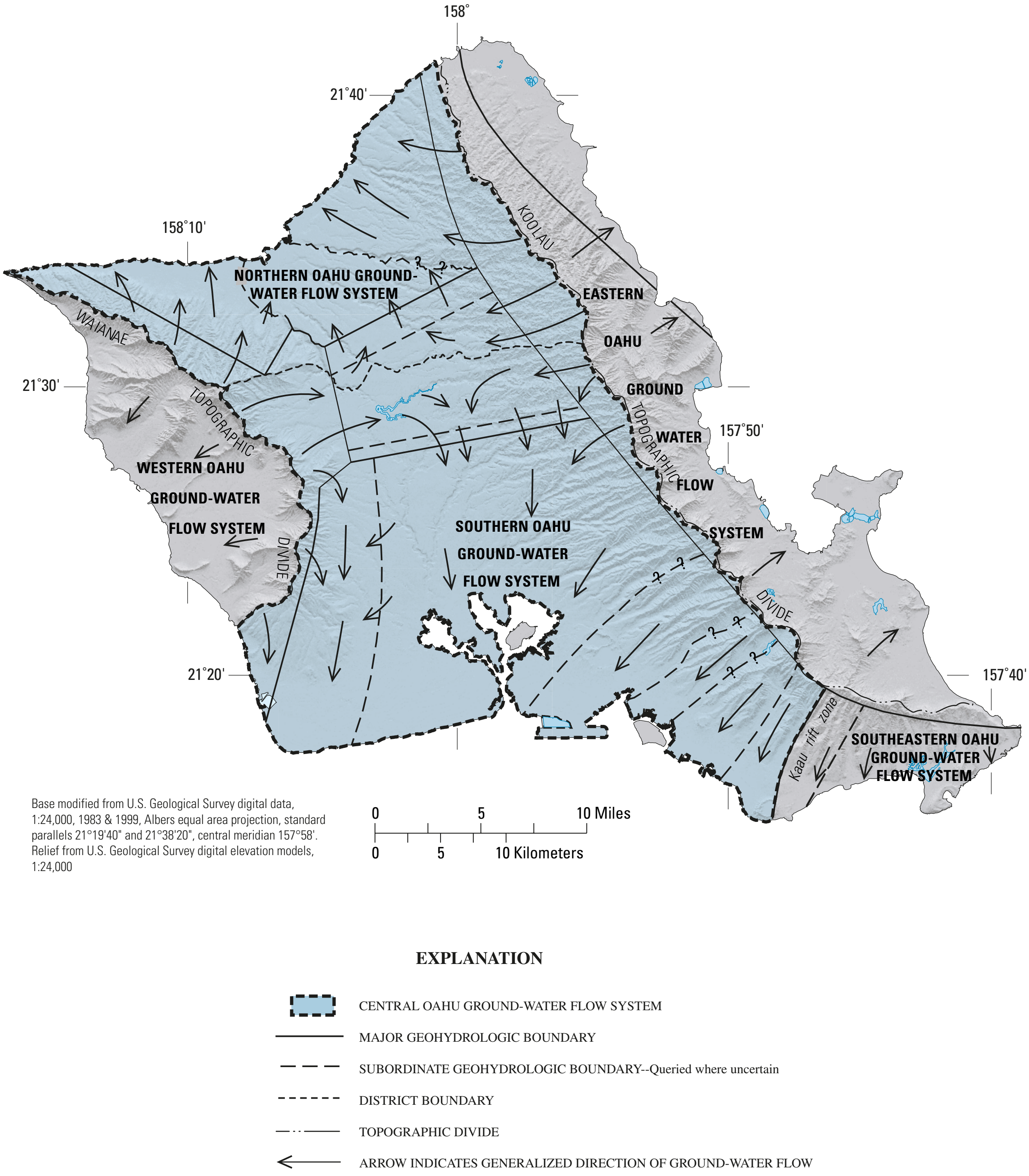

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Figure 4. Ground-water flow systems, Oahu, Hawaii (Hunt, 1996).

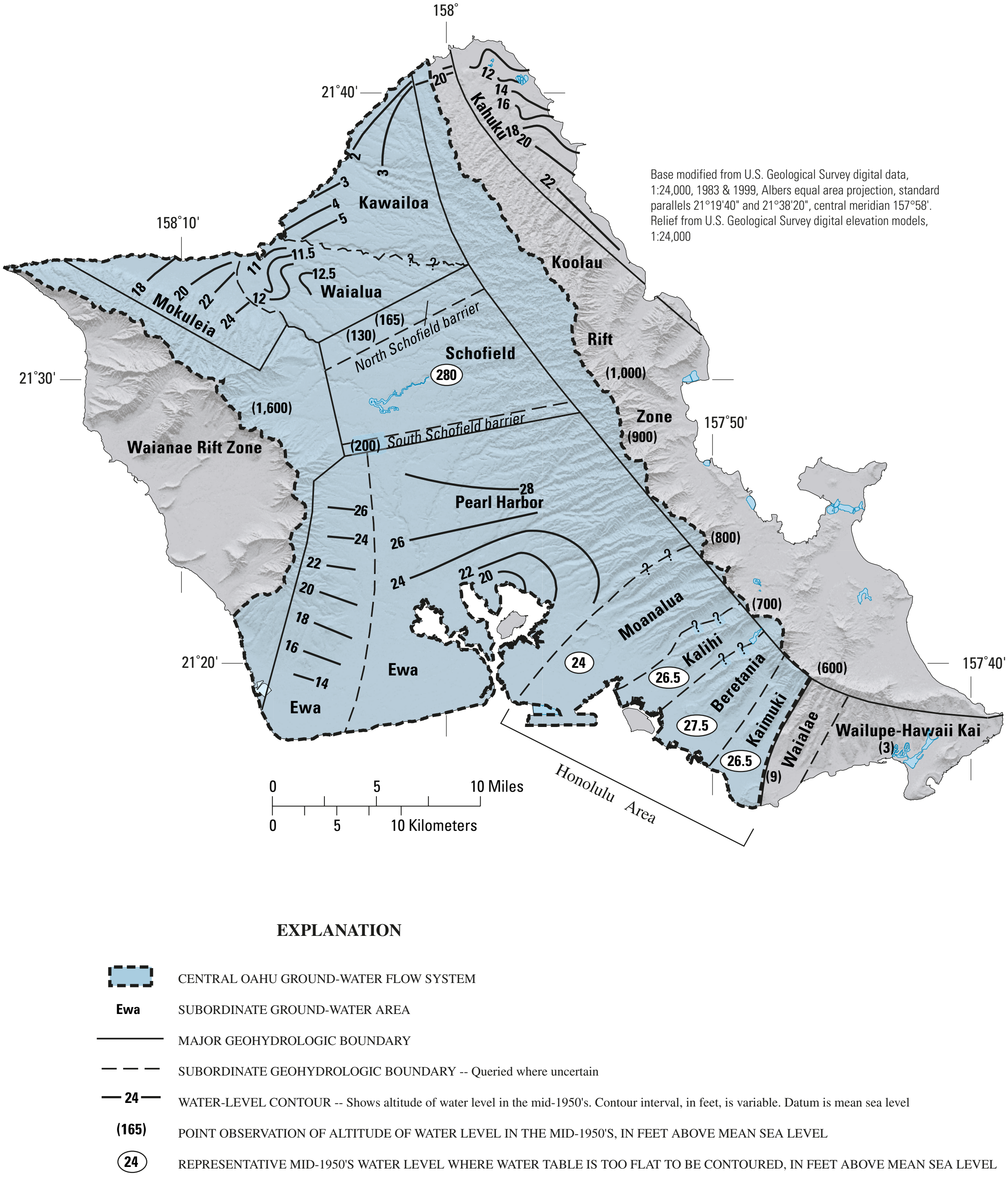

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Figure 5. Ground-water areas and potentiometric surface in the principal volcanic-rock aquifers, Oahu, Hawaii (Hunt, 1996). Ground water flows from interior mountains to the coast, generally perpendicular to potentiometric contour lines (see figure 4 for generalized flow directions).

above sea level in the central plateau and about 1,000 and 1,600 ft in the Koolau and Waianae Ranges, respectively. Ground water flows from areas of higher water level to areas of lower water level (upgradient to downgradient) and ultimately to the coast. At any point in the aquifer, ground water flowing from upgradient recharge areas is joined at the water table by recharge from land directly above. Depth to ground water from land surface ranges from zero at low elevations to as much as 2,500 ft in the mountains, with depths throughout most of the central Oahu plateau ranging from 100 to 600 ft.

The volcanic-rock aquifers are unconfined throughout most of island's interior, but are confined beneath coastal-plain sediments and larger, sediment-filled valleys such as those in the Honolulu area (fig. 3). Soil and saprolite mantle gently sloping parts of the landscape to depths that range from about 50 ft at the dry north and south ends of the central plateau to 300 ft or more in the rainy Koolau uplands (Hunt, 1996). The clay-rich saprolite is much less permeable than the unweathered basaltic lavas that form the deep aquifers. Recharging water infiltrates vertically through the soil and saprolite and then through (typically) several hundred to a few thousand feet of unsaturated, unweathered rock before reaching the deep water table. Unweathered rock is exposed in cliffs and steep valley walls, offering the opportunity to examine bed thickness and the distribution of fractures and other permeable elements in the lavas.

With regard to recharge processes and migration of surface contaminants, the Waianae and Koolau aquifers are best classified as "deep unconfined aquifers." Despite the weathered overburden and water-table depths of hundreds of feet, the volcanic-rock aquifers are as vulnerable to contamination as many shallow surficial aquifers in other settings, which are generally avoided as sources for municipal drinking-water supplies.

STUDY DESIGN AND METHODS

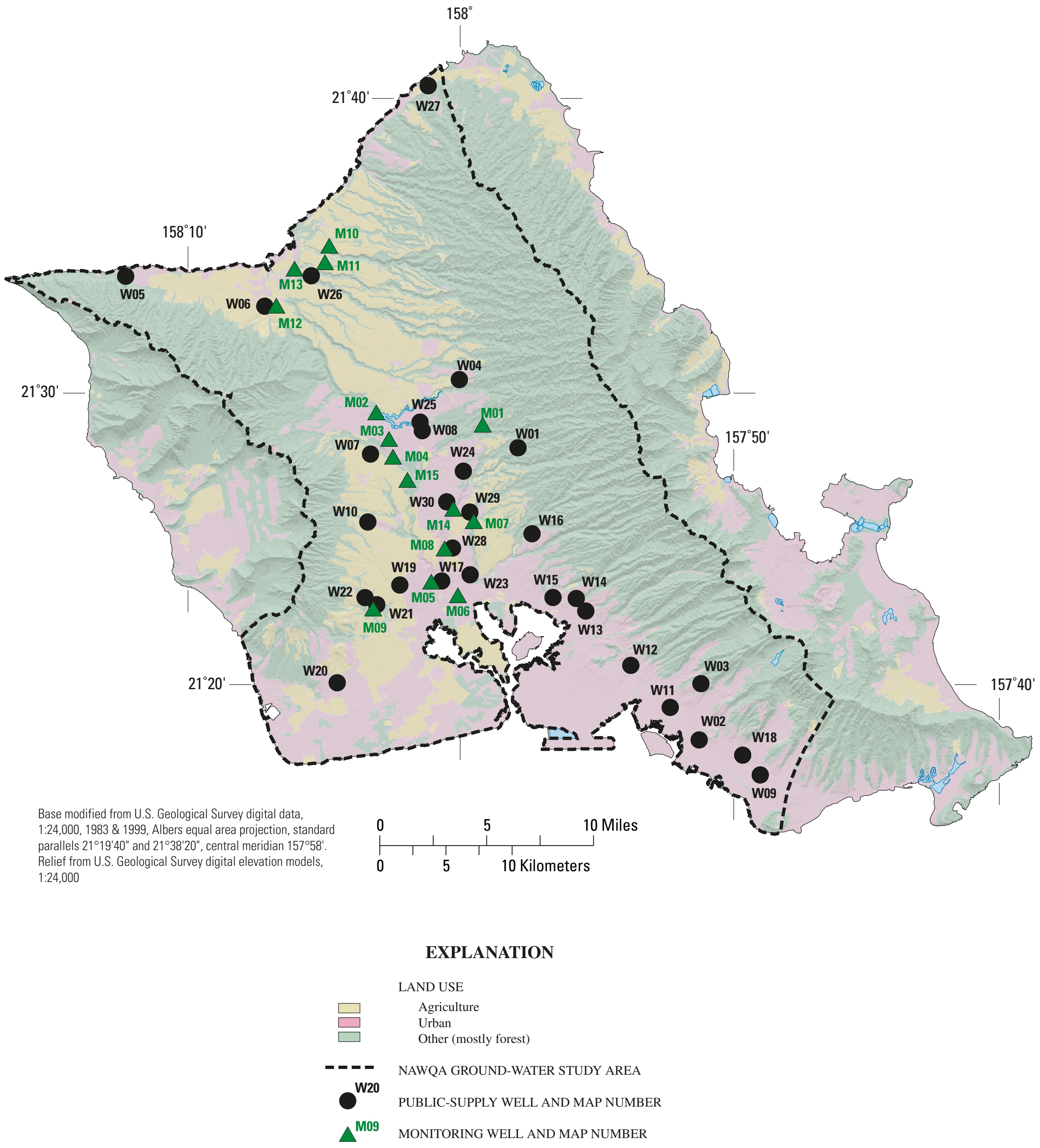
Sampling networks and laboratory methods were selected to fulfill standardized requirements of the national NAWQA program as well as local data needs. In addition to laboratory methods required nationally, several additional pesticide methods were selected for local relevance, and a custom method was used to achieve lower detection limits for two soil fumigants of longstanding interest on Oahu.

Selection of Well Networks

Two networks of wells were selected to represent conditions in the Oahu regional aquifer system (fig. 6). The first was a group of 30 public-supply wells sampled from January to July 2000. The second was a group of 15 monitoring wells sampled the following year, from April to August 2001. Because of the expense of drilling deep wells in volcanic rock, no new wells were drilled for this study; existing wells were selected for sampling instead. Depth to water from land surface ranged from –3 ft (at an artesian well) to 939 ft, with half the wells having depths to water between 89 and 591 ft.

The 30 public-supply wells comprise a "Study-Unit Survey" (Gilliom and others, 1995). Such studies employ a network of supply wells (household or public supply) to assess water quality in major aquifer systems within a study unit. Wells of a single well type (public supply) were selected at random from a list of 141 candidate wells at 53 sites, using a computerized routine by Scott (1990). The wells have pumping capacities on the order of 300 to 1,000 gal/min. By sampling a subset of public-supply wells, the Oahu Study-Unit Survey accurately assesses the drinking-water resource *as it presently is used*. However, because the wells are used to supply drinking water, they likely reflect a favorable or "clean" bias or they would be taken out of service. This favorable bias is a recognized disadvantage of studies that rely on public-supply wells (Lapham and others, 1995). In this study, however, well selection was truly random, and several wells that were out of service because of contamination were reactivated for sampling—thus lessening the clean bias and better approaching the goal of an unbiased random sampling of aquifer water quality.

Another potential source of clean bias arises from well depth. Previous studies showed that ground water in central Oahu is distinctly stratified (Visher and Mink, 1964; Tenorio and others, 1969; Hufen and others, 1980; Eyre, 1983, 1987; Voss and Wood, 1994). Water following deep flowpaths in the aquifer originated as recharge in cool, forested uplands and is older, colder, and fresher than shallower water in the aquifer. Shallower water in downgradient parts of the aquifer



Base modified from U.S. Geological Survey digital data, 1:24,000, 1983 & 1999, Albers equal area projection, standard parallels 21°19'40" and 21°38'20", central meridian 157°58'. Relief from U.S. Geological Survey digital elevation models, 1:24,000

Figure 6. Public-supply wells and monitoring wells sampled for the NAWQA study, Oahu, Hawaii, 2000–2001.

contains young irrigation-return recharge with elevated concentrations of inorganic elements, nutrients, and organic compounds. Some public-supply wells have been protectively solid-cased through this irrigation-return layer for about the first 75 to 150 ft below the water table and are open only below that. Because of this design, they draw deeper water or mixtures of deep and shallow water. Recognizing this possible depth bias, a supplemental network of 15 monitoring wells was selected as a "Special Study" aimed at sampling shallower, younger ground water that is closed off from some of the public-supply wells (most monitoring wells are open at, or just beneath, the water table). The monitoring wells supplement the public-supply wells to give a more complete picture of water-quality in the aquifer. They also provide an early warning for contaminants that have recently arrived at the water table and are on their way deeper into the flow system. Although some of the selected monitoring wells originally were installed to investigate point-source contamination, only upgradient or "far-field" wells were selected so that results reflect regional water quality and not that of the point sources. Unlike the random selection of the public-supply wells, the monitoring wells were selected arbitrarily, from a much smaller candidate list.

Sampling and Analytical Methods

Wells were sampled according to standard water-quality protocols of the U.S. Geological Survey (Koterba and others, 1995; U.S. Geological Survey, 1997). These protocols entail "clean-environment" sampling achieved by collecting and preserving water samples within a portable collection chamber (a transparent polyethylene bag stretched over a plastic pipe frame that approximates a portable "glove-box"). Powder-free vinyl gloves were worn at all sensitive stages of sample and container handling, and gloves were changed several times in the sampling process as instructed by protocols. Sampling took place inside a mobile laboratory van, providing additional shelter from wind and dust. Water was delivered from the well head to the van by Teflon tubing so that water was not exposed to the atmosphere until inside the collection chamber. A second sampling stream was diverted from the well head to an independent sampling apparatus where trace-gas samples were collected under a nitrogen atmosphere, again without air contact. Prior to sampling, physical water-quality characteristics (temperature, pH, dissolved oxygen, specific conductance) were measured during a 30 to 60 minute well-purging period to ensure that a representative sample of aquifer water was being withdrawn from the well under stable geochemical conditions. Following sampling, all tubing and accessory equipment was cleaned according to protocols and placed in sealed plastic bags and containers in preparation for the next well.

Public-supply wells typically had high-capacities (300 to 1,200 gal/min); most had line-shaft turbine pumps, a few had submersible pumps, and a few were sampled under positive artesian pressure. Supply wells were sampled by connecting Teflon tubing to a garden-hose valve using a throw-away Teflon adapter. A few monitoring wells had low-capacity pumps (5 to 25 gal/min) and were sampled in similar fashion. Monitoring wells without installed pumps were sampled using a portable downhole, positive-displacement sampling pump operating at a maximum pumping rate of about 2 gal/min. At all wells, the actual flow rate in the sample-collection chamber was restricted by valve to about 0.5 L/min.

Upon completion of sampling, ultrapure preservatives were added as necessary and samples were placed on ice and shipped via overnight courier to the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado. Samples were analyzed at NWQL using certified, quality-assured methods. A limited number of field quality-assurance (QA) samples (blanks, replicates, and spiked replicates) also were collected and analyzed. The QA results indicated only one systematic problem, the presence of toluene at low concentrations in equipment blanks run on the portable downhole sampling pump. Based on these results, toluene detections for several monitoring wells sampled by that pump were disregarded (not considered to be true detections in the environmental sample).

Laboratory methods used to analyze ground-water samples are listed in table 1. The methods include the analysis of 283 organic compounds and 55 inorganic constituents. Most analyses were conducted at the NWQL or at USGS laboratories in Reston, Virginia. Tritium and helium isotopes were analyzed at Lamont-Doherty Earth Observatory at Columbia University, New York, under contract with USGS NWQL.

Three methods were in provisional or custom status during the sampling and analysis period: two

Table 1. Laboratory methods used to analyze ground-water samples, Oahu, Hawaii, 2000–2001

[Drinking-water wells were sampled January-July 2000; monitoring wells were sampled April-August 2001; method numbers are those of the U.S. Geological Survey National Water Quality Laboratory (NWQL); Reston lab, analyzed at USGS laboratory in Reston, Virginia; EDB, 1,2-Dibromoethane; DBCP, 1,2-Dibromo-3-chloropropane; CFC, chlorofluorocarbon; SF_6, sulfur hexafluoride; methods 9002 and 9060 were in provisional status until June 2001, when they were officially approved; "permanent" gases are nitrogen, argon, oxygen, carbon dioxide, and methane]

Category	USGS method	Drinking-water wells	Monitoring wells	Remarks
INORGANICS				
Major ions	2750	Yes	Yes	--
Nutrients	2752	Yes	Yes	--
Trace elements	2710	Yes	Yes	--
ORGANICS				
Volatile organic compounds (VOCs)	2020	Yes	Yes	--
Dissolved organic carbon (DOC)	2612	Yes	Yes	--
EDB/DBCP, custom low-level	8134	Yes	Yes	Custom
Pesticides:				
Pesticides	2001	Yes	Yes	--
Moderate use pesticides and degradates	9002/2002	Yes	Yes	Provisional
Polar pesticides and metabolites	9060/2060	Yes	Yes	Provisional
Organochlorine pesticides	1324	Yes	No	--
RADIONUCLIDES				
Radium-226, -228	1262	Yes	No	--
Radon-222	1369	Yes	No	--
ENVIRONMENTAL TRACERS AND DATING				
CFC dating, deuterium/oxygen isotopes	1173	Yes	Yes	--
SF_6 dating	Reston lab	No	Yes	--
Dissolved permanent gases	Reston lab	Yes	Yes	--
Helium isotopes for tritium/helium dating	1033	Yes	Yes	--
Tritium isotope for tritium/helium dating	2112	Yes	Yes	--
Unsaturated-zone air:				
CFC dating	Reston lab	No	Yes	--
SF_6 dating	Reston lab	No	Yes	--
Permanent gases in air	Reston lab	No	Yes	--

pesticide methods under development (9002 and 9060) and later approved as official NWQL methods 2002 and 2060; and a custom method (8134) for low-level detection of the soil fumigants EDB and DBCP (1,2-dibromoethane and 1,2-dibromo-3-chloropropane).

Method 9002/2002 analyzes moderate-use pesticides and degradates by gas chromatography/mass spectrometry (GC/MS) and is described in Sandstrom and others (2001). Method 9060/2060 analyzes polar pesticides and metabolites by high-performance liquid chromatography/mass spectrometry (HPLC/MS) and is described in Furlong and others (2001). Both methods were approved in June 2001. All drinking-well samples and the first one-third of monitoring-well samples were analyzed while the methods were still in provisional status.

Custom method 8134 for low-level EDB and DBCP uses gas chromatography/mass spectrometry (GC/MS) as described in Connor and others (1998) with the exception of operating the mass spectrometer in the selected ion monitoring (SIM) mode to increase sensitivity. Aside from the SIM modification, it is identical to method 2020 for volatile organic compounds (VOCs).

Several trace atmospheric gases were employed as water tracers to estimate the age of ground water. Chlorofluorocarbons (CFCs) are anthropogenic compounds that have been released to the atmosphere over decades as a result of their use as refrigerants, propellants, solvents, and foam-blowing agents. Sulfur hexafluoride (SF_6) is manufactured for use in electrical components but also has natural sources in volcanic fluids and fluid inclusions in rocks (Busenberg and Plummer, 1997). Both dating methods work by comparing concentrations in a water sample with atmospheric concentration histories after accounting for how much of the gases would have dissolved from air into water (Plummer and Busenberg, 1999; Busenberg and Plummer, 2000). The analytical methods are extremely sensitive and measure trace concentrations several orders of magnitude lower than reporting levels for other organic-compound methods used in this study.

Results of Laboratory Analyses

Analytical results from Oahu NAWQA ground-water studies are presented in several forms:

1. Condensed summaries of results are included here to aid interpretation of the data (tables D1 and D2 in the “Water-Quality Data” section at the end of this report).

2. Complete results for approved methods, including reporting levels for all constituents, are available on the internet from the USGS Hawaii District website at URL: http://hi.water.usgs.gov/nawqa/gw.html

3. Complete results for provisional and custom methods are included here as the initial public release of these data (tables D3–D5 in the “Water-Quality Data” section at the end of this report). USGS policy requires that provisional data be publicly released in a published report that contains descriptions of the laboratory methods. Provisional data include results of pesticide methods 9002 and 9060, and custom method 8134 for low-level detection of EDB and DBCP (1,2-dibromoethane and 1,2-dibromo-3-chloropropane).

Tables D1 and D2 are condensed summaries of analytical results for the ground-water samples. These tables show only a subset of all results: only those organic compounds that were detected are listed, and non-detections are shown as blank entries instead of “less than” values (for example <.05, where the value is the minimum reporting level for the constituent). The “blank-entries” format has the advantage of making detections easily discernible in the tables.

Values preceded by the letter “E” are estimated values that are outside the calibration limits of the laboratory methods. Typically, these values are lower than the minimum reporting level of the method. In these cases the constituent is known to be present (confirmed by mass spectrometer, for example) but the exact concentration is known with less certainty than concentrations within the calibration range (Childress and others, 1999). Similarly, table entries of “M” signify that the constituent is present but the concentration is so low that no quantification can be reported with confidence. In these cases, the estimated concentration would round to zero if rounded to the same precision as the reporting level; typically, the estimated concentration is lower than the reporting level by an order of magnitude or more.

Wells are listed sequentially in table D2, whereas in table D1 they are grouped by land use and geographic locale because these factors largely determine patterns of use and release of chemicals to the environment. Group selection was not wholly objective: measurements of present and former land use were combined with subjective consideration of upgradient land use and even of the results themselves. However, the groups do make clusters of related compounds evident, as well as associations of particular compounds with particular land uses. For example, solvent compounds are associated with urban-military lands in central Oahu, and fumigant and herbicide compounds are associated with agricultural land use.

Constituents are grouped into classes on the basis of chemical properties and predominant uses as defined by the NAWQA program at the national level. Organic compounds are divided into two main categories, volatile organic compounds (VOCs) and pesticides. Pesticides are subdivided into herbicides and insecticides.

Subdivision of VOCs is somewhat problematic, however, because many of these compounds have multiple uses or are components in various end products. They can also arise as intermediates or byproducts during organic synthesis of other VOC compounds or pesticides. Actual use in a given study area can also complicate matters. For example, fumigants are classified as VOCs on the basis of their chemical composition. They are used in many locales to fumigate already harvested crops in warehouses, but on Oahu they are used fundamentally as pesticides, to kill rootworms via soil fumigation. Another class of VOCs, the trihalomethanes, are commonly viewed as disinfection byproducts because they are known to form when water is chlorinated. But they also are produced as solvents or during organic synthesis, and they have natural sources in soil and the marine environment. Regardless of the classification scheme, an important principle is that some organic compounds have multiple uses in the study area, and so the probable origin or source of detections in ground water may be unavoidably ambiguous.

The CFC (chlorofluorocarbon) and SF_6 (sulfur hexafluoride) methods were used to estimate water age or recharge date. They also provided another useful piece of information in this study: the identification of "excess" CFCs or SF_6 in some samples (tables D1 and D2). "Excess" in this context means "at concentrations greater than possible by dissolution from the atmosphere (air-water equilibrium)." Excess amounts of these trace gases are of interest in that they indicate CFC or SF_6 contamination that may have originated with other VOC or pesticide contamination, or may have followed similar environmental pathways as other compounds.

FINDINGS AND INTERPRETATIONS

Most Wells Contained Low Concentrations of Organic Compounds

Organic compounds were detected in most water samples, although compound concentrations were generally low. Out of 283 organic compounds analyzed (85 VOCs, 197 pesticides, and caffeine) 43 compounds were detected (26 VOCs, 16 pesticides, and caffeine).

Organic compounds were detected in 73 percent of public-supply wells and 100 percent of monitoring wells (table 2 and figs. 7 and 8). Supply-well detection rates for VOCs and pesticides were identical, at 63 percent. Detection rates for VOC subclasses in supply wells were: solvents and fumigants, both 40 percent; refrigerants, zero; excess CFCs and trihalomethanes, both 47 percent; and gasoline components, 13 percent. Supply-well detection rates for pesticide subclasses were 57 percent for herbicides and 13 percent for insecticides. Detection rates were higher in monitoring wells than in supply wells for all classes of organic compounds except gasoline components and insecticides (fig. 8).

Detection rates for refrigerants shown in figures 7 and 8 are from VOC method 2020 (table 1). Refrigerants were actually detected in 97 percent of supply wells and 100 percent of monitoring wells (table 2) using method 1173, which estimates ground-water age by measuring CFCs that have dissolved from the atmosphere. These high detection rates are not shown in figures 7 and 8, however, because method 1173 is ultrasensitive and not readily comparable to the other methods reported here (its minimum reporting levels are several orders of magnitude lower). What is shown in figures 7 and 8 from method 1173 are detection rates of "excess CFCs." Excess CFCs are refrigerant concentrations that exceed possible contributions from the atmosphere via air-water equilibrium and thereby indicate some source of CFC contamination.

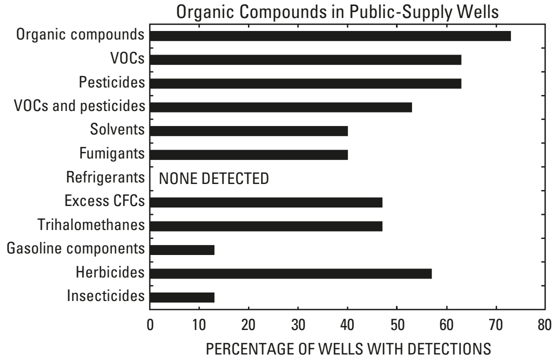


Figure 7. Detection rates for organic compound classes in 30 public-supply wells, Oahu, Hawaii, 2000–2001. Refrigerants were not detected using standard VOC method 2020 but were detected in all but one well using ultrasensitive method 1173 (CFC dating).

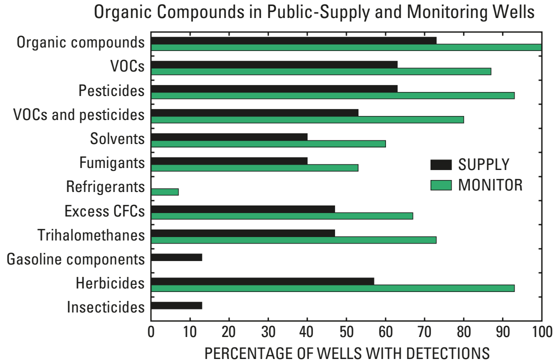


Figure 8. Comparison of detection rates for organic compound classes in 30 public-supply wells and 15 monitoring wells, Oahu, Hawaii, 2000–2001. Refrigerants were not detected in public-supply wells using standard VOC method 2020 but were detected in one monitoring well.

Table 2. Organic compound detections in untreated ground water from public-supply and monitoring wells, Oahu, Hawaii, January 2000 through August 2001

[Compounds are grouped by use, with breakdown products indented beneath parent compounds; Number of samples was one per well, but one sample for each pesticide method was ruined in preparation and affects some percentages; Method, USGS laboratory method, bold where custom or provisional; CAS, Chemical Abstract Service Number. Refrigerants were detected in all but one well using ultrasensitive method 1173; excess CFCs (chlorofluorocarbons) indicate contamination in excess of air-water equilibrium; CFC-11 and CFC-113 were detected on VOC method 2020]

Compound class, compound, and synonym (in parentheses)	Number of wells with detections		Percentage of wells with detections		Number of samples		Method	CAS
	Public supply	Monitoring	Public supply	Monitoring	Public supply	Monitoring		
Organic compounds								
At least one organic compound detected	22	15	73	100	30	15		
Two or more organic compounds detected	19	14	63	93	30	15		
At least one VOC and one pesticide detected	16	12	53	80	30	15		
Volatile organic compounds (VOCs)								
At least one VOC detected	19	13	63	87	30	15		
Two or more VOCs detected	16	12	53	80	30	15		
Solvents, organic synthesis	12	9	40	60	30	15		
Tetrachloromethane (Carbon tetrachloride)	5	6	17	40	30	15	2020	56-23-5
Dichloromethane (Methylene chloride)	2		7		30	15	2020	75-09-2
Tetrachloroethene (PCE, Perchloroethene)	5	6	17	40	30	15	2020	127-18-4
Trichloroethene (TCE)	9	8	30	53	30	15	2020	79-01-6
cis-1,2-Dichloroethene	3	5	10	33	30	15	2020	156-59-2
trans-1,2-Dichloroethene	3	3	10	20	30	15	2020	156-60-5
1,1,2-Trichloroethane (Vinyl trichloride)	3	2	10	13	30	15	2020	79-00-5
1,1,1,2-Tetrachloroethane (1,1,1,2-TCA)	3	1	10	7	30	15	2020	630-20-6
1,1-Dichloroethene (Vinylidene chloride)	1		3		30	15	2020	75-35-4
1,2-Dichloroethane (Ethylidene dichloride)		1		7	30	15	2020	107-06-2
Chlorobenzene (Monochlorobenzene)	1		3		30	15	2020	108-90-7
Fumigants	12	8	40	53	30	15		
1,2-Dibromoethane (EDB, Ethylene dibromide)	4		13		30	15	**8134**	106-93-4
1,2-Dibromo-3-chloropropane (DBCP)	5	3	17	20	30	15	**8134**	96-12-8
1,2,3-Trichloropropane (TCP)	10	8	33	53	30	15	2020	96-18-4
1,2-Dichloropropane (DCP)	12	7	40	47	30	15	2020	78-87-5
1,1-Dichloropropene (1,1-DCPe)	1		3		30	15	2020	563-58-6
Refrigerants (chlorofluorocarbons)	29	15	97	100	30	15	1173	
Excess CFCs (CFC-11,-12,-113)	14	10	47	67	30	15	1173	
Trichlorofluoromethane (CFC-11)		1		7	30	15	2020	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane (CFC-113)		1		7	30	15	2020	76-13-1
Trihalomethanes	14	11	47	73	30	15		
Tribromomethane (Bromoform)	1		3		30	15	2020	75-25-2
Dibromochloromethane	1		3		30	15	2020	124-48-1
Trichloromethane (Chloroform)	14	11	47	73	30	15	2020	67-66-3
Bromodichloromethane	2	1	7	7	30	15	2020	75-27-4
Gasoline components	4		13		30	15		
1,2,4-Trimethylbenzene (Psudocumene)	3		10		30	15	2020	95-63-6
Ethyl tert-butyl ether (ETBE)	1		3		30	15	2020	637-92-3
Methylbenzene (Toluene)	1		3		30	15	2020	108-88-3
Pesticides								
At least one pesticide detected	19	14	63	93	30	15		
Two or more pesticides detected	11	11	37	73	30	15		
Herbicides	17	14	57	93	30	15		
Atrazine	5	6	17	40	30	15	2001,**9060**	1912-24-9
Deethylatrazine	7	7	23	47	30	15	2001,**9060**	6190-65-4
Deethyldeisopropylatrazine	2	1	7	7	29	15	**9060**	3397-62-4
Deisopropylatrazine	1		3		29	15	**2060**	1007-28-9
2-Hydroxyatrazine	2	2	7	13	29	15	**9060**	2163-68-0
Diuron	5	6	17	40	29	15	**9060**	330-54-1
3(4-Chlorophenyl)-1-methyl urea	8	5	28	33	29	15	**9060**	5352-88-5
3,4-Dichloroaniline	7	1	24	7	29	15	**9002**	95-76-1
Bromacil	12	7	41	47	29	15	**9060**	314-40-9
Hexazinone	2	4	7	27	29	15	**9002**	51235-04-2
2-Chloro-2,6-diethylacetanilide		1		7	29	15	**9002**	6967-29-9
Bentazon		1		7	29	15	**9060**	25057-89-0
Imazaquin		1		7	29	15	**9060**	81335-37-7
Metsulfuron methyl		1		7	29	15	**9060**	74223-64-6
Insecticides	4		13		30	15		
Dieldrin	3		10		29	15	2001	60-57-1
p,p'-DDE	1		3		29	15	2001	72-55-9
Caffeine		4		27	29	15	**9060**	58-08-2

Number of compounds detected	Public supply	Monitoring	All wells
Organic compounds	36	30	42
VOCs	24	16	25
Pesticides	12	13	16

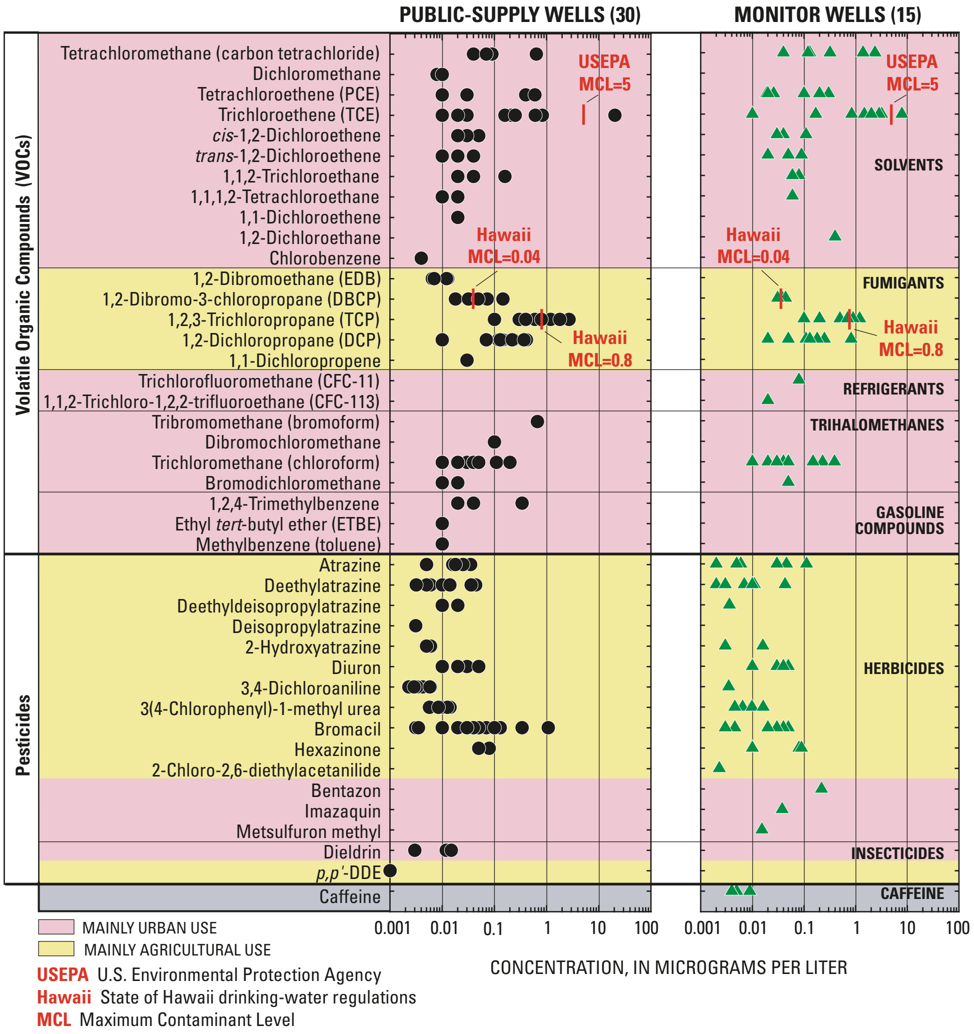


Figure 9. Concentrations of organic compounds in sampled public-supply and monitoring wells, Oahu, Hawaii, 2000–2001.

Few Concentrations Exceeded Drinking-Water Regulations

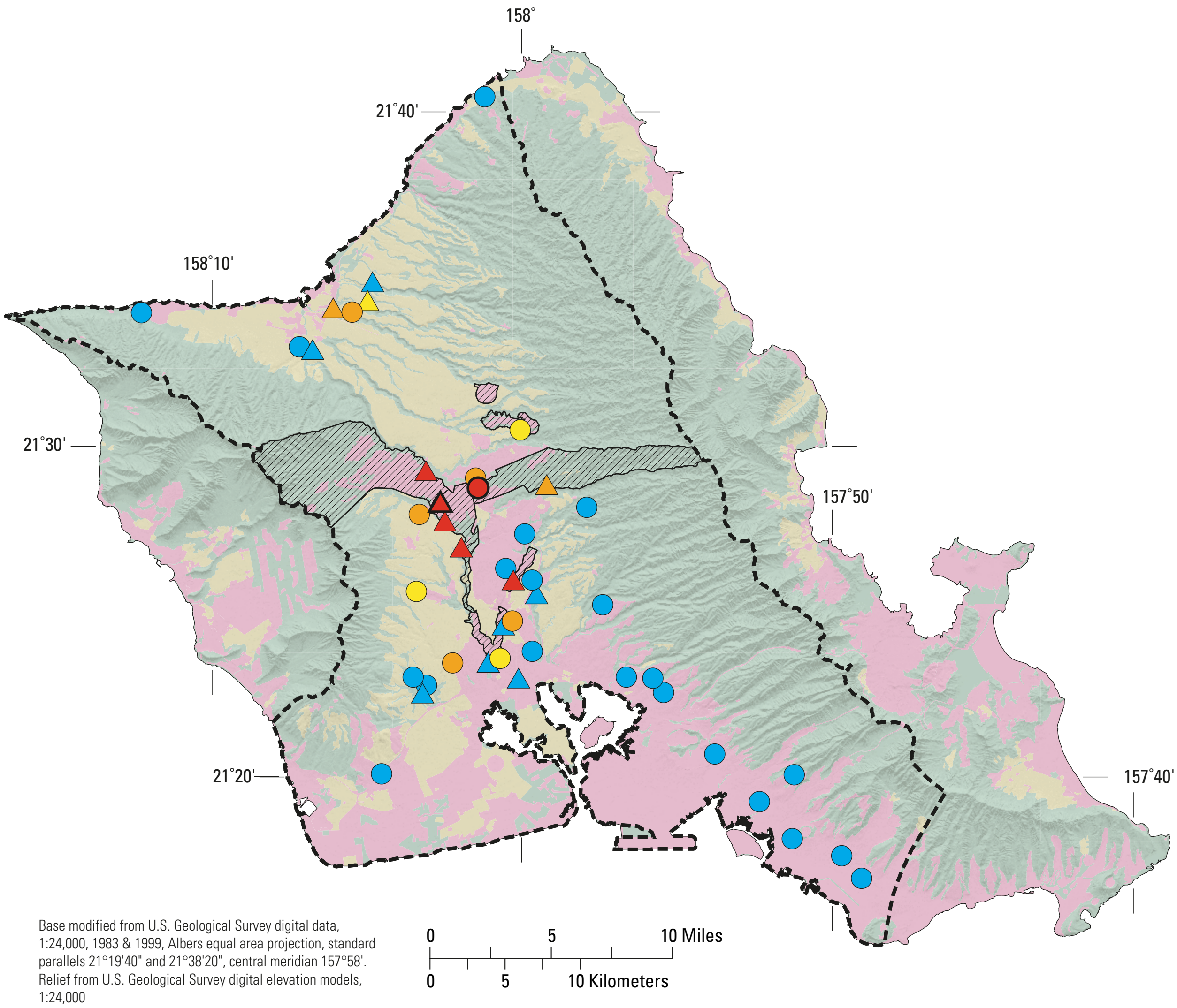
Although various compounds and elements were detected, few concentrations exceeded drinking-water regulations (for those constituents for which regulations have been established). These are shown as shaded entries in tables D1 and D2. Concentrations of organic compounds for all public-supply and monitoring wells that were sampled for the study are shown in figure 9. Comparison with Federal and State Drinking-Water Regulations (table 3 and discussion below) focuses on public-supply wells that produce drinking water, although concentrations in a few monitoring wells also exceeded regulations.

Only 2 of 30 public-supply wells (7 percent) had concentrations exceeding USEPA Maximum Contaminant Levels (U.S. Environmental Protection Agency, 2002). One central Oahu supply well (fig. 10) contained the solvent TCE (trichloroethene) at 20.4 µg/L, four times greater than the USEPA MCL of 5 µg/L. One Honolulu supply well (fig. 11) contained radon at 397 pCi/L, slightly above the proposed USEPA MCL of 300 pCi/L. The proposed MCL for radon is based on inhalation risk rather than a risk from drinking. Radon-222 is a radioactive gas that forms naturally by decay of radium-226; both are intermediate steps in the decay of uranium-238 to lead-206.

Table 3. Comparison of drinking-water regulations with organic-compound and radon concentrations in untreated ground water from public-supply wells, Oahu, Hawaii, January-July 2000

[Concentrations in micrograms per liter (µg/L), except radon in picoCuries per liter (pCi/L); concentrations exceeding drinking-water regulations are bold and shaded; compounds are arranged by use, with breakdown products indented beneath parent compounds; CAS, Chemical Abstract Service Number; MRL, Minimum Reporting Level; Median, concentration at the 50th percentile (where fewer than half of samples were detections, this value is less than the MRL or the minimum detected concentration, whichever is smaller); EPA MCL, U.S. Environmental Protection Agency Maximum Contaminant Level; Hawaii MCL, State of Hawaii MCL, only shown where different from EPA MCL; RSD5, Risk-Specific Dose at 10^{-5} cancer risk level for suspected carcinogens; HAL, Lifetime Health Advisory Level for non-carcinogens; $N_{samples}$, number of samples analyzed; E, estimated value]

Compound class, compound, and synonym (in parentheses)	CAS	Number of detections	MRL (µg/L)	Concentration range (µg/L)			Drinking-water regulations (µg/L)				Number of concentrations exceeding	
				Minimum	Median	Maximum	EPA MCL	Hawaii MCL	RSD5	HAL	EPA MCL	Hawaii MCL
Volatile organic compounds (VOCs)	**$N_{samples}$ = 30**											
Solvents, organic synthesis												
Tetrachloromethane (Carbon tetrachloride)	56-23-5	5	.06	E.04	<.04	.64	5					
Dichloromethane (Methylene chloride)	75-09-2	2	.38	E.008	<.008	E.01	5					
Tetrachloroethene (PCE, Perchloroethene)	127-18-4	5	.10	E.01	<.01	.6	5					
Trichloroethene (TCE)	79-01-6	9	.038	E.01	<.01	**20.4**	5				**1**	
cis-1,2-Dichloroethene	156-59-2	3	.038	E.02	<.02	E.05	70					
trans-1,2-Dichloroethene	156-60-5	3	.032	E.01	<.01	E.04	100					
1,1,2-Trichloroethane (Vinyl trichloride)	79-00-5	3	.06	E.02	<.02	.16	5					
1,1,1,2-Tetrachloroethane (1,1,1,2-TCA)	630-20-6	3	.030	E.01	<.01	E.02			10			
1,1-Dichloroethene (Vinylidene chloride)	75-35-4	1	.04	E.02	<.02	E.02	7					
1,2-Dichloroethane (Ethylidene dichloride)	107-06-2	0	.13	<.13	<.13	<.13	5					
Chlorobenzene (Monochlorobenzene)	108-90-7	1	.028	E.004	<.004	E.004	100					
Fumigants												
1,2-Dibromoethane (EDB, Ethylene dibromide)	106-93-4	4	.0037	.0065	<.0037	E.0128	.05	.04				
1,2-Dibromo-3-chloropropane (DBCP)	96-12-8	5	.0077	.018	<.0077	**.146**	.2	.04				**3**
1,2,3-Trichloropropane (TCP)	96-18-4	10	.16	E.1	<.1	**2.7**		.8		40		**3**
1,2-Dichloropropane (DCP)	78-87-5	12	.068	E.01	<.01	.41	5					
1,1-Dichloropropene (1,1-DCPe)	563-58-6	1	.026	E.03	<.03	E.03						
Refrigerants (chlorofluorocarbons)												
Trichlorofluoromethane (CFC-11)	75-69-4	0	.09	<.09	<.09	<.09				2000		
1,1,2-Trichloro-1,2,2-trifluoroethane (CFC-113)	76-13-1	0	.06	<.06	<.06	<.06						
Trihalomethanes												
Tribromomethane (Bromoform)	75-25-2	1	.06	<.06	<.06	<.06	80					
Dibromochloromethane	124-48-1	1	.18	E.1	<.1	E.1	80					
Trichloromethane (Chloroform)	67-66-3	14	.052	E.01	<.01	.20	80					
Bromodichloromethane	75-27-4	2	.048	E.01	<.01	E.02	80					
Gasoline components												
1,2,4-Trimethylbenzene (Psudocumene)	95-63-6	3	.056	E.02	<.02	.34						
Ethyl tert-butyl ether (ETBE)	637-92-3	1	.054	E.01	<.01	E.01						
Methylbenzene (Toluene)	108-88-3	1	.05	E.01	<.01	E.01	1000					
Pesticides and caffeine	**$N_{samples}$ = 29**											
Atrazine	1912-24-9	5	.001	.005	<.001	.035	3					
Deethylatrazine	6190-65-4	7	.002	E.005	<.002	E.044						
Deethyldeisopropylatrazine	3397-62-4	2	.0599	E.01	<.01	E.02						
Deisopropylatrazine	1007-28-9	1	.0737	E.003	<.003	E.003						
2-Hydroxyatrazine	2163-68-0	2	.1927	E.005	<.005	E.006						
Diuron	330-54-1	5	.0793	.010	<.01	.05				10		
3(4-Chlorophenyl)-1-methyl urea	5352-88-5	8	.0915	.01	<.01	.01						
3,4-Dichloroaniline	95-76-1	7	.005	E.002	<.002	E.006						
Bromacil	314-40-9	12	.0807	E.003	<.003	E1.08				90		
Hexazinone	51235-04-2	2	.008	.05	<.008	.08						
2-Chloro-2,6-diethylacetanilide	6967-29-9	0	.008	<.008	<.008	<.008						
Bentazon	25057-89-0	0	.0193	<.0193	<.0193	<.0193				200		
Imazaquin	81335-37-7	0	.103	<.103	<.103	<.103						
Metsulfuron methyl	74223-64-6	0	.1138	<.1138	<.1138	<.1138						
Insecticides												
Dieldrin	60-57-1	3	.001	E.003	<.001	.015			.02			
p,p'-DDE	72-55-9	1	.006	E.001	<.001	E.001			1			
Caffeine	58-08-2	0	.0805	<.0805	<.0805	<.0805						
Radon	**$N_{samples}$ = 30**											
Radon (pCi/L)	14859-67-7	30	26	40	104	**397**	300				**1**	



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EXPLANATION

LAND USE

- ▭ Agriculture
- ▭ Urban
- ▭ Other (mostly forest)

▨ SELECTED MILITARY INSTALLATIONS

- - - - NAWQA GROUND-WATER STUDY AREA

○ PUBLIC-SUPPLY WELL

△ MONITORING WELL

TRICHLOROETHENE (TCE) CONCENTRATION IN GROUND WATER, IN MICROGRAMS PER LITER

- ● Not detected - minimum reporting level = 0.038
- ● Low - less than 0.1
- ● Medium - 0.1 to 1
- ● High - 1 to 5
- ● Exceeds U.S. Environmental Protection Agency maximum contaminant level of 5

Figure 10. Distribution of trichloroethene (TCE), Oahu, Hawaii. One public supply well in central Oahu had a concentration exceeding the U.S. EPA Maximum Contaminant Level.

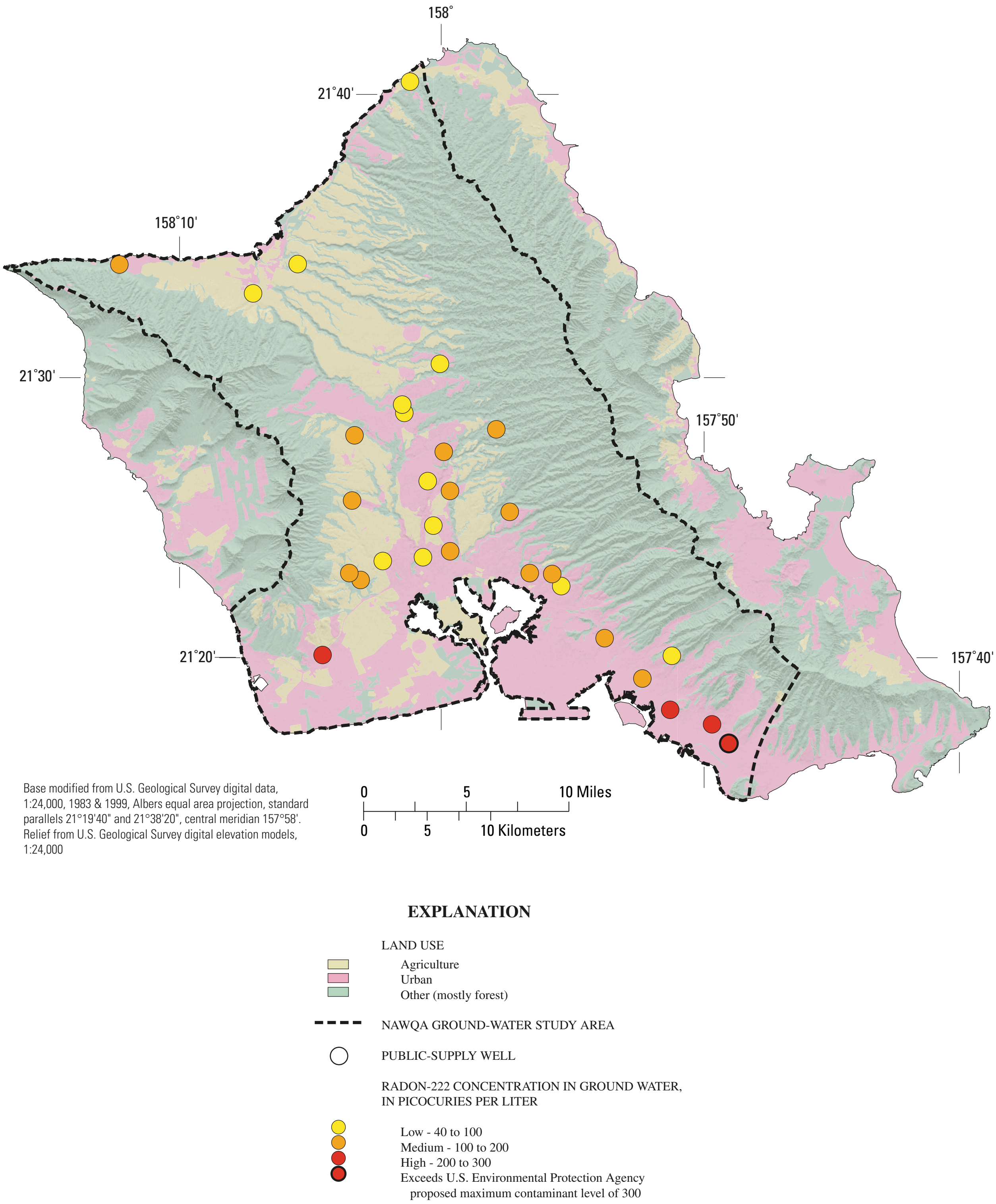

Figure 11. Distribution of radon-222, Oahu, Hawaii. One public-supply well in Honolulu had a concentration exceeding the proposed U.S. EPA Maximum Contaminant Level.

Four of 30 public-supply wells (13 percent) exceeded State MCLs for fumigants, which are lower than USEPA MCLs (State of Hawaii, 1999). State MCLs were exceeded in three central Oahu supply wells each for 1,2,3-trichloropropane (TCP; fig. 12) and 1,2-dibromo-3-chloropropane (DBCP; fig. 13). Two of these wells contained both compounds (table D1), and two more wells contained one compound each, for a total of four public-supply wells in which fumigants exceeded state MCLs. Maps for 1,2-dibromoethane (EDB) and 1,2-dichloropropane (DCP) are included here because of longstanding local interest in fumigant contamination in central Oahu (figs. 14 and 15).

Two public-supply wells had inorganic concentrations (table D2) that exceeded USEPA Secondary Drinking Water Regulations, which are non-enforceable guidelines concerned mainly with aesthetic qualities such as taste and odor of the water. One well had a chloride concentration of 263 mg/L, slightly above the maximum guideline of 250 mg/L, and one well had pH lower than the minimum guideline of 6.5.

Constituents of prominent human-health concern nationally appear to pose little problem on Oahu. Nitrate was below drinking-water limits at all wells, with the maximum nitrate concentration of 5.24 mg/L as N (table D2) being about half the USEPA drinking-water MCL of 10 mg/L. All arsenic concentrations were less than the 0.9 µg/L minimum reporting limit and therefore well below the USEPA drinking-water MCL of 10 µg/L. The gasoline oxygenate MTBE (methyl *tert*-butyl ether), which has caused much concern in some parts of the continental United States, is not currently used as a gasoline additive in Hawaii and was not detected by Oahu NAWQA sampling.

Detection Rates Were Highest in the Nation for Fumigants and Among the Highest for Solvents, VOCs, and Insecticides

Out of over 80 NAWQA Study-Unit Surveys nationwide that sampled for VOCs, Oahu ranked first in fumigant detections, third in solvent detections, and fourth in overall VOC detections. These rankings used data screened to report detections only above a common assessment level of 0.2 µg/L, so that results from early NAWQA study units with higher reporting limits could be included in the comparison. The screened detection rates in Oahu public-supply wells were 30, 20, and 47 percent for fumigants, solvents, and VOCs, compared to 40, 40, and 63 percent for the raw, unscreened detection rates.

Herbicide detections in Oahu public-supply wells ranked 51st and insecticide detections 12th out of over 90 Study-Unit Surveys that sampled for pesticides. These rankings were based on unscreened data. Notably, the pesticide rankings do not reflect two supplemental pesticide methods used in many 1997 Study Units but not in earlier studies begun in 1991 and 1994. Over 75 percent of Oahu herbicide detections were from these supplemental methods (methods 9002 and 9060, table D1) and are not factored into the national herbicide rankings.

Commonly Detected Solvents, Fumigants, and Herbicides Have Histories of Intensive Use

Organic compounds detected most commonly and in highest concentrations have been in use on Oahu from the mid-1900s or earlier. Trichloromethane (chloroform) was the most prevalently detected VOC, with a detection rate of 47 percent in public-supply wells (table 2 and fig. 16). High concentrations of chloroform occurred together with other solvents and appear to have originated primarily from solvent use or breakdown of solvent compounds. Lower concentrations of chloroform may have originated as impurities or breakdown of other VOCs or pesticides, or as a disinfection byproduct of water chlorination.

Other solvents commonly detected were trichloroethene (TCE), tetrachloroethene (PCE), and tetrachloromethane (carbon tetrachloride), which were detected in 30, 17, and 17 percent of supply wells, respectively (fig. 16). These are among the leading solvents used historically in the United States for cleaning, degreasing, and textile dry-cleaning. Solvents were used intensively at military installations in central Oahu dating back to at least the 1940s, and various potential sources of solvents have been investigated, including aircraft and automotive maintenance and engine rebuilding shops, drum-disposal and burn areas, and laundries (Harding Lawson Associates, 1995). However, specific source sites responsible for solvent contamination of public-supply wells in central Oahu were not found in more than a decade of investigations (U.S. Environmental Protection Agency, 2000). Potential civilian-sector sources of solvents in central Oahu include commercial automotive repair and painting shops, dry cleaners, and industrial or automotive

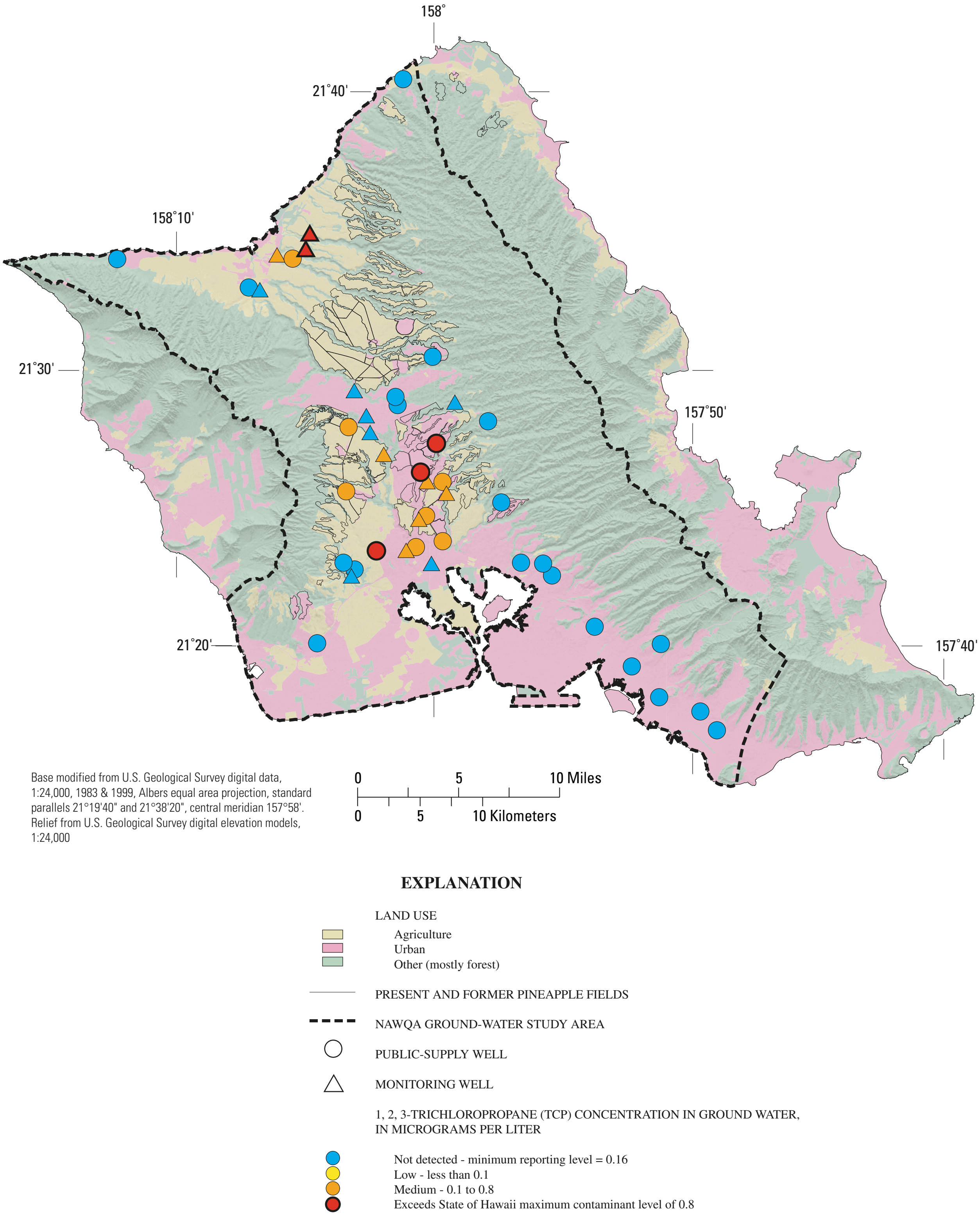

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Figure 12. Distribution of 1,2,3-trichloropropane (TCP), Oahu, Hawaii. Three public-supply wells in central Oahu had concentrations exceeding the State of Hawaii Maximum Contaminant Level.

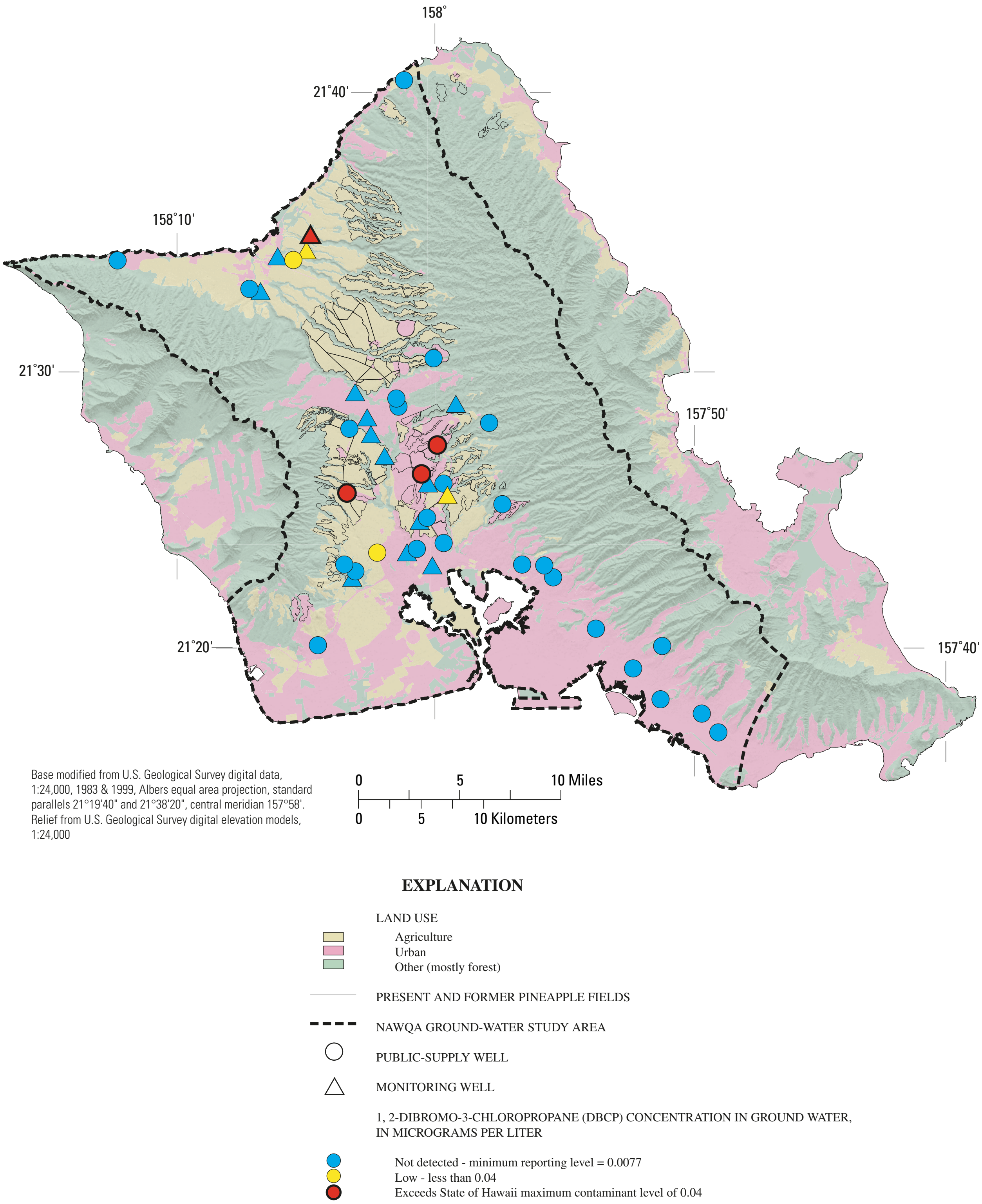

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Figure 13. Distribution of 1,2-dibromo-3-chloropropane (DBCP), Oahu, Hawaii. Three public-supply wells in central Oahu had concentrations exceeding the State of Hawaii Maximum Contaminant Level.

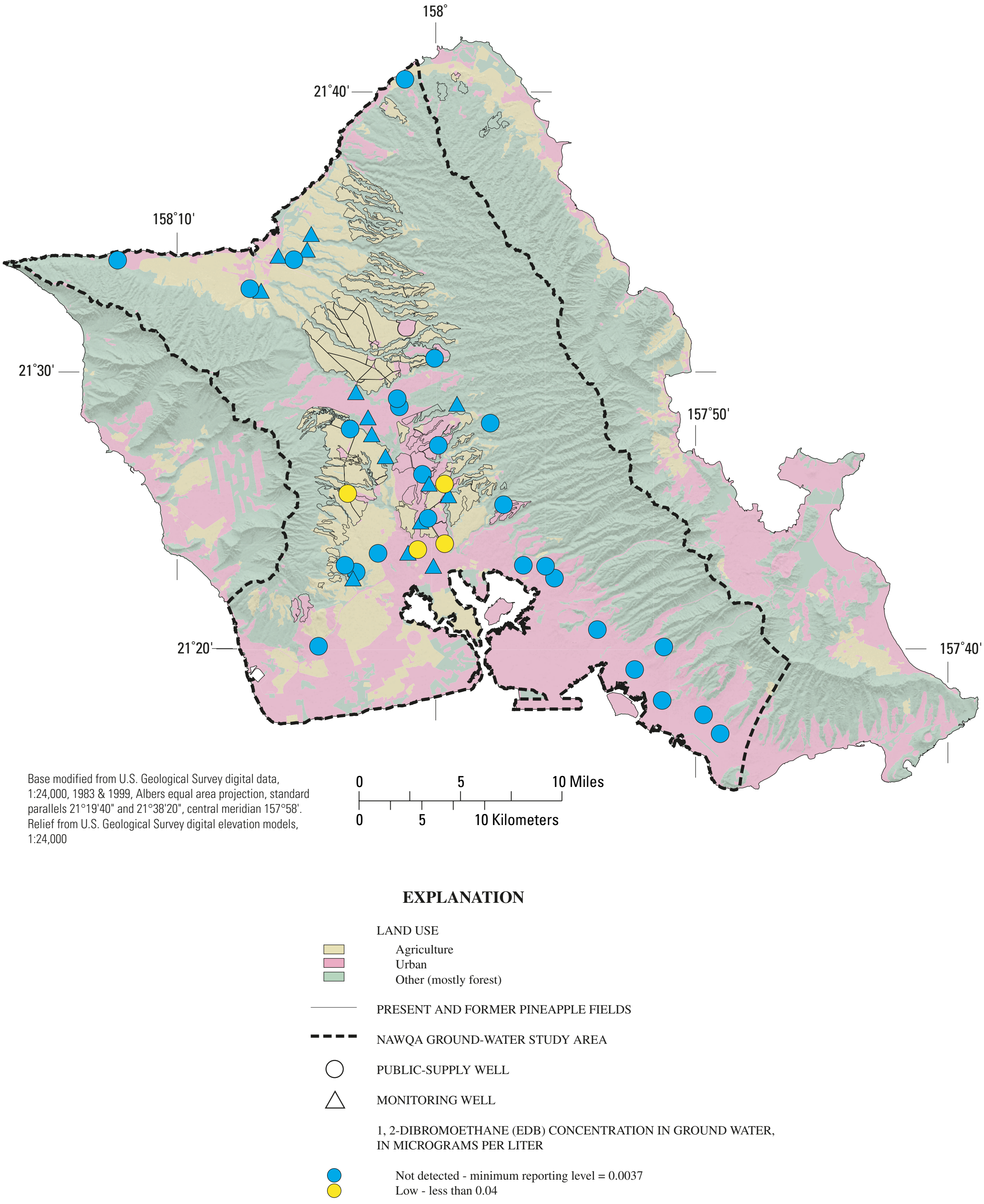

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Figure 14. Distribution of 1,2-dibromoethane (EDB), Oahu, Hawaii. EDB was only detected in the southern part of central Oahu.

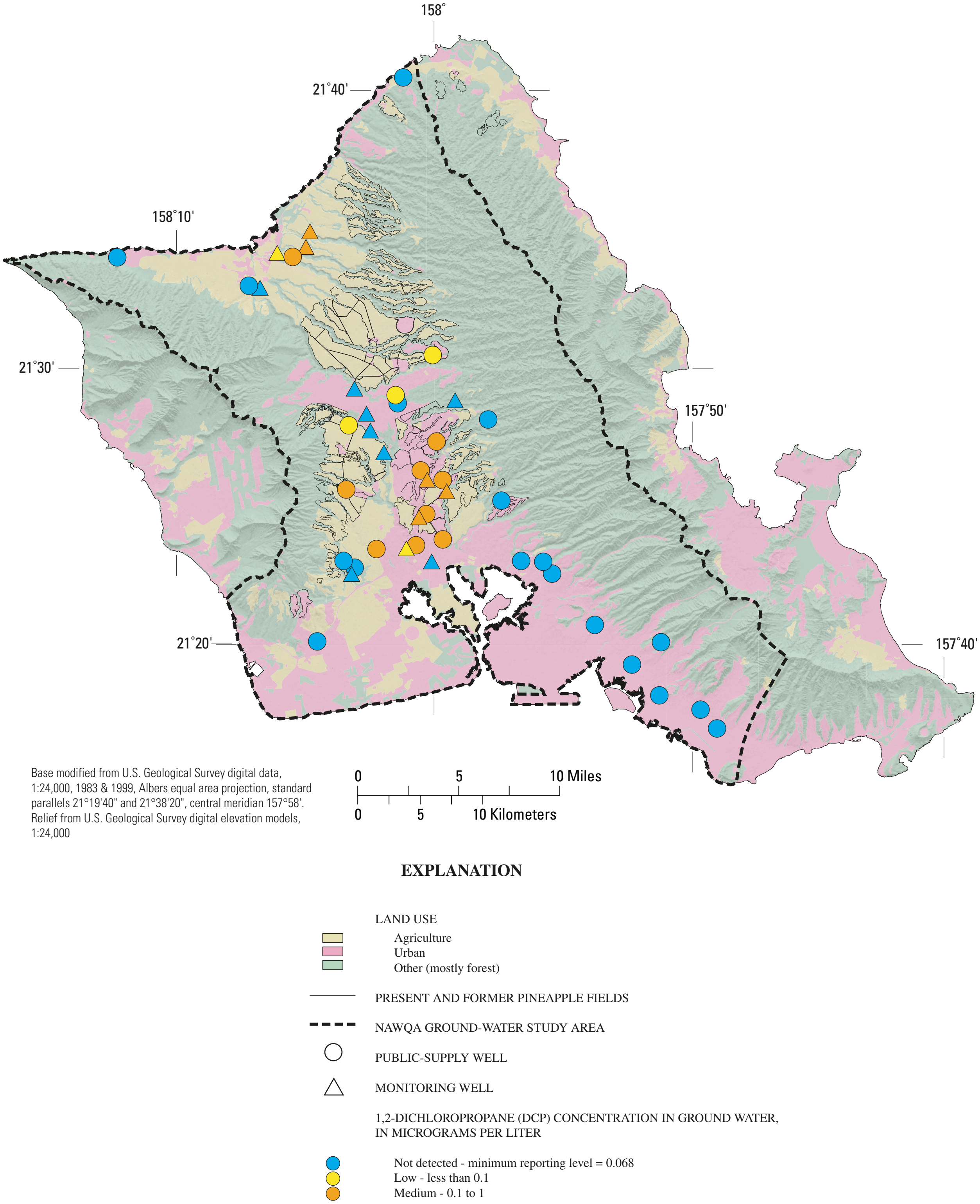

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Figure 15. Distribution of 1,2-dichloropropane (DCP), Oahu, Hawaii. Concentrations were greatest in central Oahu, in a pattern similar to that of 1,2,3-trichloropropane (TCP).

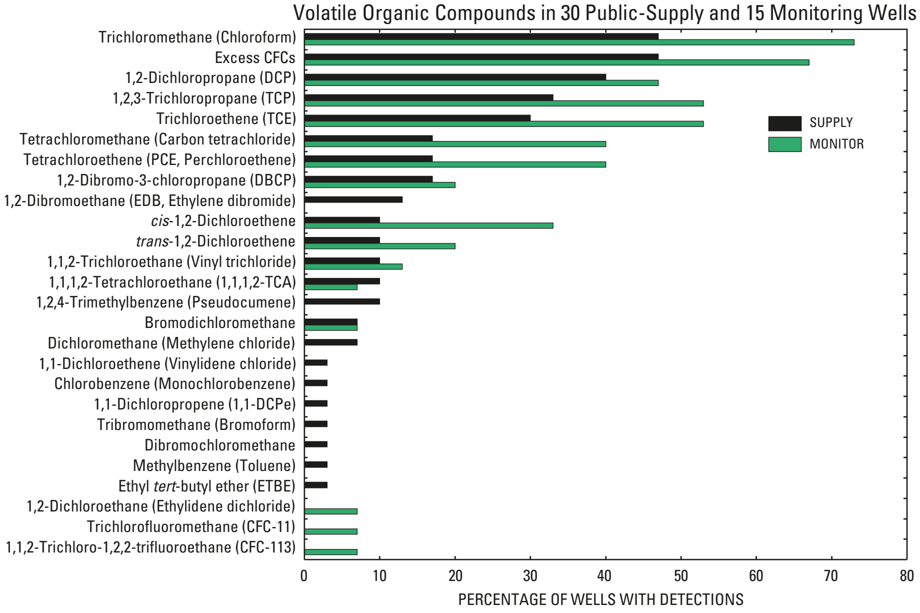

Figure 16. Detection rates for volatile organic compounds (VOCs), Oahu, Hawaii.

maintenance incidental to mechanized agriculture in the area.

The VOC fumigant compounds 1,2-dichloropropane (DCP) and 1,2,3-trichloropropane (TCP) were detected in 40 and 33 percent of supply wells, respectively (fig. 16). Detected less frequently were 1,2-dibromo-3-chloropropane (DBCP) and 1,2-dibromoethane (EDB), in 17 and 13 percent of supply wells. Several fumigant formulations used on Oahu pineapple fields contained DCP, including the fumigant DD (a dichloropropane-dichloropropene mixture that was used from 1943 to 1977), Telone, and Telone II. The DD formulation also contained TCP as an impurity of as much as 7 percent by weight (Oki and Giambelluca, 1987; Orr and Lau, 1987). EDB was used on Oahu from 1948 to 1983, whereas DBCP was used from 1959 to 1977. The greater number of detections and higher concentrations of DCP and TCP (in comparison to EDB and DBCP) may reflect greater persistence (lesser tendency to volatilize or break down; Oki and Giambelluca, 1987), the earlier introduction of DD fumigant (J. Mink, personal commun., 1985, as cited in Oki and Giambelluca, 1987), or the fact that DD was applied at rates 4 to 20 times greater per acre than EDB and DBCP, respectively (Yim and Dugan, 1975).

Fourteen herbicides or herbicide breakdown products were detected (table 2 and fig. 17). Bromacil was the most prevalent, detected in 41 percent of public-supply wells, followed by diuron and atrazine at 17 percent, and hexazinone at 7 percent. All four compounds have been used in pineapple cultivation and all but bromacil were used for sugarcane. Much greater amounts of herbicide have been applied to sugarcane than to pineapple, and diuron and atrazine have been used in greater amounts than bromacil or hexazinone (State of Hawaii, 1969; Pacific Biomedical Research Center, 1975; Takahashi, 1982). Dates of introduction on Oahu are not available but diuron was probably applied first, after becoming available in 1954, followed by atrazine in 1958, bromacil in 1962, and hexazinone in 1976 (Oki and Brasher, 2003).

Herbicide breakdown products were detected, several of them more commonly than their parent compounds. Two diuron breakdown products were detected: 3(4-chlorophenyl)-1-methyl urea and 3,4-dichloroanaline, in 28 and 24 percent of supply wells, both more than the parent compound. Four atrazine breakdown products were detected, the most common being deethylatrazine in 23 percent of supply wells (again, more than the parent compound).

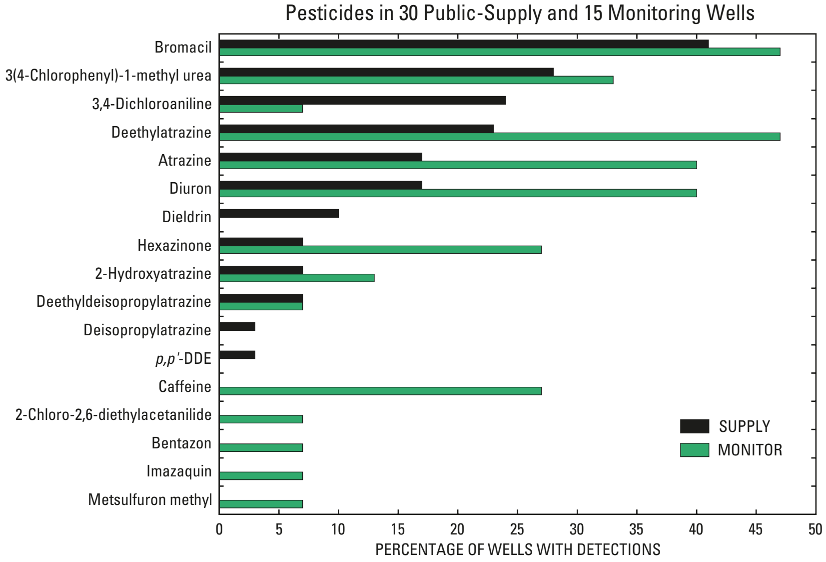

Figure 17. Detection rates for pesticide compounds, Oahu, Hawaii.

Gasoline Components and Insecticides Were Detected in Few Wells

Gasoline components were unexpectedly scarce (table 2 and figs. 7 and 8), given the heavily urbanized character of much of the study area. Methylbenzene (toluene) and ethyl-*tert*-butyl-ether (ETBE, a gasoline oxygenate) were detected in one Honolulu public-supply well (table D1 and fig. 16), and three supply wells contained 1,2,4-trimethylbenzene (one in Honolulu and two in central Oahu). The presence of both toluene and ETBE together at the one well is strongly suggestive of gasoline contamination. But 1,2,4-trimethylbenzene is also common in solvents and paint thinners so its presence alone, without additional gasoline components, cannot be attributed unequivocally to gasoline. Similarly, the presence of 1,2-dibromoethane (EDB) in four central Oahu supply wells is not strongly suggestive of gasoline contamination without the presence of other gasoline compounds. In addition to its use as a nematicide fumigant in central Oahu, EDB also was used historically in leaded gasoline, as a component of the anti-knock additive tetraethyl lead. Some investigators have reasoned that a possible source of EDB from known gasoline leaks in central Oahu cannot be ruled out (Oki and Giambelluca, 1987). The four supply wells in which EDB was detected in this study also contained 2 to 3 other fumigants but no additional gasoline components (table D1).

Only two insecticides were detected in ground water (table 2 and fig. 17). Dieldrin was detected in three public-supply wells in urban Honolulu (table D1) and *p,p'*-DDE was detected in one supply well in central Oahu. Dieldrin has been used on Oahu to control termites and also is a breakdown product of the termiticide aldrin (Brasher and Anthony, 2000). NAWQA ecology studies have detected dieldrin in fish tissue and in bed sediment from Oahu streams. The second compound, *p,p'*-DDE is a breakdown product of *p,p'*-DDT, which was used for insect control in pineapple cultivation on Oahu and probably for other purposes as well. DDT was widely used in the United States until it was banned in 1972, and is highly persistent in the environment. Despite three decades of non-use, DDT and its breakdown products were detected in bed sediment and fish tissue by Oahu NAWQA ecology studies (Brasher and Anthony, 2000).

Volatile Organic Compounds Were Higher in Concentration Than Pesticides

Maximum VOC concentrations were more than an order of magnitude greater than maximum pesticide concentrations (fig. 9). Furthermore, whereas only one pesticide concentration (bromacil) was above 1 µg/L, twelve VOC concentrations exceeded that value: six from trichloroethene, two from tetrachloromethane, and four from 1,2,3-trichloropropane (table D1).

Several possible reasons could explain why VOC concentrations were higher than pesticide concentrations. Perhaps the simplest is application rate. Of the compounds applied for agriculture, about five times more fumigants than herbicides have been applied by weight (State of Hawaii, 1969; Pacific Biomedical Research Center, 1975; Takahashi, 1982). Another reason may be that some VOC contamination originated from concentrated point-source spills or disposal. This mode of release is likely for solvents, which had the highest concentrations of any compounds. In contrast, agricultural chemicals were released widely in nonpoint-source applications that exposed them to dilution and degradation over vastly greater surface areas. Finally, some of the VOC compounds may be more resistant to degradation than pesticides and hence more persistent in the environment.

Land Use, Locale, and Aquifer Vulnerability are Main Factors in Contamination

Organic compounds and nutrients were detected with greater frequency and at higher concentrations in central Oahu than in urban Honolulu or near upland forests. Furthermore, characteristic suites of chemicals were associated with particular land uses and locales (table D1).

1. Solvents were mainly associated with urban and military lands in central Oahu (fig. 18).

2. Fumigants and herbicides were associated with agricultural lands in central Oahu, including former agricultural lands that have been converted to residential urban use (figs. 19 and 20).

3. Insecticides (fig. 21) were detected in urban Honolulu and in one well in central Oahu.

4. Nutrient concentrations were highest beneath agricultural lands in central Oahu, following much the same pattern as fumigants and herbicides (figs. 22 and 23).

These associations were tested statistically (table 4) and are shown in figures 24 and 25. Tests were performed for differences in median values between pairs of well groups defined in table D1 (1=forest; 2=urban Honolulu; 3=urban-military central Oahu; 4=agricultural central Oahu). Regarding organic compounds (fig. 24), the median number of compounds was not significantly different at the 95-percent confidence level between forest and urban Honolulu well groups, but these two groups were significantly different from the urban-military and agricultural central Oahu groups (table 4). The two central Oahu groups did not differ by median number of compounds, but when compounds were divided into VOCs and pesticides (fig. 25), urban and agricultural central Oahu groups differed statistically from each other and from the forest and urban Honolulu groups as well. In these tests, fumigants were excluded from the VOC class and included with pesticides because the fumigants are applied agriculturally. Median nutrient concentrations also showed important differences between paired groups, and urban Honolulu differed from central Oahu in tritium concentration (table 4).

The strong correspondence between water quality and land use is an expected outcome and a main focus of the NAWQA program. Land use is a principal determinant of chemical release to the environment, whether by nonpoint-source agricultural application of fumigants, herbicides, and fertilizers; by nonpoint leaching of urban termiticides; or by point-source releases of solvents or fuels. Also unsurprising is that wells in and near the upland forest contained few organic compounds (table D1), given that there is little opportunity for chemical release to the environment in these areas.

Besides land use, aquifer vulnerability and rapid ground-water flow rates also play a role in contamination on Oahu. Most of the central Oahu area where organic compounds are prevalent is a recharge zone, with no confining units between land surface and the deep unconfined aquifer. Much of the earth material in the intervening unsaturated zone is highly permeable and this makes the deep aquifer vulnerable to contamination, even where depth to the water table is as much as 500 to 1,000 ft. Apparent recharge dates from CFCs and SF_6 were “young” for almost all samples, with only one pre-1940 date out of 45 wells (table D1). The young apparent ages and the prevalence of organic compounds highlight the vulnerability of Hawaiian unconfined basalt aquifers to contamination: water recharges from land surface to the deep water table on a timescale of a few decades or less and carries anthropogenic chemicals with it.

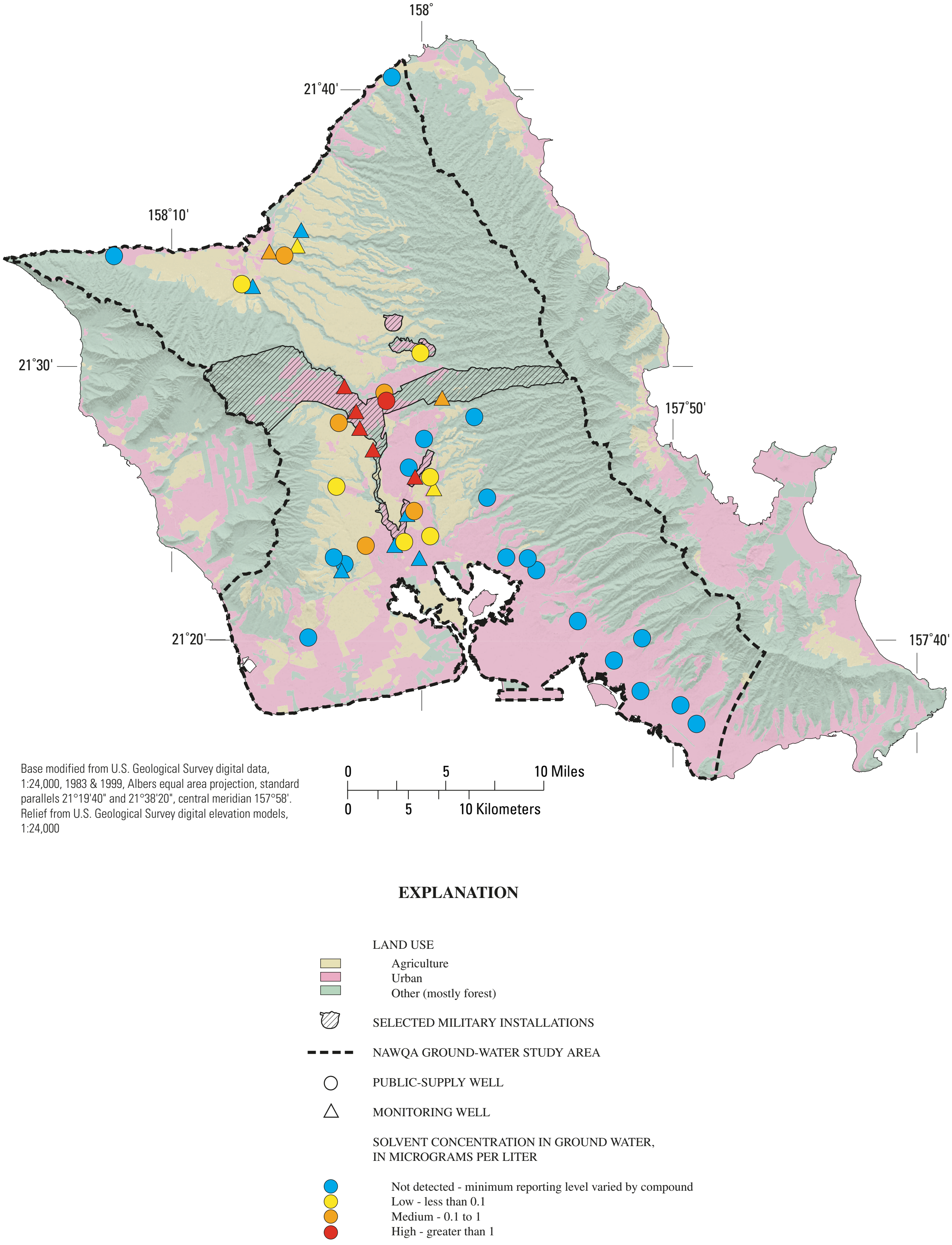

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Figure 18. Distribution of solvents, Oahu, Hawaii. Concentrations were highest in and downgradient from urban-military lands in central Oahu.

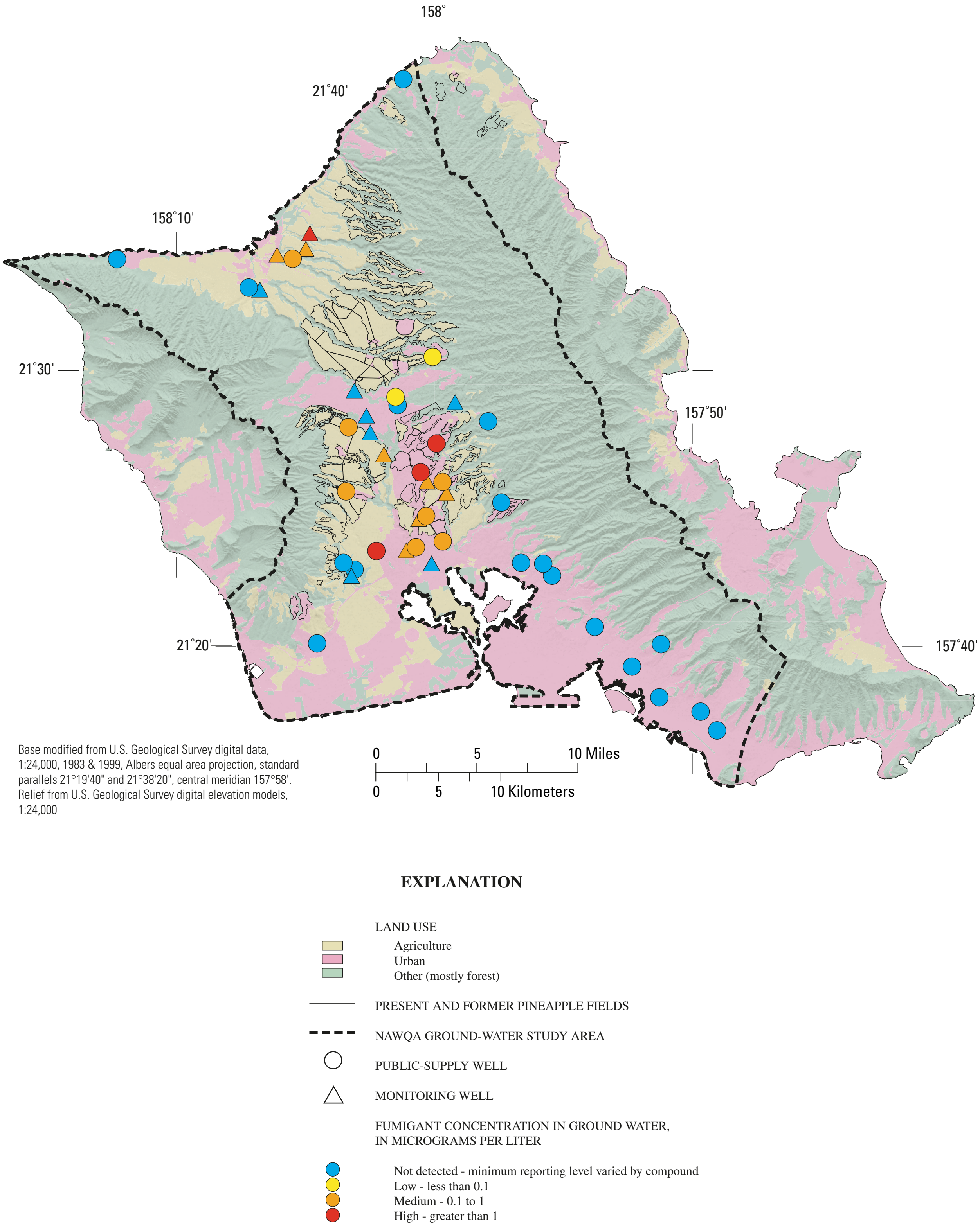

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Figure 19. Distribution of fumigants, Oahu, Hawaii. Concentrations were highest in and downgradient from present and former pineapple fields in central Oahu.

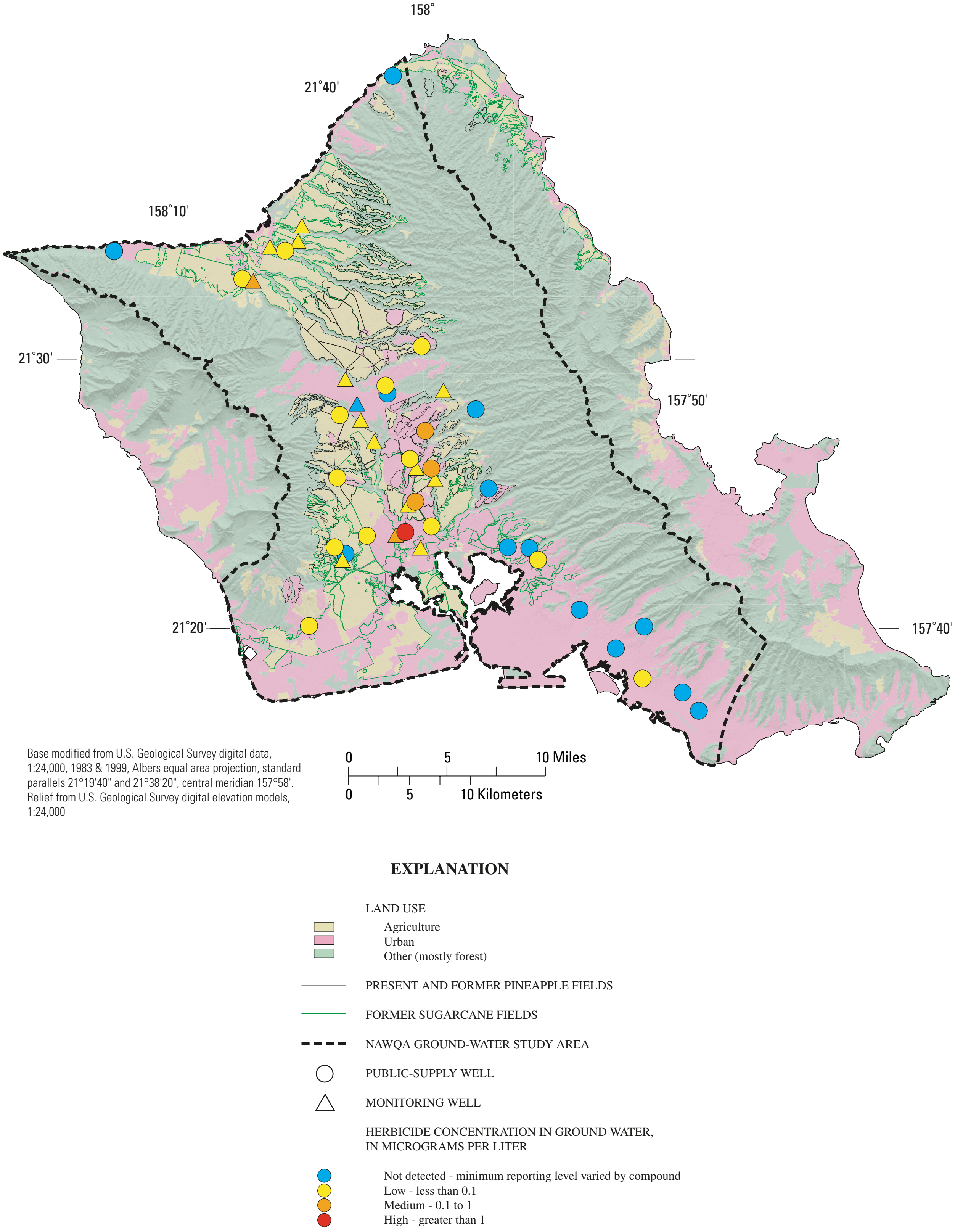

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Figure 20. Distribution of herbicides, Oahu, Hawaii. Concentrations were highest in present and former agricultural lands in central Oahu.

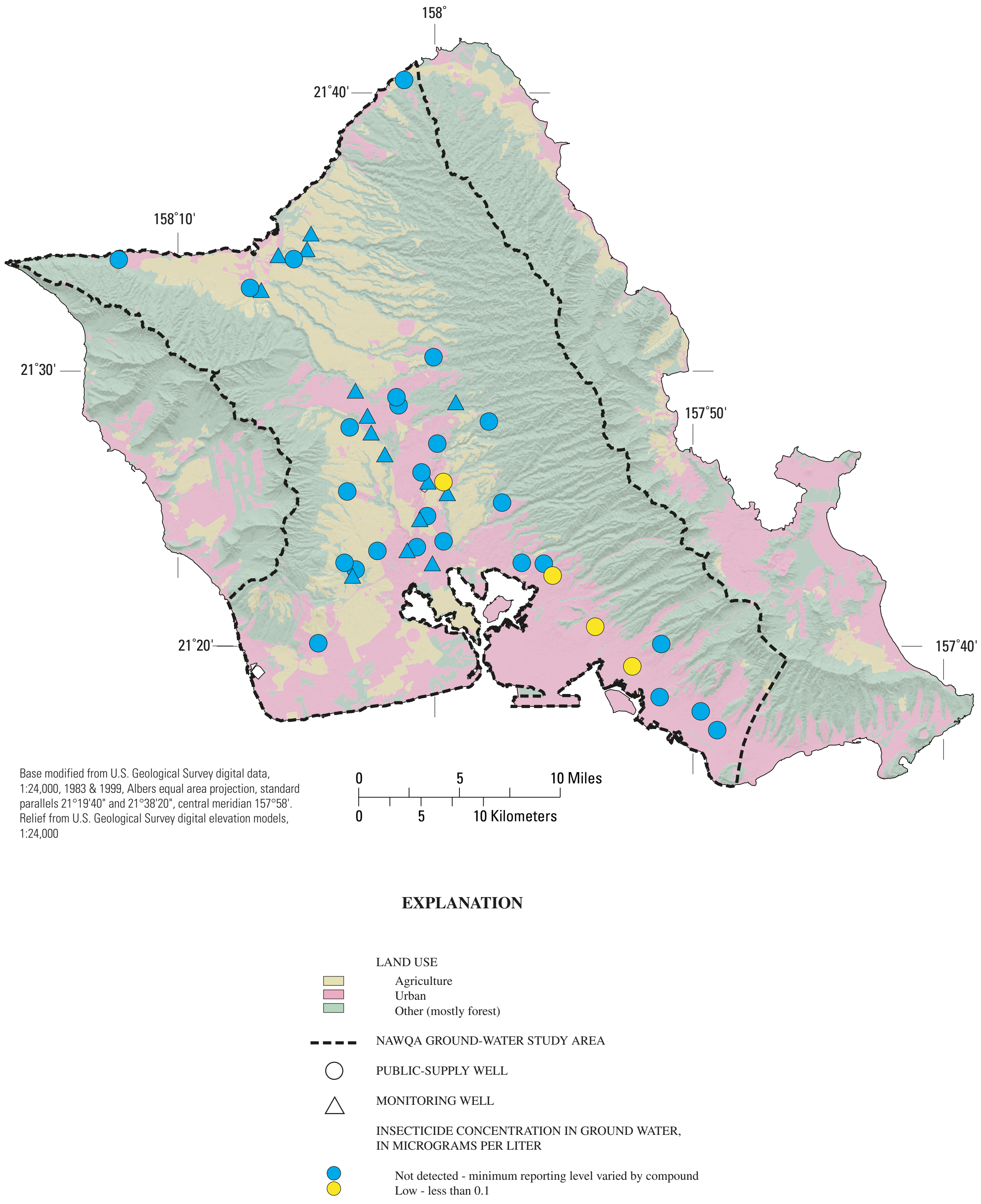

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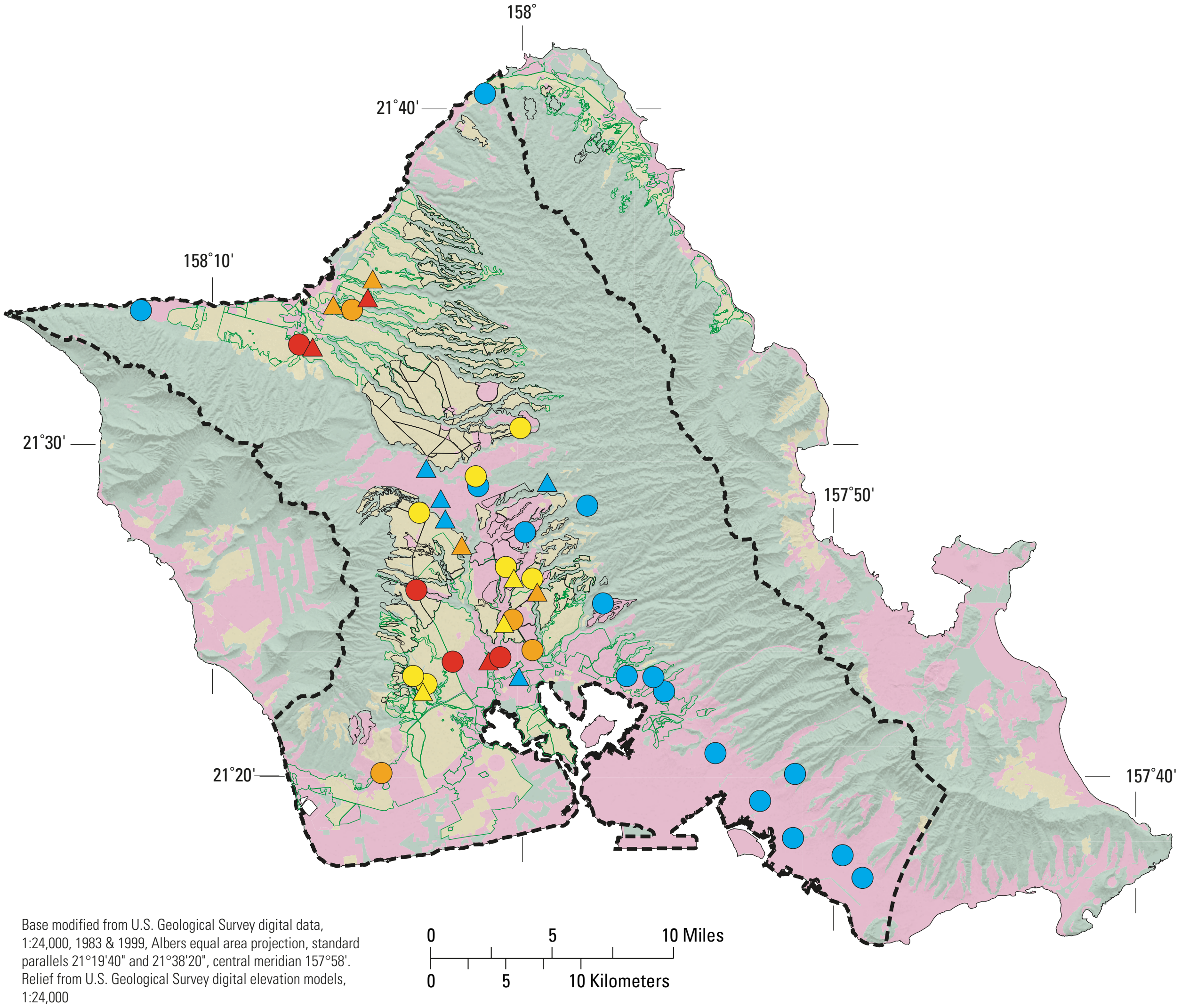
Figure 21. Distribution of insecticides, Oahu, Hawaii. Insecticides were detected at three wells in Honolulu (dieldrin) and one well in central Oahu (*p,p'*-DDE).



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EXPLANATION

LAND USE
- 🟨 Agriculture
- 🟪 Urban
- 🟩 Other (mostly forest)

— PRESENT AND FORMER PINEAPPLE FIELDS

— FORMER SUGARCANE FIELDS

- - - NAWQA GROUND-WATER STUDY AREA

○ PUBLIC-SUPPLY WELL

△ MONITORING WELL

NITRATE CONCENTRATION IN GROUND WATER, IN MILLIGRAMS PER LITER AS N
- 🔵 Natural background - 0.1 to 1
- 🟡 Low - 1 to 2
- 🟠 Medium - 2 to 3
- 🔴 High - 3 to 5.5

Figure 22. Distribution of nitrate, Oahu, Hawaii. Concentrations were highest in and downgradient from present and former agricultural lands in central Oahu.

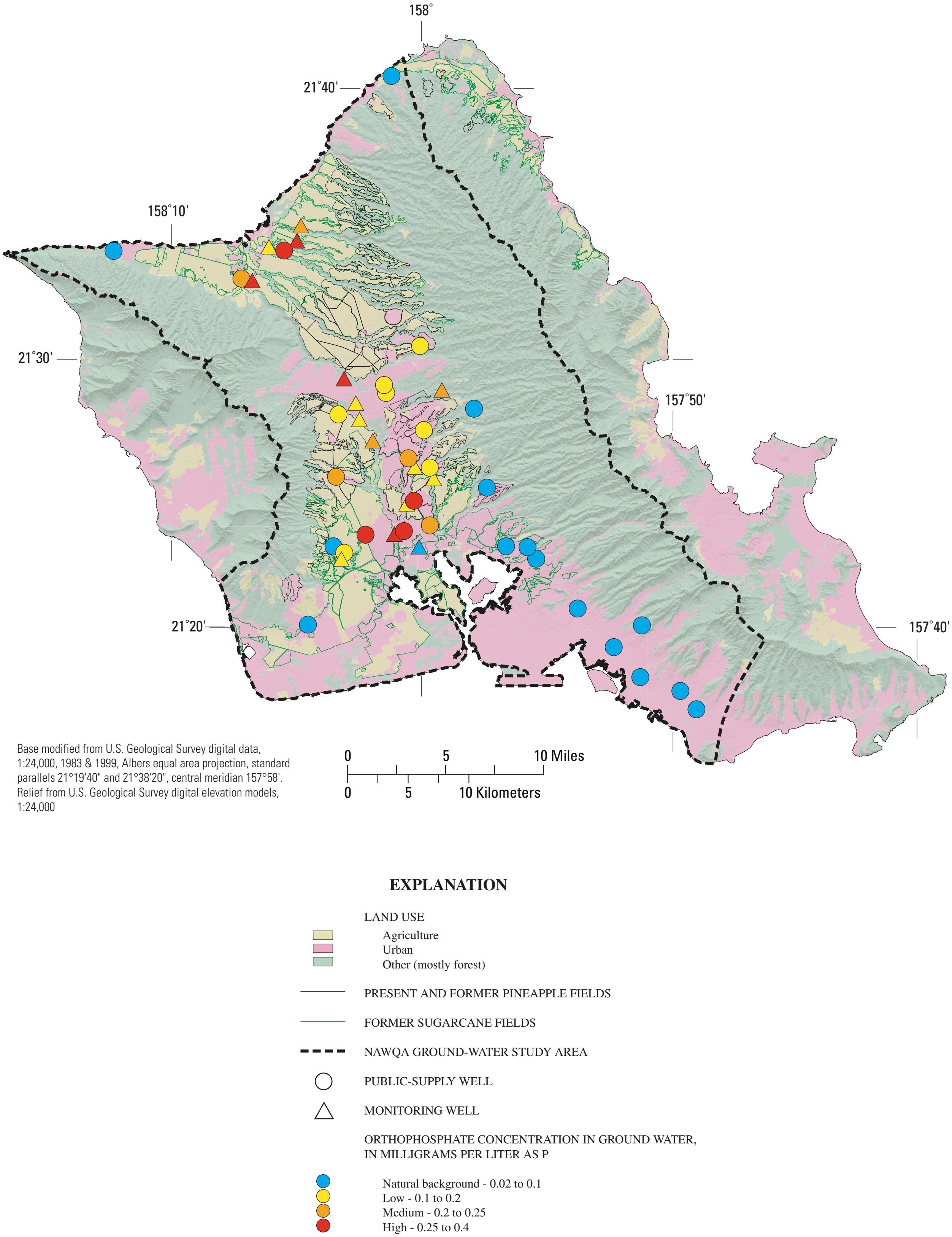

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Figure 23. Distribution of orthophosphate, Oahu, Hawaii. Concentrations were highest in and downgradient from present and former agricultural lands in central Oahu.

Table 4. Wilcoxon rank-sum test of differences between well groups defined on the basis of land use and locale, Oahu, Hawaii, January 2000 through August 2001

[Two-sided Wilcoxon test is a non-parametric test for difference between two groups of data; P-value is the probability that the group medians are the same, and values less than 0.05 (bold and shaded) indicate with greater than 95% confidence that the group medians do indeed differ; *, value is close to 95% confidence level (within 2.5%); VOC, volatile organic compound. See table D1 for detailed information on the well groups]

Do median values for pairs of well groups differ with 95% or greater confidence for these chemical attributes ?						
Well groups	**Chemical attributes**					
	Number of organic compounds	Number of VOCs (excluding fumigants)	Number of pesticides and fumigants	Nitrate concentration	Orthophosphate concentration	Tritium concentration
Between Group 1-Forest and:						
Group 2-Urban Honolulu	No	No	No	No	**Yes**	No
Group 3-Urban-military central Oahu	**Yes**	**Yes**	**Yes**	No	**Yes**	No
Group 4-Agricultural central Oahu	**Yes**	No	**Yes**	**Yes**	**Yes**	No
Between Group 2-Urban Honolulu and:						
Group 3-Urban-military central Oahu	**Yes**	**Yes**	**Yes**	No *	**Yes**	**Yes**
Group 4-Agricultural central Oahu	**Yes**	**Yes**	**Yes**	**Yes**	**Yes**	**Yes**
Between Group 3-Urban-military central Oahu and:						
Group 4-Agricultural central Oahu	No	**Yes**	**Yes**	**Yes**	No	No
P-values from Wilcoxon rank-sum test from which the above answers were determined:						
Between Group 1-Forest and:						
Group 2-Urban Honolulu	0.38	0.79	0.087	0.94	**0.030**	0.81
Group 3-Urban-military central Oahu	**0.0023**	**0.0046**	**0.011**	0.099	**0.0007**	0.13
Group 4-Agricultural central Oahu	**0.0026**	0.15	**0.0011**	**0.0010**	**0.0030**	0.38
Between Group 2--Urban Honolulu and:						
Group 3-Urban-military central Oahu	**0.0004**	**0.0004**	**0.031**	0.0505 *	**0.0000**	**0.0044**
Group 4-Agricultural central Oahu	**0.0004**	**0.046**	**0.0002**	**0.0001**	**0.0000**	**0.022**
Between Group 3-Urban-military central Oahu and:						
Group 4-Agricultural central Oahu	0.92	**0.0000**	**0.0009**	**0.0014**	0.92	0.17

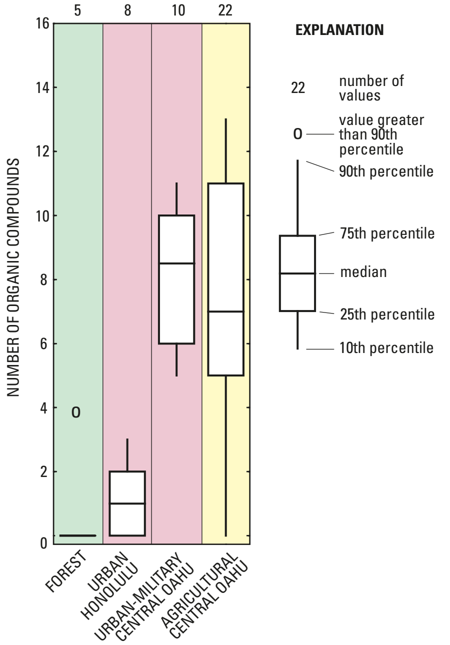


Figure 24. Number of organic compounds detected in wells grouped by land use and locale, Oahu, Hawaii. Numbers of compounds were greater in urban and agricultural central Oahu well groups than in forest and urban Honolulu well groups.

In contrast to central Oahu, few organic compounds were detected in the deep aquifer beneath urban Honolulu despite the high urban density there. Several factors probably contribute to the lack of organic contamination. One factor is aquifer vulnerability: most of urban Honolulu lies downgradient from mountain recharge zones and is instead in the zone of aquifer discharge near the coast. Much of the city is underlain by sedimentary confining units that retard vertical recharge and contaminant transport and divert ground-water flow laterally to the shore through shallow sedimentary aquifers that are not used as drinking-water sources. Land-use planning is another factor: urban Honolulu lands that do lie over upland recharge zones are mainly residential, with little commercial, industrial, or military use. This reflects nearly a century of sound urban planning and watershed protection by State and County agencies that restricted facilities with high contamination potential to coastal areas and away from upland recharge zones. A final factor is that urban residential lands in the Honolulu uplands likely receive much less chemical loading than urban-military and agricultural lands in central Oahu, and typically less mobile chemicals would be used in urban residential areas. This is certainly true compared to fumigant and herbicide application over agricultural lands (Takahashi, 1982; Green

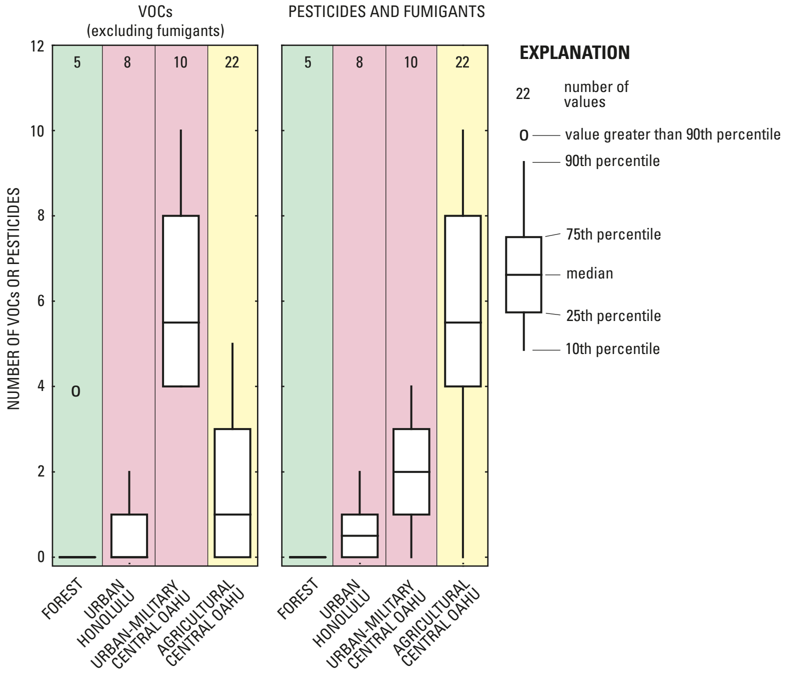


Figure 25. Number of volatile organic compounds (VOCs) and pesticides detected in wells grouped by land use and locale, Oahu, Hawaii. The number of VOCs (excluding fumigants) was greatest in the urban-military central Oahu well group. The number of pesticides and fumigants was greatest in the agricultural central Oahu well group.

and others, 1977) and probably true for nutrients as well. Residential lands in the Honolulu uplands also have fewer potential VOC sources than do the urban-military lands of central Oahu or the urban commercial and industrial lands along the south coast. Insecticides are the only chemical class having higher loading in urban residential areas, most notably the termiticides. An alternate explanation for the lack of contaminants in Honolulu wells is the age of ground water there. Most wells had CFC dates in the 1960s (table D1) and it is possible that contaminants are on their way but have not yet been detected.

Ground Water Carries Nutrients and Chemicals to Streams and Coastal Waters

Elevated concentrations of nitrate and phosphorus were associated with agricultural lands in central Oahu (figs. 22 and 23). Natural background concentrations in the study area are less than about 1 mg/L for nitrate as N (Visher and Mink, 1964) and 0.1 mg/L for orthophosphate as P. Concentrations higher than these are anthropogenic, resulting from over a century of agricultural fertilizer application.

Many orthophosphate concentrations (fig. 23) were greater than the USEPA recommended goal of 0.1 mg/L for avoiding nuisance plant growth (eutrophication) in moving waters. Nutrient concentrations were found to be higher in stream base flow than in storm flow by NAWQA surface-water studies, and the higher concentrations were attributed to discharge of nutrient-laden ground water (Tomlinson and Miller, in press). The organic compounds 1,2-dibromoethane (EDB), bromacil, atrazine, and de-ethylatrazine also were higher in base flow than in storm flow, raising concerns about possible effects of organic compounds on aquatic organisms.

Besides streams, discharging ground water also carries nutrients and chemicals into estuaries and nearshore marine waters. Nutrients are a particular concern with respect to coral reefs. The coral-reef ecosystem is highly nutrient-sensitive and can be degraded where excess nutrients promote excessive algal growth that displaces or interferes with the growth of healthy corals. Another concern is the proliferation of invasive species. Several species of nuisance seaweed have plagued Hawaii in recent years, and elevated nutrient concentrations are a suspected factor in their proliferation.

Well Type and Depth are Less Significant Factors Than Land Use and Locale

The principal reason for sampling monitoring wells was to gain a more complete distribution of sampling depths by sampling shallower ground water that is cased off from most public-supply wells. However, cursory analysis of the two well networks revealed few patterns unequivocally related to well type or depth that cannot be explained equally or more so by the location of wells and nearby land use. Put another way, location and land-use factors would have to be removed sufficiently to permit valid tests on well-type and depth influences.

Monitoring wells did differ statistically from supply wells in depth to open interval at a 95-percent confidence level (table 5 and figure 26). Median depth below water to the top of the open interval was 0 ft for monitoring wells and 60 ft for supply wells. The two well types did not differ significantly by depth to water from land surface.

Detection rates were higher in monitoring wells than in supply wells for all classes of organic compounds except gasoline components and insecticides (fig. 8). Although the median number of compounds in monitoring wells (8) was twice that in supply wells (4), this difference was not significant at the 95-percent confidence level but was nearly so, at 94-percent (table 5, p-value of 0.062). Differences in median VOC and pesticide concentrations also were not significant at 95-percent confidence but would be significant if confidence levels were relaxed to about 90 percent (p-values were 0.11 and 0.10). Figure 27 aids in understanding these findings: although median values are quite different between well groups for number of compounds, VOCs, and pesticides, the paired distributions overlap enough to reduce the statistical significance of the differences. The small sample sizes of the data sets also reduce statistical significance, particularly the 15-well sample count for monitoring wells.

Several factors besides depth may contribute to differences between the two well types, or may diminish statistical differences. Perhaps foremost among them is the biased spatial distribution of the monitoring wells. In contrast to the widespread, randomly selected spatial distribution of the public-supply wells, the monitoring wells are clustered in central Oahu where the predominance of chemicals were detected. Because this area has seen intensive use or application of solvents, fumigants, and herbicides, the monitoring-well network is biased towards detection of these compounds. The few compounds detected more commonly in public-supply wells (gasoline components and insecticides) were detected in

Table 5. Wilcoxon rank-sum test of differences between public-supply and monitoring wells, Oahu, Hawaii, January 2000 through August 2001

[Two-sided Wilcoxon test is a non-parametric test for difference between two groups of data; P-value is the probability that the group medians are the same; values less than 0.05 (bold and shaded) indicate with greater than 95% confidence that the group medians do indeed differ; *, value is close to 95% confidence level (within 2.5%); VOC, volatile organic compound; mg/L, milligrams per liter]

Chemical or physical attribute	**Do median values for supply wells and monitoring wells differ with 95% or greater confidence ?**	P-value	Median value out of 30 public-supply wells	Median value out of 15 monitoring wells
Organic compounds and nutrients				
Number of organic compounds	No *	0.062 *	4	8
Number of VOCs (excluding fumigants)	No	0.11	1	2
Number of pesticides (plus fumigants)	No	0.10	2	4
Nitrate concentration (mg/L)	No	0.215	0.92	1.9
Orthophosphate concentration (mg/L)	**Yes**	**0.014**	0.1	0.2
Land use within 500 meters of well				
Percentage of urban land use	**Yes**	**0.013**	54	15
Percentage of agricultural land use	No	0.18	1	34
Percentage of former agricultural land use	No	0.60	55	44
Well geometry				
Depth to top of open interval of well below water (feet)	**Yes**	**0.0000**	60	0
Depth to water from land surface (feet)	No	0.99	320	340
Water age and tracers				
CFC (chlorofluorocarbon) recharge date	**Yes**	**0.013**	1966	1976
Tritium concentration (tritium units)	**Yes**	**0.038**	0.26	0.63
Oxygen-18 isotopic ratio (per mill)	No	0.53	-3.2	-3.1

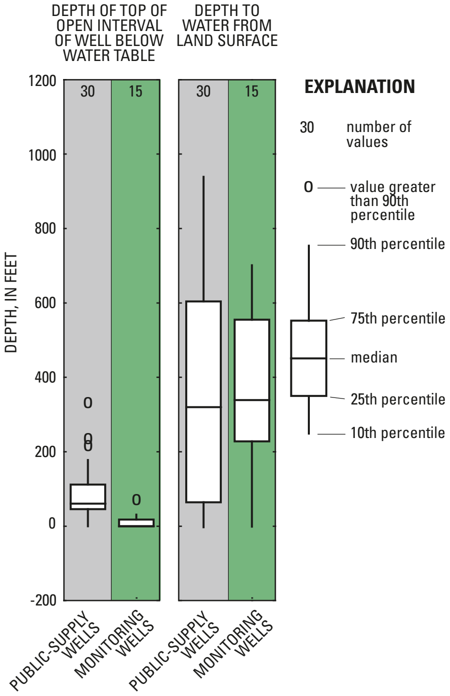


Figure 26. Comparison of physical characteristics between public-supply wells and monitoring wells, Oahu, Hawaii. Depth below water table to the top of the well's open interval was less for monitoring wells than supply wells. Depth to water from land surface did not differ statistically between the two types of wells.

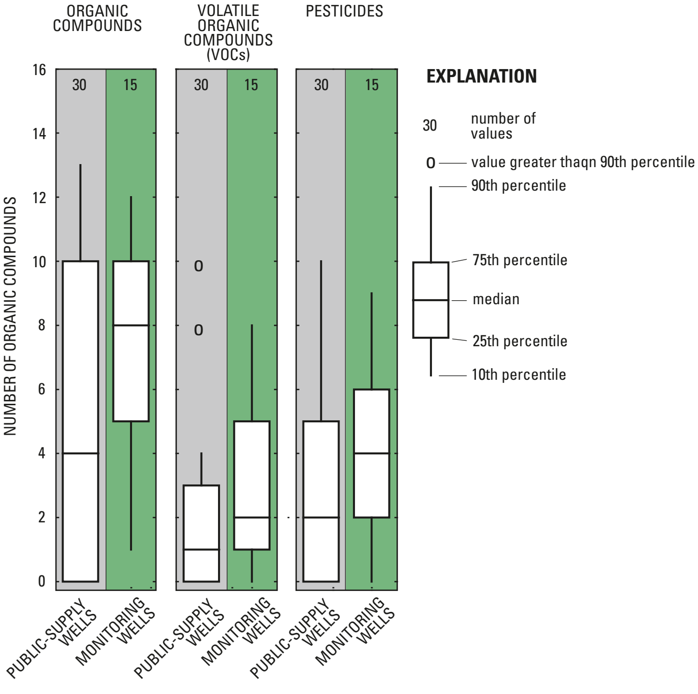


Figure 27. Comparisons between public-supply wells and monitoring wells for number of organic compounds, number of volatile organic compounds (VOCs), and number of pesticides, Oahu, Hawaii. Apparent differences between the two types of wells were not statistically significant at the 95-percent confidence level, but were nearly so.

Table 6. Spearman rank correlation of selected chemical and physical attributes within public-supply and monitoring well networks, Oahu, Hawaii, January 2000 through August 2001

[Correlation coefficient is non-parametric Spearman rho coefficient computed on rank-transformed data; larger magnitudes indicate stronger correlations; P-value is probability that the null hypothesis is true (no correlation); values less than 0.05 (bold and shaded) indicate correlations that are significant at greater than 95% confidence level; *. value is close to 95% confidence level (within 2.5%); nominal number of data pairs was 30 for public-supply wells and 15 for monitoring wells; lesser numbers are due to missing data; VOC, volatile organic compound; CFC, chlorofluorocarbon, N, number of wells]

Chemical and physical attributes, paired	Number of data pairs	Public-supply wells, N=30		Monitoring wells, N=15	
		Correlation coefficient	P-value	Correlation coefficient	P-value
Correlation with percent urban land use within 500 meters of well					
Number of organic compounds and urban use	30, 15	-0.27	0.15	-0.17	0.52
Number of VOCs (excluding fumigants) and urban use	30, 15	-0.18	0.32	0.32	0.24
Number of pesticides (plus fumigants) and urban use	30, 15	-0.22	0.23	-0.40	0.13
Nitrate concentration and urban use	30, 15	-0.37	**0.045**	-0.41	0.12
Correlation with percent agricultural land use within 500 meters of well					
Number of organic compounds and agricultural use	30, 15	0.49	**0.0085**	0.33	0.22
Number of organic compounds and former agricultural use	30, 15	0.50	**0.0075**	0.27	0.32
Number of VOCs (excluding fumigants) and agricultural use	30, 15	0.32	0.081	-0.40	0.13
Number of VOCs (excluding fumigants) and former agricultural use	30, 15	0.19	0.31	-0.54	**0.044**
Number of pesticides (plus fumigants) and agricultural use	30, 15	0.46	**0.014**	0.61	**0.023**
Number of pesticides (plus fumigants) and former agricultural use	30, 15	0.63	**0.0007**	0.74	**0.006**
Nitrate and agricultural use	30, 15	0.57	**0.0021**	0.68	**0.011**
Nitrate and former agricultural use	30, 15	0.65	**0.0005**	0.84	**0.0018**
Correlation with nitrate concentration					
Number of organic compounds and nitrate	30, 15	0.83	**0.0000**	0.41	0.13
Number of VOCs (excluding fumigants) and nitrate	30, 15	0.60	**0.0011**	-0.21	0.42
Number of pesticides (plus fumigants) and nitrate	30, 15	0.88	**0.0000**	0.74	**0.0058**
Correlation with depth to water from land surface					
Number of organic compounds and depth to water	30, 15	0.19	0.31	-0.01	0.95
Number of VOCs (excluding fumigants) and depth to water	30, 15	0.15	0.43	0.65	**0.015**
Number of pesticides (plus fumigants) and depth to water	30, 15	0.17	0.35	-0.66	**0.013**
Nitrate and depth to water	30, 15	0.20	0.28	-0.46	0.086
CFC recharge date and depth to water	29, 15	-0.36	0.056 *	-0.05	0.83
Tritium and depth to open water	29, 15	0.29	0.13	0.10	0.72
Correlation with depth to open interval of well below water					
Number of organic compounds and depth to open interval	30, 15	-0.22	0.24	-0.13	0.63
Number of VOCs (excluding fumigants) and depth to open interval	30, 15	-0.13	0.48	-0.37	0.17
Number of pesticides (plus fumigants) and depth to open interval	30, 15	-0.22	0.24	0.34	0.21
Nitrate and depth to open interval	30, 15	-0.18	0.32	0.22	0.42
CFC recharge date and depth to open interval	29, 15	-0.11	0.56	0.31	0.25
Tritium and depth to open interval	29, 15	-0.27	0.16	-0.30	0.26
Correlation with CFC recharge date (larger date=younger)					
Number of organic compounds and CFC recharge date	29, 15	0.51	**0.0075**	0.18	0.50
Number of VOCs (excluding fumigants) and CFC recharge date	29, 15	0.50	**0.0077**	-0.02	0.93
Number of pesticides (plus fumigants) and CFC recharge date	29, 15	0.44	**0.020**	0.46	0.086
Nitrate and CFC recharge date	29, 15	0.34	0.075 *	0.49	0.066 *
Orthophosphate and CFC recharge date	29, 15	0.25	0.18	0.32	0.23
Tritium and CFC recharge date	28, 15	0.33	0.085	0.17	0.52
Correlation with tritium "water age" (larger concentration=younger)					
Number of organic compounds and tritium	29, 15	0.52	**0.0057**	0.42	0.12
Number of VOCs (excluding fumigants) and tritium	29, 15	0.44	**0.019**	0.43	0.11
Number of pesticides (plus fumigants) and tritium	29, 15	0.43	**0.024**	0.08	0.76
Nitrate and tritium	29, 15	0.34	0.074 *	0.15	0.58
Orthophosphate and tritium	29, 15	0.56	**0.003**	0.64	**0.018**
Delta 18-oxygen/16-oxygen ratio and tritium	29, 15	0.29	0.13	0.12	0.66

urban Honolulu, again probably reflecting a difference in locale more than a difference due to well type or depth.

Various land-use and well attributes were subjected to correlation analysis to determine influences on water-quality results by well type (table 6). Strongest correlations were with agricultural land use and included the number of organic compounds, VOCs, and pesticides, as well as nitrate concentration (orthophosphate had similar results as nitrate). Most of these correlations were significant for supply wells and for monitoring wells. Organic compounds, VOCs, and pesticides were also strongly correlated with nitrate concentration (though this appears again to simply reflect the influence of agricultural land use) and with younger waters as indicated by apparent CFC recharge date and tritium concentration.

There may be important differences between monitoring and supply wells that are not obvious by comparing the two groups in their entirety. For example, three "recent-use" herbicides (bentazon, imazaquin, and metsulfuron methyl) were detected only in monitoring wells (table D1). The three compounds have been used on Oahu only since about 1990 and their detection may reflect early arrival at the water table and preferential detection in monitoring wells with shallow open intervals. Additional depth-related patterns in water quality might be discerned by exhaustive comparison of specific pairs of adjacent wells and careful consideration of compound breakdown products.

Most Ground Water Appears to be 10 to 50 Years Old, But Ages are Problematic

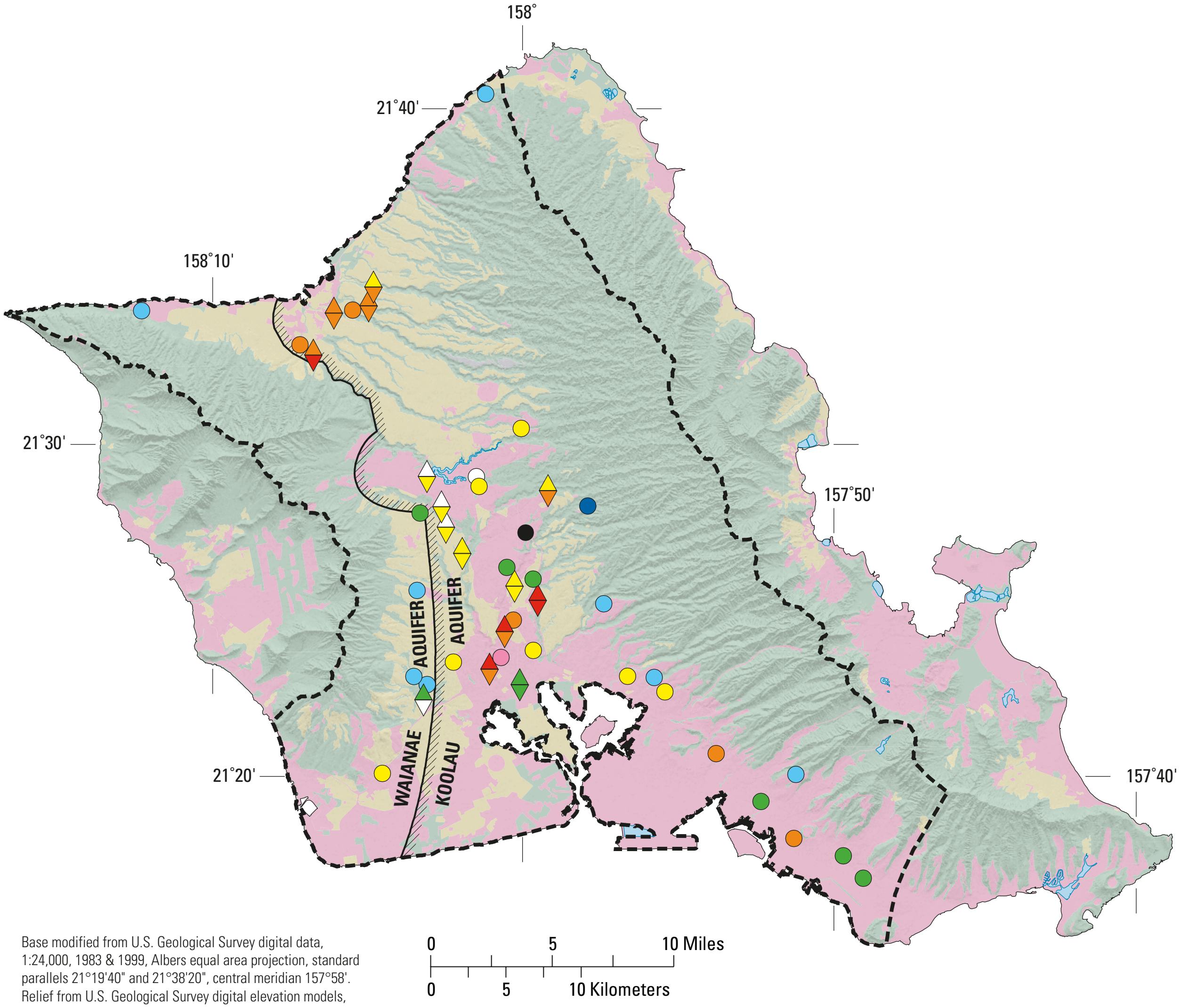
Water samples from all 45 wells sampled had some component of young water less than 50 years old, as indicated by CFC or SF_6 dates within this time span or by the presence of post-1953 bomb tritium (table D1 and figs. 28 and 29). Tritium-helium dating also was attempted but results are not reported here because of interference by natural terrigenic helium from the volcanic rocks.

Each dating method has limitations and potential interferences. The CFC (chlorofluorocarbon) and SF_6 (sulfur hexafluoride) methods date waters recharged since about 1941 and 1970, respectively, by comparing concentrations of these trace atmospheric gases dissolved in ground water with histories of atmospheric concentrations (Plummer and Busenberg, 1999). However, apparent ages can be biased by old air in the unsaturated zone and by contamination or degradation processes. The tritium method measures radioactive hydrogen-3 isotope (^3H) incorporated in the water molecule and truly tracks water through the hydrologic cycle. Tritium forms naturally in the upper atmosphere and is incorporated in rainfall at low background concentrations. It was also added to the atmosphere by nuclear weapons testing starting in 1953 and peaking in 1962 at concentrations several hundred-fold above background in rain. Tritium can be used to date ground water in only the most general sense on Oahu, by distinguishing "pre-bomb" (pre-1953) water from younger water containing higher concentrations of bomb tritium.

Tritium concentrations generally were lowest (0–0.3 tritium units, or TU) in Honolulu, in the Waianae aquifer, and in the eastern side of the central plateau (table D1 and fig. 29). These samples include possible pre-bomb waters (concentrations less than 0.1 TU) and probable mixtures of old water with small to moderate fractions of post-bomb water (0.1–0.3 TU). Highest tritium concentrations (0.4–1.8 TU) were scattered throughout the rest of the central plateau and at a few wells in the Koolau uplands. Values from 0.4 to 1 TU likely signify post-bomb water or mixtures of pre-bomb and post-bomb waters. Values greater than 1 TU also could mark mixtures of old and young waters, but are not readily distinguishable from entirely young waters recharged since about 1980. These interpretations are based on measurements of tritium in Hawaiian rain (fig. 30A) and concentrations representing radioactive decay of those initial tritium amounts (fig. 30B) up to 2001, when the second set of Oahu wells was sampled. The rain concentrations are annual values from measurements at Hilo, Hawaii from 1952 to 1990, with other years estimated by correlation with stations at Ottawa, Canada, and Midway Island (data and decay calculations are from M.A. Scholl, U.S. Geological Survey, written commun., 2003). Scholl's assumed pre-bomb background concentration of 1.0 TU has been replaced here by a value of 0.6 TU (average of five Oahu rain samples from 1953; Von Buttlar and Libby, 1955 as cited in Hufen and others, 1980).

Apparent recharge dates from CFC and SF_6 methods were post-1950 with two exceptions: a pre-1940s date and a 1947 date, both in the Koolau uplands of central Oahu (table D1 and fig. 28). Most dates were in the 1950s to 1980s time span. Older dates (1940s-1960s) were generally clustered in Honolulu, in the Waianae aquifer, and more toward the uplands in central Oahu. Younger dates (1970s-1990s) were generally clustered in central Oahu, with mostly 1970s dates near the top of the central plateau, and 1980s-1990s dates at lower elevations to the north and south. This general pattern of older dates in the uplands and younger dates downgradient is opposite the usual pattern expected in a ground-water flow system. Usually, younger dates mark newly recharged water in more active upland recharge zones, and older dates downgradient reflect travel time and aging of the water along flow paths. Interpretation of the Oahu pattern requires detailed consideration of recharge processes and timing as well as possible artifacts.

The CFC and SF_6 recharge dates are termed "apparent" because they can differ from true dates of recharge for a number of reasons. One distinction is that the dates reported here assume simple piston-flow displacement of older water by younger water in the hydrologic system, with no mixing of waters of different ages. In reality, mixed-age samples are expected as the rule and not the exception because most of the wells have open intervals tens to hundreds of feet long and will not obtain "point" samples of aquifer water.



Base modified from U.S. Geological Survey digital data, 1:24,000, 1983 & 1999, Albers equal area projection, standard parallels 21°19'40" and 21°38'20", central meridian 157°58'. Relief from U.S. Geological Survey digital elevation models, 1:24,000

EXPLANATION

LAND USE

🟨 Agriculture
🟪 Urban
🟩 Other (mostly forest)

- - - NAWQA GROUND-WATER STUDY AREA

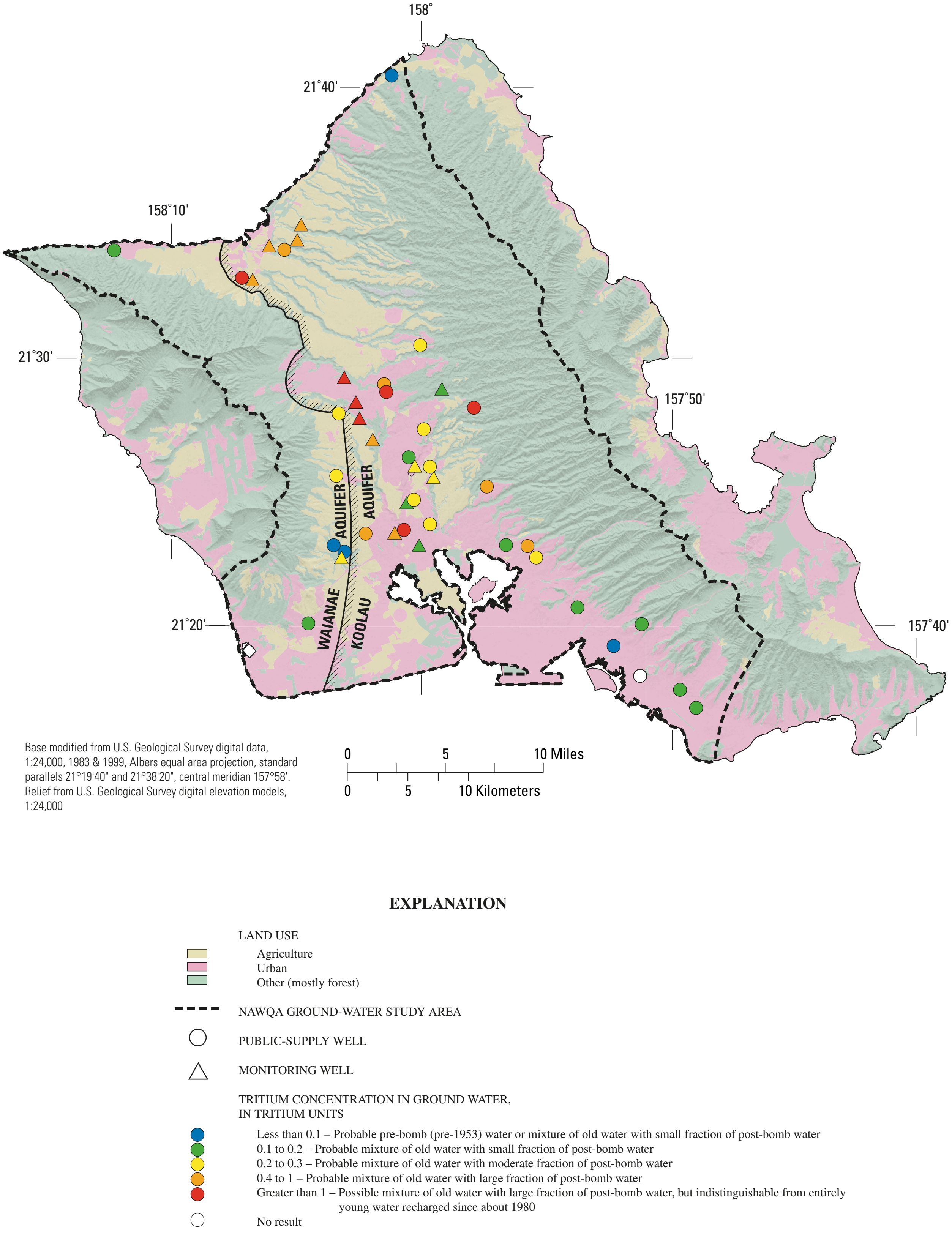
○ PUBLIC-SUPPLY WELL SAMPLED FOR CFCs

△ CFC ▽ SF_6 MONITORING WELL SAMPLED FOR CFCs AND SF_6

APPARENT RECHARGE DATE OF GROUND WATER, IN CALENDAR YEARS

● Pre-1940
● 1940s
● 1950s
● 1960s
● 1970s
● 1980s
● 1990s
● 2000s
○ No Result (Excess CFC or SF6 contamination at concentrations greater than possible by atmospheric deposition)

Figure 28. Distribution of apparent recharge dates from CFC (chlorofluorocarbon) and SF_6 (sulfur hexafluoride) methods, Oahu, Hawaii. Younger dates were clustered mostly in central Oahu.



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EXPLANATION

LAND USE

- 🟨 Agriculture
- 🟪 Urban
- 🟩 Other (mostly forest)

- - - - NAWQA GROUND-WATER STUDY AREA

○ PUBLIC-SUPPLY WELL

△ MONITORING WELL

TRITIUM CONCENTRATION IN GROUND WATER, IN TRITIUM UNITS

- 🔵 Less than 0.1 – Probable pre-bomb (pre-1953) water or mixture of old water with small fraction of post-bomb water
- 🟢 0.1 to 0.2 – Probable mixture of old water with small fraction of post-bomb water
- 🟡 0.2 to 0.3 – Probable mixture of old water with moderate fraction of post-bomb water
- 🟠 0.4 to 1 – Probable mixture of old water with large fraction of post-bomb water
- 🔴 Greater than 1 – Possible mixture of old water with large fraction of post-bomb water, but indistinguishable from entirely young water recharged since about 1980
- ○ No result

Figure 29. Distribution of tritium concentrations, Oahu, Hawaii. Low concentrations were clustered mainly in the Waianae aquifer, in Honolulu, and in a north-south band in south-central Oahu.

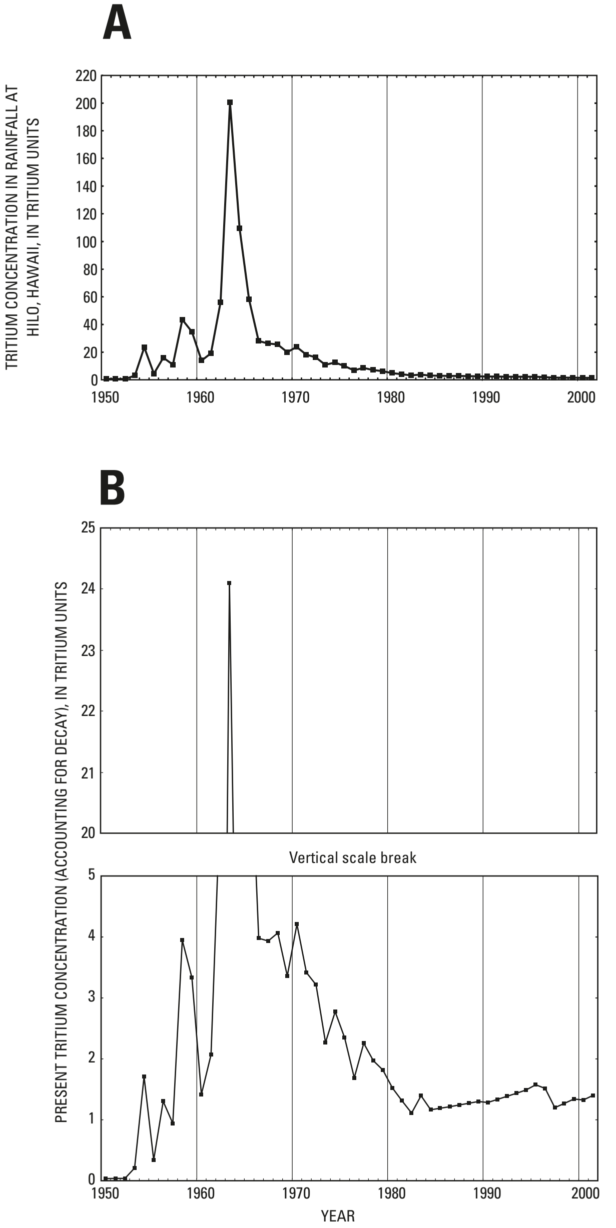


Figure 30. Tritium concentration in rain at Hilo, Hawaii (A) and after accounting for radioactive decay of tritium from the initial rain concentrations in the intervening years to present (B). Data and decay calculations are by Martha Scholl (USGS, written commun., 2003).

This appears to be borne out by the tritium data, which suggest mixed waters for many samples (fig. 29). “Unmixing” calculations are possible to some extent, but are complex and have not been attempted as of this writing.

Another distinction is that CFC and SF_6 dates mark the time when recharge was sequestered below the water table and no longer in contact with air, not the time when water first infiltrated below ground. Dissolved CFC and SF_6 concentrations are imparted under equilibrium with the last air contacted, which is unsaturated-zone air just above the water table and not the atmosphere at land surface. A time lag will be introduced as atmospheric air penetrates into the unsaturated zone. Air can migrate by diffusion (a slow process) through soil and weathered overburden and by advection (a faster process) through fractures and other permeable pathways in response to barometric pumping, wind, and thermal influences. Unsaturated-zone air will be older than atmospheric air and will impart an apparent date that is older than the true date of recharge (Plummer and Busenberg, 1999; Busenberg and Plummer, 2000). This old bias is most pronounced in thick unsaturated zones such as on Oahu, although it would be lessened where there is rapid advection of air through high-permeability pathways in the basaltic lavas. At 60 m (200 feet) depth to water in Snake River basalts beneath playa lake sediments, CFC ages were biased old by 20-23 years because of slow air diffusion (Plummer and Busenberg, 1999).

Degradation of CFCs also can impart an old bias. Chlorofluorocarbons degrade in anaerobic environments under sulfate-reducing or methanogenic conditions (Plummer and Busenberg, 1999). Degradation does not appear probable in Oahu saturated aquifers because all ground-water samples contained dissolved oxygen and no methane. However, CFCs may degrade in parts of the unsaturated zone. Some exposures of red saprolite in the study area contain greenish-gray bands where iron has been reduced from its ferric state (red) to its ferrous state (green). This suggests that anaerobic reducing conditions existed in the saprolite, most likely within perched water bodies.

Additional sources of CFCs or SF_6 besides the atmosphere can make apparent ages younger than true ages. Many water samples had concentrations in excess of possible atmosphere-water equilibrium concentrations (table D1). The excess concentrations could indicate anthropogenic contamination of CFCs or SF_6, or a natural terrigenic source of SF_6 from rocks or igneous fluids (Busenberg and Plummer, 2000). Only a few samples had excess concentrations sufficient to prevent dating, but other samples could have a young bias if partly contaminated.

Because CFC or SF_6 ages are set at the water table, they should not reflect infiltration time through the unsaturated zone. Instead, ages should correspond to the time it takes for water to move deeper into the aquifer once it has reached the water table, and to flow laterally downgradient to intercepting wells. Estimates of lateral pore velocity in the study area include 4 ft/d by Orr and Lau (1987) and 5-15 ft/d by Eyre (1987), a range of 0.28 to 1.0 mi/yr. Estimates for piston-flow infiltration time through the unsaturated zone in central Oahu include 3 years (Eyre, 1987), 8-10 years (also Eyre, 1987), and 15-20 years (Orr and Lau, 1987). The 3-year estimate was for infiltration through 50 feet of saprolite and 100 feet of unsaturated basalt at a dry, low-elevation site. The 8-year estimate was apportioned as 7 years for infiltration through 100 feet of saprolite and 1 year through 400 feet of unsaturated basalt. The 15-20 year estimate cited 13.5 years through 120 feet of saprolite and 5.25 years through 700 feet of unsaturated basalt. Eyre (1987) reviewed several rapid water-level responses to rainfall, on the order of months to a year, and inferred that these reflected piston-flow displacements of water from the bottom of the saprolite moisture profile rather than contributions of new water through the entire unsaturated zone via fractures, macropores, and other rapid pathways. He did equate the fast responses to infiltration time through unweathered basalt beneath the saprolite.

The unexpected pattern of older CFC dates in the uplands and younger dates downgradient (fig. 28) probably reflects artifacts as well as actual recharge processes. Some of the older CFC recharge dates appear to be biased by old unsaturated zone air, the best examples being the 1947 and pre-1940 dates at wells W01 and W24 in the Koolau uplands. These ages are contradicted by moderate to high tritium concentrations that indicate appreciable components of younger post-bomb (post-1953) water in the samples, and by the presence at W24 of fumigants and herbicides not introduce until the 1940's and 1950s (table D1 and fig. 29). Furthermore, wells W01 and W24 lie 4.5 and 6 miles from the probable ground-water divide near the Koolau mountain crest. Using the range of lateral travel times cited earlier (0.28-1.0 mi/yr), maximum travel times over these distances would be 18-21 years at the slower rate and 5-6 years at the faster rate. These are much shorter durations than the apparent CFC ages of 53 and 60+ years.

The Koolau uplands are mantled by a thick (100-300 feet) layer of clay-rich saprolite that is much less permeable than the unweathered basaltic lavas that comprise the deep aquifers. The saprolite thins at lower elevations, to about 50 feet or less at the north and south ends of the central Oahu plateau, and is also thinner in the drier Waianae uplands than in the wetter Koolau uplands. Vertical diffusion of air through the saprolite would be much slower where it is thickest, resulting in older unsaturated-zone air and older apparent CFC and SF_6 ages in the Koolau uplands compared to other areas. Even water recharging within the last decade or so could be tagged with an older apparent CFC age by equilibrating with old unsaturated-zone air at the water table. Alternately, CFC degradation could be more prevalent in the thicker, wetter saprolite of the Koolau uplands than in drier areas.

Apparent CFC and SF_6 dates may be less biased and closer to true recharge dates in other areas where saprolite is thinner. Furthermore, stream valleys at the dry north and south ends of the central plateau have vertical walls as much as 150 feet high that expose layers of permeable, unweathered basaltic lavas, and valley walls in Honolulu expose partly weathered rock. Unweathered valley walls should allow advective ventilation of young unsaturated-zone air that would impart truer apparent recharge ages. Notably, apparent CFC and SF_6 recharge dates in the Waianae aquifer and in Honolulu are somewhat more in line with tritium data than in the Koolau uplands.

Irrigation may have contributed to young CFC and SF_6 ages in downgradient areas of central Oahu by supplying large volumes of young recharge. This would represent an actual hydrologic process rather than an artifact. High-rate furrow irrigation of sugarcane prevailed until conversion to low-rate drip irrigation in the mid-1980s. Return recharge from furrow irrigation in central Oahu was estimated at 84-97 in/yr, far exceeding natural recharge recharge of 4-5 in/yr in those areas and surpassing rates in much wetter mountainous areas (Giambelluca, 1986). Volumetrically, much of the upper layer of ground water beneath former sugarcane fields may have originated as pre-1985 irrigation-return recharge, with comparatively little recharge from rainfall or drip irrigation having been added in later years. Clusters of apparent dates in the 1970s and 1980s could reflect a large influx of irrigation-return recharge before irrigation rates were reduced sharply. If "old" ground water was pumped and applied to fields, this might explain waters in the southeast corner of central Oahu that have low tritium concentrations but CFC and SF6 dates in the 1970s-1990s (figs. 28 and 29). The CFC and SF6 signatures would be "reset" younger by exposure with the atmosphere and unsaturated-zone air, whereas the tritium dates would not be reset; the water would maintain an "old" tritium signature.

Irrigation may also have contributed to organic and nutrient contamination in central Oahu. Application of water in excess of plant needs would tend to leach or flush contaminants from the soil to deep aquifers rather than allowing them to stay in the soil and degrade more fully or be removed by plant uptake. Leaching would tend to be greater where more irrigation water was applied

Complex Mixtures of Organic Compounds Were Prevalent

Mixtures of organic compounds in ground water are of particular interest for human-health reasons. Toxicologists have evaluated health risks and established drinking-water regulations for many single compounds but risks associated with compound mixtures are far less known and may be greater than those of single compounds in some cases (Carpenter and others, 1998; Bartsch and others, 1998). NAWQA datasets provide a recent opportunity for evaluating the occurrence of compound mixtures in the environment as, for example, in Stackleberg and others (2001) and Squillace and others (2002).

Compound mixtures were prevalent in Oahu ground-water samples (fig. 31). Multiple organic compounds were detected in 63 percent of public-supply wells and 93 percent of monitoring wells (table 2). Mixtures of VOCs and pesticides were detected in 53 percent of public-supply wells and 80 percent of monitoring wells. Wells having higher concentrations tended to contain greater numbers of compounds (table D1). Many wells in central Oahu contained several classes of compounds such as solvents, fumigants, and pesticides (fig. 32). Samples with high solvent concentrations contained multiple solvents (fig. 33), as many as ten. Samples with high fumigant concentrations contained three to four fumigants (fig. 34) as well as herbicides and solvents, mostly at trace concentrations below reporting levels. Herbicides also tended to occur together (fig. 35), with as many as ten herbicides and breakdown products detected in one sample.

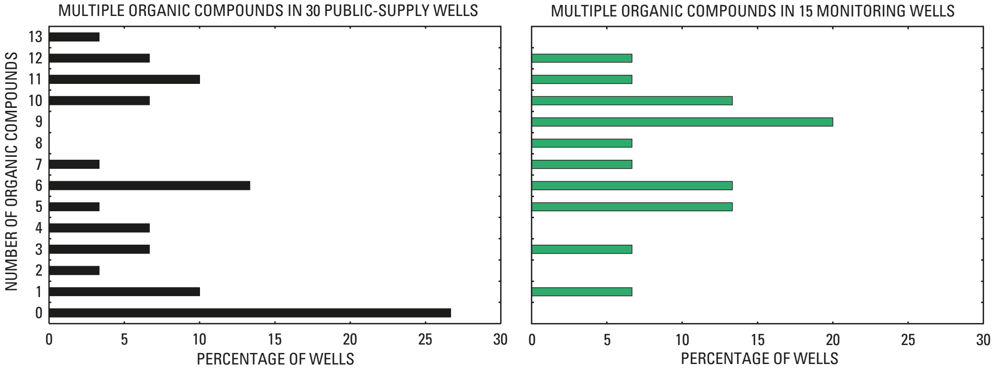
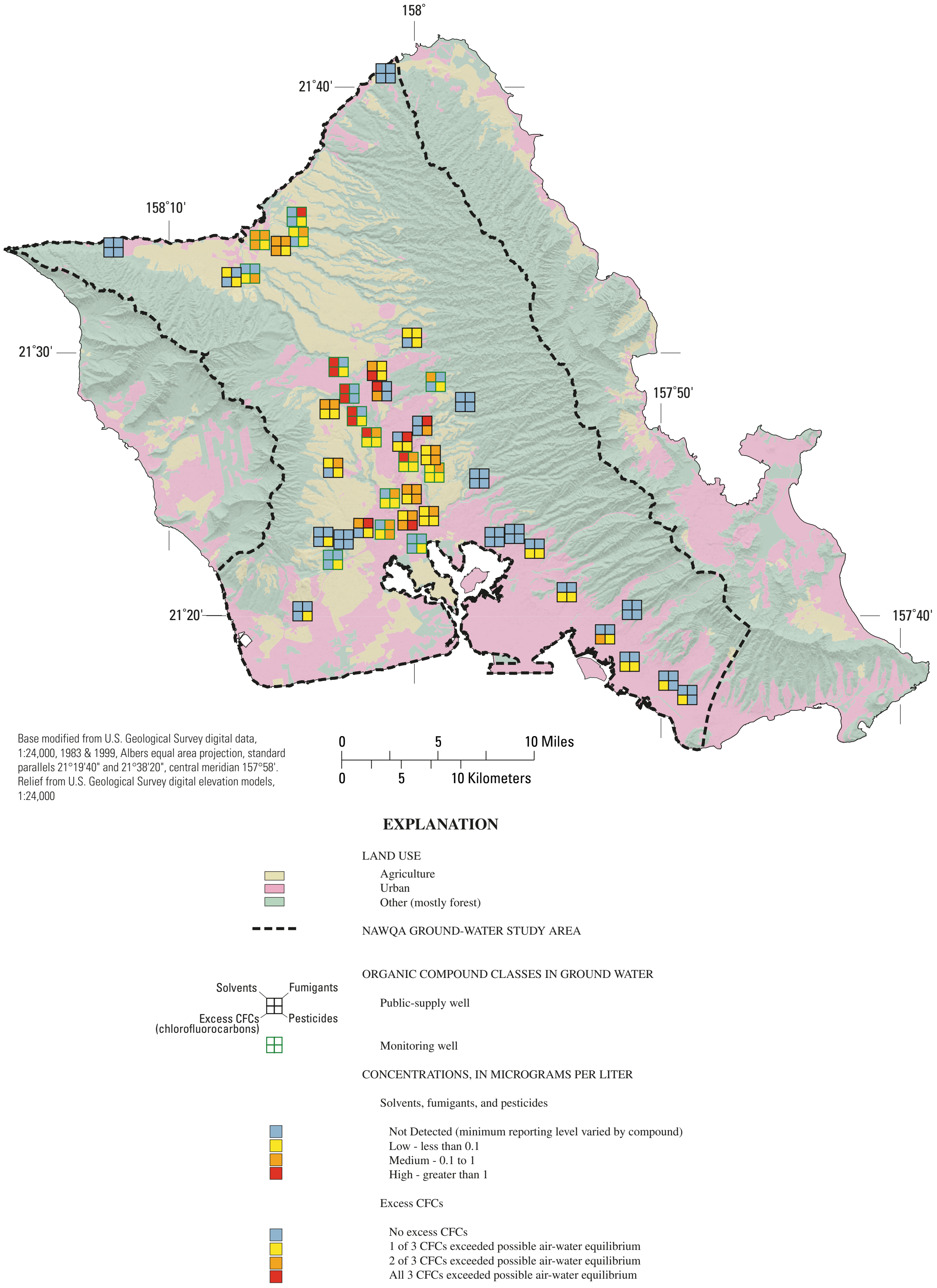
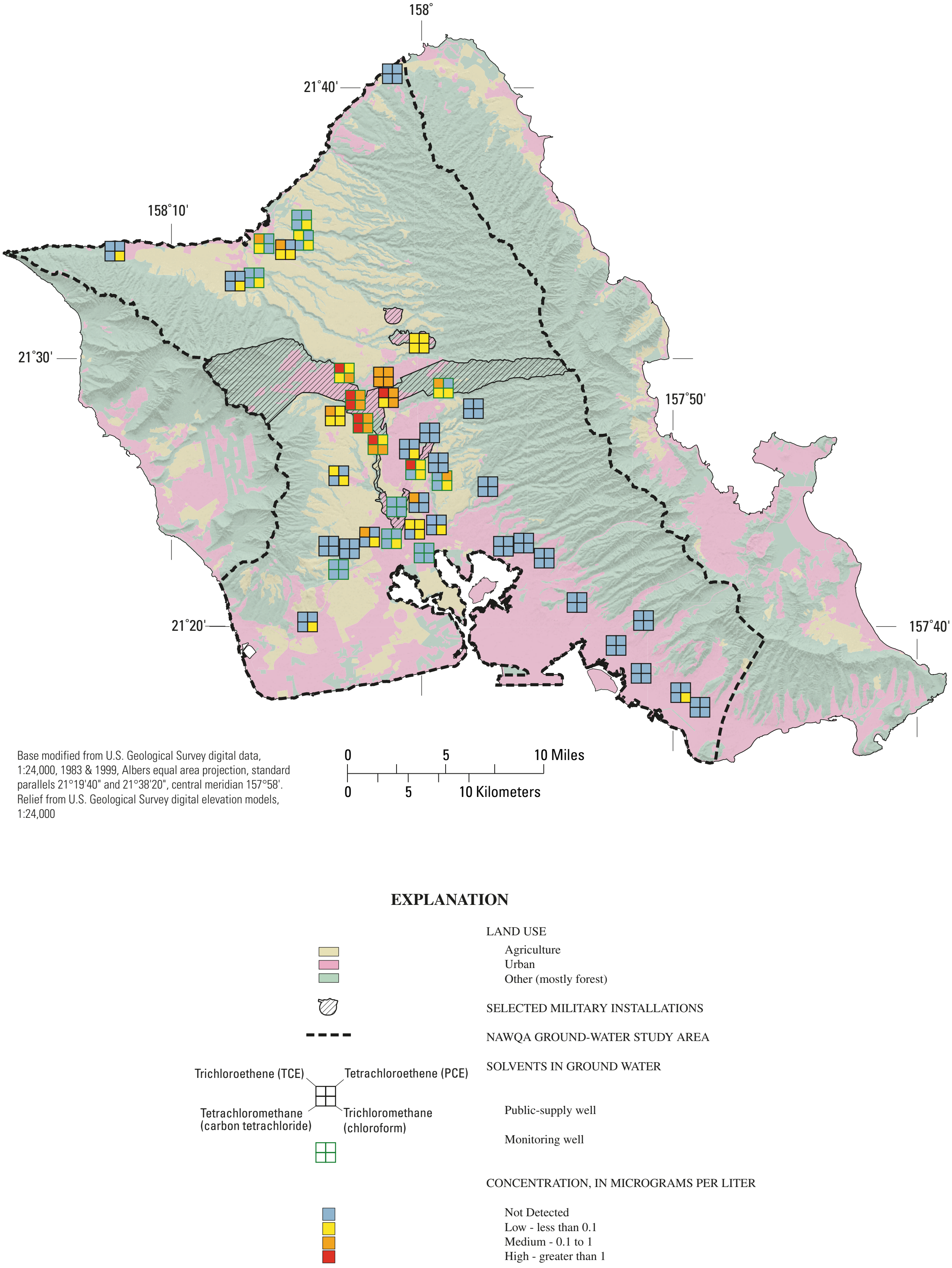


Figure 31. Compound mixtures in public-supply and monitoring wells, Oahu, Hawaii. Most wells contained two or more organic compounds. As many as 13 compounds were detected in one public-supply well.



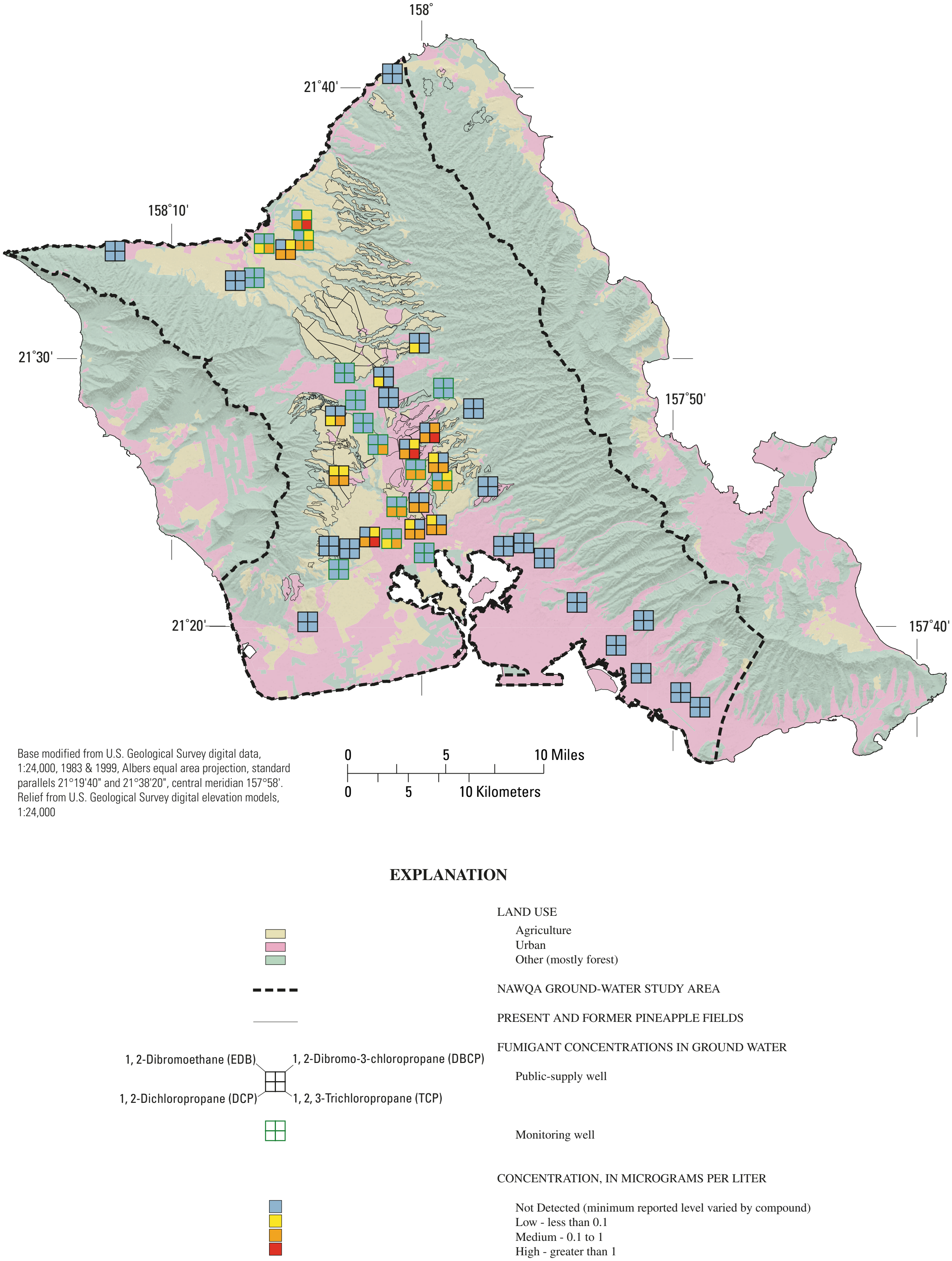
Base modified from U.S. Geological Survey digital data, 1:24,000, 1983 & 1999, Albers equal area projection, standard parallels 21°19'40" and 21°38'20", central meridian 157°58'. Relief from U.S. Geological Survey digital elevation models, 1:24,000

Figure 32. Distribution of organic compound mixtures in public-supply and monitoring wells, Oahu, Hawaii. Wells in urban-military and agricultural lands in central Oahu had the highest concentrations and greatest number of compound classes.



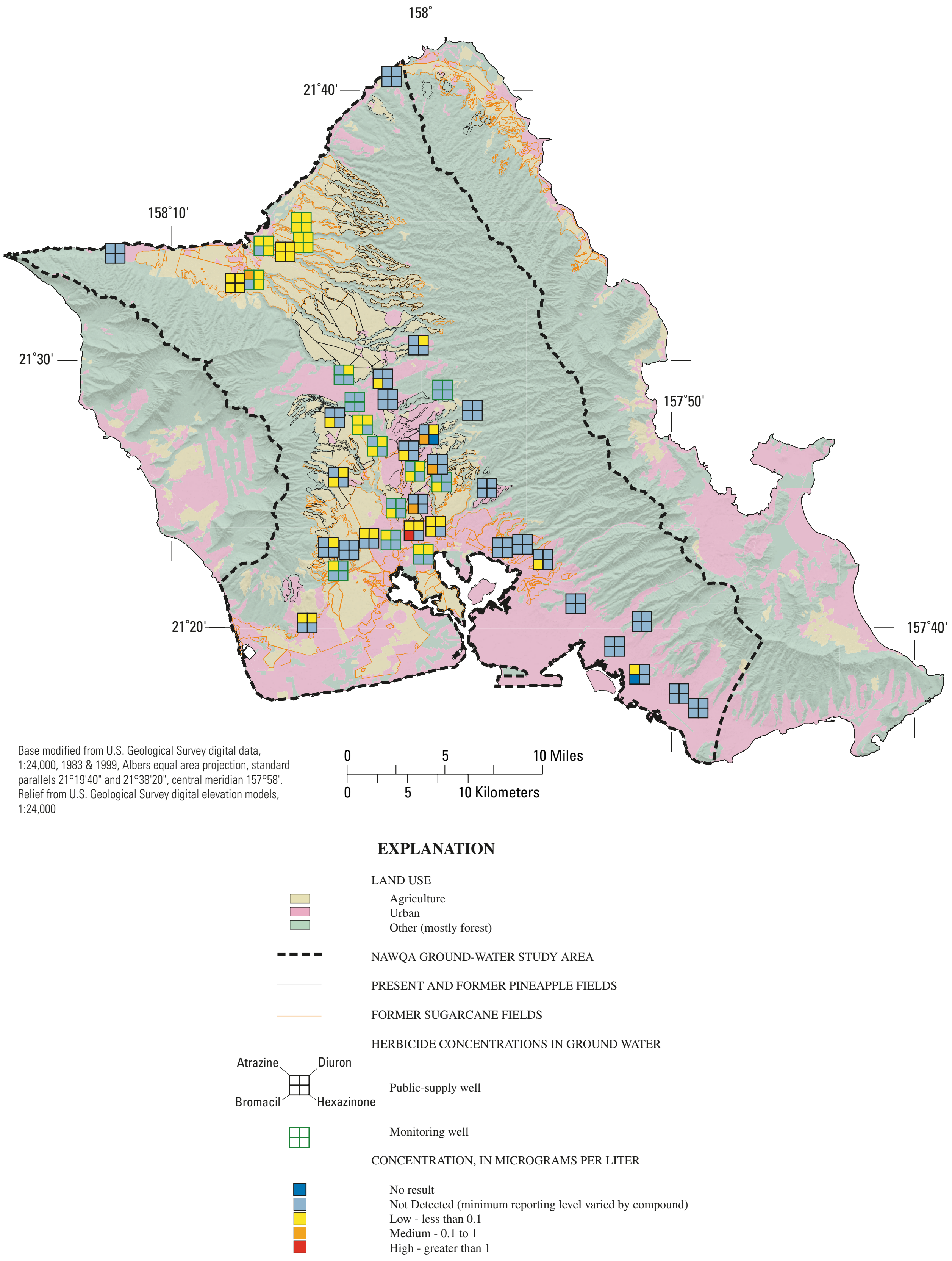
Base modified from U.S. Geological Survey digital data, 1:24,000, 1983 & 1999, Albers equal area projection, standard parallels 21°19'40" and 21°38'20", central meridian 157°58'. Relief from U.S. Geological Survey digital elevation models, 1:24,000

Figure 33. Distribution of solvent mixtures, Oahu, Hawaii. Wells in urban-military lands in central Oahu had the highest concentrations and greatest number of solvent compounds.



Base modified from U.S. Geological Survey digital data, 1:24,000, 1983 & 1999, Albers equal area projection, standard parallels 21°19'40" and 21°38'20", central meridian 157°58'. Relief from U.S. Geological Survey digital elevation models, 1:24,000

Figure 34. Distribution of fumigant mixtures, Oahu, Hawaii. Wells in or downgradient from present and former pineapple fields in central Oahu had the highest concentrations and greatest number of fumigant compounds.



Base modified from U.S. Geological Survey digital data, 1:24,000, 1983 & 1999, Albers equal area projection, standard parallels 21°19'40" and 21°38'20", central meridian 157°58'. Relief from U.S. Geological Survey digital elevation models, 1:24,000

Figure 35. Distribution of herbicide mixtures, Oahu, Hawaii. Wells in present and former agricultural lands in central Oahu had the highest concentrations and greatest number of herbicide compounds.

Some possible explanations for the widespread detection of compound mixtures are obvious, others are less so. Composition and use of particular product formulations are probable factors. For example, co-occurrence of multiple solvent compounds in a sample could reflect the use and release of several individual solvents, solvent blends, or manufacturing impurities or intermediates. Impurities found in commercial trichloroethene products include chloroform, carbon tetrachloride, tetrachloroethene, cis-1,2-dichloroethene, trans-1,2-dichloroethene, 1,1,2-trichloroethane, 1,1,1,2-tetrachloroethane, 1,2-dichloroethane, 1,1-dichloroethene, bromodichloromethane, bromodichloroethene, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, pentachloroethane, and benzene (U.S. Dept. of Health and Human Services, 2002). Notably, the first 10 of these 15 compounds were present in central Oahu water samples having the highest trichloroethene concentrations (table D1). Similarly, 1,2-dichloropropane (DCP) and 1,2,3-trichloropropane (TCP) are both components in DD fumigant and tended to be detected together (fig. 34).

Degradation is a likely explanation for the presence of some compounds. Several herbicide breakdown products were detected along with their parent compounds (table D1), and some solvent compounds are known breakdown products of others. For example, tetrachloromethane (carbon tetrachloride) breaks down into trichloromethane (chloroform) and dichloromethane. Breakdown products of tetrachloroethene (PCE) include trichloroethene (TCE), 1,1-dichloroethene, *cis*-1,2-dichloroethene, and trans-1,2-dichloroethene.

Mixed land use and coalescing contaminant plumes may have contributed mixtures of disparate compounds (for example, agricultural chemicals *and* industrial solvents). Although land use near Oahu NAWQA wells was characterized (table D1), each well's results need not correspond only to land use directly above it. Complicating factors include the length and depth of the well’s open interval and the pumping rate. The longer the open interval and the deeper it is below the water table, the more likely that the well will intercept ground water originating farther upgradient in the watershed than water recharging from directly above. Even if the well is open at the water table, a long open interval will draw a mixture of waters recharged both locally and upgradient. And the greater the pumping rate, the more water will be drawn from farther away. As a result, contributing recharge areas of many wells encompass a mix of land uses. This is more true of public-supply wells than the monitoring wells, which were pumped at much lower rates and generally had shorter open intervals. In central Oahu, the end result of these factors is that wells are likely to contain a mix of agricultural fumigants and herbicides from local recharge and industrial solvents carried in dilute ground-water plumes from upgradient urban-military areas.

Application practices may have contributed to detections of compound mixtures. Fumigant-herbicide mixtures may simply reflect that both have been applied on agricultural lands. Co-occurrence of multiple fumigants could reflect sequential application of single fumigants or application of fumigant mixtures; for example 1,2-dibromo-3-chloropropane (DBCP) typically was applied together with DD fumigant in the study area (Yim and Dugan, 1975). Detection of herbicide mixtures could similarly reflect application of multiple herbicides, either in succession or in combination.

Although solvent-class compounds might not be expected in ground water beneath rural or agricultural lands, they are commonly being detected by the NAWQA program nationwide (Squillace and others, 1999, 2002). Co-occurrence of trace-level solvents with fumigants and herbicides in central Oahu could reflect mixing of multiple urban and agricultural contaminant plumes. However, application practices and composition of fumigant and herbicide formulations may also be contributing factors. Regarding application practices, fumigants were sometimes mixed with diesel fuel, paint thinner, or white gas on Oahu (Orr and Lau, 1987; U.S. Department of Health and Human Services, 1995). Solvent-class compounds are not main components of diesel fuel or white gas, but "paint thinner" is a general term encompassing formulations that do contain solvent compounds. Regarding composition, many pesticide formulations contain "adjuvants," a general term for additives that act as carrier solvents, dispersal or wetting agents, or in a host of other capacities. Solvent-class compounds and CFCs are known adjuvants or manufacturing intermediates in pesticide synthesis. Pesticide labeling laws do not require disclosure of compounds other than the main active ingredient, however, and so other components are lumped together under the term "inert ingredients" despite the fact that they may comprise as much as 95 percent of the formulation by weight and are not necessarily "inert" with respect to human health or the environment. Additives or intermediates in product formulations provide a plausible explanation for widespread co-occurrence of trace-level solvents with fumigants and herbicides in central Oahu.

Chloroform And CFC Contamination Were Closely Associated With Other Compounds

Widespread detections of trichloromethane (chloroform) and excess CFCs do not correspond to any explicit, known use in the study area. Co-occurrence of chloroform and excess CFCs with other solvents, fumigants, and pesticides suggests that they may have originated mainly as intermediates or impurities in other products, or by degradation of parent compounds in the environment.

Chloroform was the most commonly detected organic compound in this study, being present in 47 percent of public-supply wells and 73 percent of monitoring wells (table 2 and fig. 16). Chloroform is one of a class of compounds known as trihalomethanes that form when water containing organic compounds is disinfected with chlorine. Recharge of chlorinated water from leaking distribution pipes, lawn watering, or wastewater effluent is thought to contribute chloroform to ground water in many areas (Squillace and others, 1999; Bender and others, 2000). But chloroform is a common solvent itself, a feedstock or intermediate in organic synthesis of other VOCs and pesticides, and a breakdown product of tetrachloromethane (carbon tetrachloride). Complicating the situation further, chloroform has natural sources in the terrestrial and marine environments, being produced in soil (Laturnus and others, 2000) and by macroalgae that also produce other trihalomethanes (Nightingale and others, 1995). These natural sources can account for only the lowest, trace-level concentrations observed in the NAWQA sampling, however.

Most water samples in which chloroform was detected also contained other solvents, fumigants, or pesticides. Chloroform was at highest concentration where solvents such as trichloroethene or carbon tetrachloride also were highest (table D1) and was at trace concentrations below 0.1 µg/L where it otherwise co-occurred with fumigants, pesticides, or trace concentrations of solvents. These relations suggest that most chloroform contamination in the study area originated together with other compounds (especially solvents) or by their breakdown. A disinfection origin cannot be ruled out for some detections, however, particularly for trace concentrations and where chloroform was the only compound detected (or one of only a few compounds detected). It is unlikely that chloroform forms pervasively in soil in the study area because it was mostly undetected in wells that reflect "background" conditions, such as those in forested areas and urban Honolulu (table D1). A disinfection origin for trihalomethanes is strongly suggested for only one well, W05, which contains all four trihalomethanes (table D1). If disinfection is the origin, it probably was a sampling artifact rather than a true measure of trihalomethanes in the aquifer because there is no known disposal of chlorinated water upgradient from the well. Water is chlorinated at the wellhead and, although it was disconnected during sampling, residual concentrations of trihalomethanes may have somehow contaminated the sample. Alternately, all four trihalomethanes could truly be present in ground water from a marine algae source of the compounds. Well W05 is located where prevailing winds blow ocean spray onto the land most days of the year. The likelihood of this source carrying trihalomethanes to ground water at the observed concentrations could be clarified by analysis of rainwater samples from the area.

Excess CFCs (chlorofluorocarbon refrigerants) were present in 47 percent of public-supply wells and 67 percent of monitoring wells (table 2 and fig. 16). Most of these samples also contained solvents, fumigants, or pesticides (table D1). CFCs are known manufacturing intermediates or additives in other VOCs and pesticides, and this may explain the co-occurrence of excess CFCs with these other compounds. If not already present in other chemical products, CFCs may partition preferentially from the atmosphere into highly concentrated VOCs or pesticides in the environment (such as in shallow soil) and thence into water at higher concentrations than would be possible by single-component, air-water equilibrium (Cook and Solomon, 1997). Notably, a common application practice for fumigants and some pesticides is to cover the application with plastic sheeting (a "vapor barrier") to enhance pesticide potency by inhibiting evaporation and maintaining a high concentration in the soil. This practice may provide a favorable environment for enhanced partitioning of CFCs from the atmosphere into the fumigant or pesticide within the shallow soil. A localized spill or disposal of concentrated solvent to shallow soils could represent a similarly favorable environment for enhanced partitioning of CFCs from the atmosphere to the solvent and thence to ground water.

Organic Contamination Reflects Decades-Old Releases And Former Land Use

Apparent recharge dates from CFC and SF_6 methods ranged from pre-1940s to present, with most dates in the 1950s to 1980s time span (table D1 and fig. 28). Although there is uncertainty in some of the dates, if they are roughly representative then most organic and nutrient contamination in central Oahu probably originated from applications or spills 20-50 years old or older. Where land use has changed during this period, water quality more likely reflects former land use than present land use.

If it takes several decades for water to flow through the hydrologic system, flushing of organic compounds will take even longer, on the order of decades to a century. Transport of organic compounds is delayed by retardation (the tendency for a compound to adsorb to soil particles or natural organic carbon in the soil and desorb later) and dispersion (solute spreading). Retardation delays the time of peak concentration of a compound in ground water beyond the average travel time of water alone. And because of dispersion, once the peak concentration has passed a certain point in the aquifer, concentration will decline gradually in a long, tapering tail. For example, using computer simulation, Orr and Lau (1987) estimated that DBCP concentrations in a central Oahu well would increase from 1983 through 2000 before beginning a long decline thereafter.

For the most part, it is probably too soon for chemicals associated with recent land-use changes (such as the residential urbanizition of central Oahu) to have been detected in most wells. It may also be possible that urban chemicals have migrated to ground water already but that a "recent-urban signature" is difficult to recognize against the background of older contamination.

Monitoring Wells May Be Useful For Early Detection

Three "recent-use" herbicides were detected in monitoring wells: bentazon, imazaquin, and metsulfuron methyl (table D1 and fig. 17). The compounds were detected in only one well each. These herbicides are used primarily for turf grass maintenance and have been used on Oahu only since about 1990 (Robert Boesch, Hawaii Department of Agriculture, oral commun., 2002). Their detection indicates that they have leached to deep ground water within a decade or so, which is reasonable because they were detected in a dry area where saprolite is thin.

Monitoring wells that are open only a short depth below the water table have the best chance of characterizing recent contaminant transport associated with present land use. Although it takes some time for recharge to make its way from land surface to the deep aquifer, monitoring wells offer the best opportunity for collecting an isolated sample of the youngest water presently arriving at the water table. This type of "early warning" role for monitoring wells may be useful for evaluating whether newly introduced chemicals leach to deep ground-water before fully degrading. There also may be a role for direct monitoring at the deep water table where wastewater is reused via land application. Wastewater indicators (inorganic major and trace elements; pharmaceuticals and personal care products; caffeine) could be diagnostic in identifying or quantifying the wastewater fraction in recharge arriving at the water table.

POLICY IMPLICATIONS

Although the USGS NAWQA program has no regulatory role, results from the program may be useful to policy makers and others involved in land-use planning, engineering, chemical handling and application, and human health.

Most organic and nutrient contamination in Oahu's deep aquifers appears to reflect decades-old releases and close association with agricultural and military land uses. To a large degree, most of the observed contamination appears to be an "old" problem associated with outmoded or banned practices. Chemical application and handling have improved markedly in recent decades in comparison to standards prevailing in the mid-1900s when most of the observed contamination probably originated. Pesticides and soil fumigants having high toxicity or environmental persistence have been discontinued and replaced with compounds that are less toxic or degrade quicker. Requirements for the use, storage, and disposal of solvents and fuels are much more stringent than in the 1940s and 1950s, when common practice was for disposal directly on the ground, to sumps that drained to the shallow subsurface, or to landfills in drums or other containers. Present users of large volumes of chemicals, (such as agriculture, industry, and the military) follow strict handling and disposal procedures that were yet to be developed a half century ago. And compared to previous decades, there is now a much greater awareness among the general public of the need for proper disposal of household solvents, paint thinners, and pesticides.

Recent land-use changes on Oahu may bring new issues or new compounds to greater prominence in the future. A notable change is the ongoing large-scale conversion of former agricultural lands in central Oahu to residential suburban use. On the basis of results from this study, it appears to be too early to discern a distinct water-quality signature that may accompany the newer suburban land use. However, the newer urban land use likely will contribute much less chemical loading to soil and ground water than former agricultural use, in which fertilizers and pesticides were applied intensively and high-rate irrigation enhanced leaching.

Another notable land-use change is the ongoing decentralization of former mono-crop sugarcane cultivation to diversified-crop agriculture. Several issues accompany this change: the attendant decentralization of pesticide use and oversight; use of a greater variety of pesticides than the few used by large-scale plantations; differences in pesticide and fertilizer leaching associated with a diversity of crops and irrigation regimes. Again, results from the 2000-2001 NAWQA ground-water samples have little direct bearing on these mechanisms because their effects have yet to reach the deep water table to any large degree. However, the detection of several recent-use herbicides in this study seems to illustrate the utility of shallow-penetration monitoring wells for gaining an early warning of anticipated water-quality changes.

Re-use of treated wastewater by land application is being considered in Hawaii, and a pilot program is already underway in central Oahu. The method has several desirable aspects, one being that it provides additional recharge to aquifers and another being the environmental and cost advantages of not discharging the effluent to streams or piping it to the coast for offshore disposal. Effects on ground-water quality are not fully known, however, and detailed studies of effects will likely accompany any large-scale reuse/application progam. Direct monitoring of ground water would appear to be a likely component in such studies, using shallow-penetration monitoring wells to sample deep ground water, and even shallower monitoring wells or lysimeters in soil and saprolite to obtain younger water samples that would show earlier effects. New laboratory methods are available to detect compounds such as pharmaceuticals and personal care products that are present in wastewater, and stable isotopes and inorganic major and trace elements also may show particular wastewater signatures. Similar approaches would be useful in evaluating the leaching potential of new pesticides under full-scale field conditions.

Finally, the health of nearshore marine waters is a focus of increasing interest nationally and in Hawaii. Most concern is with surface-water loads of sediment and nutrients delivered to coastal waters by streams. However, the role of ground water in carrying nutrient and other chemical loads to nearshore waters cannot be overlooked. Stream contributions are large in magnitude but are episodic, whereas ground-water contributions are steady and ongoing every day of the year. Best management practices that reduce nutrient runoff and leaching can help reduce nutrient loads to nearshore waters. Perhaps foremost in importance are the need to avoid overapplication of fertilizers and to time applications so as to avoid high-intensity rainfall events that cause surface runoff and enhance leaching through soils.

SUMMARY AND CONCLUSIONS

Water quality in the main drinking-water source aquifers of Oahu was assessed by a one-time sampling of untreated ground water from 30 public-supply wells and 15 monitoring wells. Organic compounds were detected in 73 percent of public-supply wells, but mostly at low concentrations below drinking-water regulations and even below minimum laboratory reporting levels. Of 43 organic compounds detected, 26 were volatile organic compounds (VOCs), 16 were pesticides, and the remaining compound was caffeine. Subclasses of VOCs that were prevalent throughout the area included solvents, fumigants, and trihalomethanes.

In contrast, gasoline components and refrigerants were detected in very few wells using standard VOC methods. Of the two pesticide subclasses, herbicides were prevalent and insecticides were scarce.

Characteristic suites of chemicals were associated with particular land uses. In central Oahu, solvents were associated with urban and military lands whereas fumigants, herbicides, and fertilizer components nitrate and phosphorus were associated with agricultural lands. Somewhat unexpectedly, very little contamination was detected in areas of highest urban density in Honolulu, most likely as a consequence of sound land-use planning, favorable aquifer structure, and less intensive application of chemicals (or of less mobile chemicals) compared to agricultural areas.

Water quality was within drinking-water regulations in all but a few cases. Concentrations exceeding USEPA Maximum Contaminant Levels (MCLs) included the solvent trichloroethene and the radionuclide Radon-222 in one public-supply well each. Concentrations of soil fumigants 1,2,3-trichloropropane (TCP) and 1,2-dibromo-3-chloropropane (DBCP) exceeded State of Hawaii MCLs (which are lower than Federal MCLs) in four supply wells. Complex mixtures of organic compounds were common: most water samples contained multiple solvents, fumigants, or herbicides, and many samples contained compounds from two or all three of these classes. With regard to aquatic-health quidelines, phosphorus concentrations in much of central Oahu were greater than the USEPA recommended goal for avoiding nuisance plant growth in moving waters. Nutrients, VOCs, and pesticides carried to streams and coastal waters by ground water may affect stream ecology or the health of coral reefs.

Most organic and nutrient contamination appears to reflect decades-old releases and former land use. Apparent recharge dates for ground-water samples ranged from pre-1940 to the present, with most dates falling in the 1950s to 1980s time span. Several widely detected compounds were discontinued from use as long ago as the 1970s but have yet to be flushed from the ground-water system. Although large tracts of central Oahu have been converted from sugarcane to residential urban use since the 1950s, water quality more closely reflects the former agricultural land use, and it appears to be too early to detect a water-quality signature characteristic of the newer urban use.

Emerging local issues in ground-water quality include ongoing organic and nutrient leaching, proposed land application of treated wastewater effluent, and the ongoing decentralization of former mono-crop sugarcane cultivation to diversified-crop agriculture, with attendant decentralization of oversight in pesticide application and handling. Shallow-penetration monitoring wells could be a valuable component in ongoing water-quality monitoring efforts for these and other issues.

REFERENCES CITED

Bartsch, R., Forderkunz, S., Reuter, U., Sterzl-Eckert, H., and Griem, H., 1998, Maximum workplace concentration values and carcinogenicity classification for mixtures: Environmental Health Perspectives, v. 106, supplement 6, p. 1291–1293.

Bender, D.A., Zogorski, J.S., Luo, Wentai, Pankow, J.F., Majewski, M.S., and Baker, R.J., 2000, Atmosphere-water interaction of chloroform, toluene, and MTBE in small perennial urban streams, *in* Air & Waste Management Association Conference and Exposition, 93rd, Salt Lake City, Utah, June 18-22, 2000 [Proceedings]: Sewickley, Penn., Air & Waste Management Association [CD-ROM] Paper # 706.

Brasher, A.M., and Anthony, S.S., 2000, Occurrence of organochlorine pesticides in stream bed sediment and fish from selected streams on the island of Oahu, Hawaii, 1998: U.S. Geological Survey Fact Sheet 140-00, 6 p.

Busenberg, E., and Plummer, L.N., 1997, Use of sulfur hexafluoride as a dating tool and as a tracer of igneous and volcanic fluids in ground water: Geological Society of America, Salt Lake City, 1997, Abstracts and Programs, v. 29(6), p. A-78.

Busenberg, E., and Plummer, L.N., 2000, Dating young groundwater with sulfur hexafluoride—Natural and anthropogenic sources of sulfur hexafluoride: Water Resources Research, v. 36, no. 10, p. 3011–3030.

Carpenter, D.O., Arcaro, K.F., Bush, B., Niemi, W.D., Pang, S., and Vakharia, D.D., 1998, Human health and chemical mixtures—An overview: Environmental Health Perspectives, v. 106, supplement 6, p. 1263–1270.

Childress, C. J., Foreman, W.T., Connor, B. F., and Maloney, T. J., 1999, New reporting procedures based on long-term method detection levels and some considerations for interpretations of water-quality data provided by the U. S. Geological Survey National Water Quality Laboratory: U.S. Geological Survey Open-File Report 99-193, 19 p.

Connor, B.F., Rose, D.L., Noriega, M.C., Murtagh, L.K., and Abney, S.R., 1998, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of 86 volatile organic compounds in water by gas chromatography/mass spectrometry, including detections less than reporting limits: U.S. Geological Survey Open-File Report 97-829, 78 p. [USGS laboratory method 2020]

Cook, P.G. and Solomon, D.K., 1997, Recent advances in dating young groundwater—chlorofluorocarbons, $^3H/^3He$, and 85 Kr: Journal of Hydrology, v. 191, p. 245–265.

Dale, R.H. and Takasaki, K.J., 1976, Probable effects of increasing pumpage from the Schofield ground-water body, island of Oahu, Hawaii: U.S. Geological Survey Water-Resources Investigations Report 76-47, 45 p.

Eyre, P.R., 1983, The effects of pumpage, irrigation return, and regional ground-water flow on the water quality at Waiawa water tunnel, Oahu, Hawaii: U.S. Geological Survey Water-Resources Investigations Report 83-4097, 44 p.

Eyre, P.R., 1987, Source of salts in the Waianae part of the Pearl Harbor Aquifer near Barbers Point water tunnel, Oahu, Hawaii: U.S. Geological Survey Water-Resources Investigations Report 87-4247, 48 p.

Furlong, E.T., Anderson, B.D., Werner, S.L., Soliven, P.P., Coffey, L.J., and Burkhardt, M.R., 2001, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of pesticides in water by graphitized carbon-based solid-phase extraction and high-performance liquid chromatography/mass spectrometry: U.S. Geological Survey Water-Resources Investigations Report 01-4134, 73 p. [USGS laboratory method 2060]

Giambelluca, T.W., 1986, Land-use effects on the water balance of a tropical island: National Geographic Research, v. 2, no. 2, p. 125–151.

Giambelluca, T.W., Nullet, M.A., and Schroeder, T.A, 1986, Rainfall atlas of Hawaii: State of Hawaii Dept. of Land and Natural Resources Report R76, 267 p.

Gilliom, R.J., Alley, W.M., and Gurtz, M.E., 1995, Design of the National Water-Quality Assessment Program—Occurrence and distribution of water-quality conditions: U.S. Geological Survey Circular 1112, 33 p.

Green, R.E., Goswami, K.P., Mukhtar, M., and Young, H.Y., 1977, Herbicides from cropped watersheds in stream and estuarine sediments in Hawaii: Journal of Environmental Quality, v. 6, no. 2, p. 145–154.

Harding Lawson Associates, 1995, Final sampling and analysis plan for Operable Unit 2 Phase II remedial investigation, Schofield Army Barracks, Island of Oahu Hawaii: Prepared for U.S. Army Environmental Center, Aberdeen Proving Ground, MD, report and appendixes variously paged.

Hufen, T.H., Eyre, P.E., and McConachie, W., 1980, Underground residence times and chemical quality of basal groundwater in Pearl Harbor and Honolulu aquifers, Oahu, Hawaii: University of Hawaii Water Resources Research Center Technical Report No. 129, Honolulu, Hawaii, 75 p.

Hunt, C.D., Jr., 1996, Geohydrology of the island of Oahu, Hawaii: U.S. Geological Survey Professional Paper 1412-B, 54 p.

Klasner, F., and Mikami, D., 2003, Land use on the island of Oahu, Hawaii, 1998: U.S. Geological Survey Water-Resources Investigations Report 02-4301, 20 p.

Koterba, M.T, Wilde, F.D., and Lapham, W.W., 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program: Collection and documentation of water-quality samples and related data: U.S. Geological Survey Open-File Report 95-399, 113 p.

Lapham, W.W., Wilde, Franceska, D., and Koterba, M.T., 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—Selection, installation, and documentation of wells, and collection of related data: U.S. Geological Survey Open-File Report 95-398, 69 p.

Laturnus, F.L., Lauritsen, F.R., and Gron, C., 2000, Chloroform in a pristine aquifer system—Toward an evidence of biogenic origin: Water Resources Research, v. 36, no. 10, p. 2999–3009.

Lau, L.S., 1987, Organic chemical contamination of Oahu groundwater: University of Hawaii Water Resources Research Center Technical Report No. 181, Honolulu, Hawaii, 153 p.

Nichols, W.D., Shade, P.I., and Hunt, C.D., Jr., 1996, Summary of the Oahu, Hawaii, regional aquifer system analysis: U.S. Geological Survey Professional Paper 1412-A, 61 p.

Nightingale, P.D., Malin, G, and Liss, P.S., 1995, Production of chloroform and other low-molecular-weight halocarbons by some species of macroalgae: Limnology and Oceanography, v. 40, p. 180–689.

Oki, D.S., and Brasher, A.M.D., 2003, Environmental setting and the effects of natural and human-related factors on water quality and aquatic biota, Oahu, Hawaii: U.S. Geological Survey Water-Resources Investigations Report 03-4156, 98 p.

Oki, D.S., and Giambelluca, Thomas W., 1987, DBCP, EDB, and TCP contamination of ground water in Hawaii: Ground Water, v. 25, no. 6, p. 693–702.

Oki, D.S., Gingerich, S.B., and Whitehead, R.L., 1997, *in* Ground water atlas of the United States - Alaska, Hawaii, Puerto Rico and the U.S. Virgin Islands, U.S. Geological Survey Hydrologic Investigations Atlas 730-N. --- Hawaii chapter

Orr, S., and Lau, L.S., 1987, Trace organic (DBCP) transport simulation of Pearl Harbor Aquifer, Oahu, Hawaii: Multiple mixing-cell model, Phase I: University of Hawaii Water Resources Research Center Technical Report No. 174, Honolulu, Hawaii, 60 p.

Pacific Biomedical Research Center, 1975, Hawaii epidemiologic studies program, Annual report no. 8, January through December 1974, Honolulu, University of Hawaii, 176 p.

Plummer, L.N., and Busenberg, E., 1999, Chlorofluorocarbons, Chapter 15: in Cook, P., and Herczeg, A.L., eds., Environmental Tracers in Subsurface Hydrology, Boston, Kluwer Academic Publishers, p. 441–478.

Presley, T.K., Sinton, J.M., and Pringle, Malcolm, 1997, Postshield volcanism and catastrophic mass wasting of the Waianae Volcano, Oahu, Hawaii: Bulletin of Volcanology, v. 58, p. 597–616.

Sandstrom, M.W., Stroppel, M.E., Foreman, W.T., and Schroeder, M.P., 2001, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of moderate-use pesticides and selected degradates in water by C-18 solid-phase extraction and gas chromatography/mass spectrometry: U.S. Geological Survey Water-Resources Investigations Report 01-4098, 70 p. [USGS laboratory method 2002]

Scott, J.C., 1990, Computerized stratified random site-selection approaches for design of a ground-water-quality sampling network: U.S. Geological Survey Water-Resources Investigations Report 90-4101, 109 p.

Squillace, P.J., Moran, M.J, Lapham, W.W., Price, C.V., Clawges, R.M., and Zogorski, J.S., 1999, Volatile organic compounds in untreated ambient groundwater of the United States, 1985–1995: Environmental Science and Technology, v. 33, p. 4176–4187.

Squillace, P.J., Scott, J.C., Moran, M.J., Nolan, B.T., and Kolpin, D.W., 2002, VOCs, pesticides, nitrate, and their mixtures in groundwater used from drinking water in the United States: Environmental Science and Technology, v. 36, p. 1923–1930.

Stackleberg, P.E., Kauffman, L.J., Ayers, M.A., and Baehr, A.L., 2001, Frequently co-occurring pesticides and volatile organic compounds in public supply and monitoring wells, southern New Jersey, USA: Environmental Toxicology and Chemistry, v. 20, no. 4, p. 843-865.

State of Hawaii, 1969, Evaluation of pesticide problems in Hawaii (Appendix): State of Hawaii, Department of Agriculture, 113 p.

State of Hawaii, 1999, Amendment and compilation of chapter 11-20, Hawaii Administrative rules (relating to potable water systems), State of Hawaii, Department of Health, no pagination, accessed December 9, 2002 at URL: http://www.hawaii.gov/health/about/rules/11-20.pdf

Stearns, H.T., and Vaksvik, K.N., 1935, Geology and ground-water resources of the island of Oahu, Hawaii: Hawaii Division of Hydrography Bulletin 1, 479 p.

Swain, L.A., 1973, Chemical quality of ground water in Hawaii: State of Hawaii, Department of Land and Natural Resources Report R48, 54 p.

Takahashi, W., 1982, Pesticide usage patterns in Hawaii, 1977: Pesticide Hazard Assessment Project, Pacific Biomedical Research Center, University of Hawaii, Honolulu, 92 p.

Takasaki, K.J., 1977, Elements needed in design of a ground-water-quality monitoring network in the Hawaiian Islands: U.S. Geological Survey Water-Supply Paper 2041, 23 p. and fold-out maps.

Tenorio, P.A., Young, R.H.F., and Whitehead, H.C., 1969, Identification of return irrigation water in the subsurface—Water quality: University of Hawaii Water Resources Research Center Technical Report No. 33, Honolulu, Hawaii, 90 p.

Tomlinson, M.S., Miller, L.D., in press, Water quality of selected streams on the island of Oahu, Hawaii, 1999–2001-The effects of land use and ground-water/surface-water interactions: U.S. Geological Survey Scientific Investigations Report 2004-5048.

U.S. Department of Health and Human Services, 1995, Public health assessment, Del Monte Corporation (Oahu Plantation) Kunia, Honolulu County, Hawaii, CERCLIS NO. HID980637631: Public Health Service Agency for Toxic Substances and Disease Registry, Atlanta, Georgia, accessed July 31, 2002 at URL: http://www.atsdr.cdc.gov/HAC/PHA/delmonte/dmc_p1.html#back_a

U.S. Department of Health and Human Services, 2002, Hazardous substances data base: National Institutes of Health, accessed July 31, 2002 at URL: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB

U.S. Environmental Protection Agency, 2000, Final close-out report, Schofield Army Barracks, Oahu, Hawaii: Superfund Records Center 3315-00044, DD40, 18 p. plus appendixes.

U.S. Environmental Protection Agency, 2002, National Primary Drinking Water Regulations: EPA 816-F-02-013, updated July 2002, 7 p, accessed May 27, 2003 at URL: http://www.epa.gov/safewater/mcl.html

U.S. Geological Survey, 1997 to present, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A9, 2 v., variously paged. [Also available online at URL: http://pubs.water.usgs.gov/twri9A. Chapters originally were published from 1997–1999; updates and revisions are ongoing and are summarized at URL: http://water.usgs.gov/owq/FieldManual/mastererrata.html

Visher, F.N., and Mink, J.F., 1964, Ground-water resources in southern Oahu, Hawaii: U.S. Geological Survey Water-Supply Paper 1778, 133 p.

Von Buttlar, H., and Libby, W.F., 1955, Natural distribution of cosmic ray produced tritium: Journal of Inorganic Nuclear Chemistry, v. 1, no. 1, p. 75–91.

Voss, C.I., and Wood, W.W., 1994, Synthesis of geochemical, isotopic, and groundwater modelling analysis to explain regional flow in a coastal aquifer of southern Oahu, Hawaii: Proceedings, International Atomic Energy Agency meeting “Mathematical models and their applications to isotope studies in groundwater hydrology,” June 1–4, 1993, Vienna, Austria, IAEA-TECDOC-777, p. 147–178.

Wentworth, C.K., 1951, Geology and ground-water resources of Honolulu-Pearl Harbor area, Oahu, Hawaii: Board of Water Supply, City and County of Honolulu, 111 p.

Yim, S.K., and Dugan, G.L., 1975, Quality and quantity of nonpoint pollution sources in rural surface water runoff on Oahu: University of Hawaii Water Resources Research Center Technical Report No. 93, Honolulu, Hawaii, 60 p.