

**AMBIENT GROUNDWATER MONITORING AND ASSESSMENT PROGRAM
CALIFORNIA AQUIFER SUSCEPTIBILITY (CAS) ASSESSMENT
STATE WATER RESOURCES CONTROL BOARD**

EXECUTIVE SUMMARY

The State Water Resources Control Board (SWRCB), in coordination with the Department of Health Services (DHS) and the Department of Water Resources (DWR), is implementing the California Aquifer Susceptibility (CAS) assessment to determine the water quality and relative susceptibility of groundwater that serves as a source for public water supplies to potentially contaminating activities (PCAs). CAS is part of the Ambient Groundwater Monitoring and Assessment (GAMA) Program and will employ groundwater age-dating techniques and low-level analyses for volatile organic compounds (VOCs). The fundamental premise of this assessment is that groundwater age can be used as a guide for assessing aquifers in terms of susceptibility. The age of groundwater may be defined as the time since the water was recharged and isolated from the atmosphere. Tritium/helium-3 techniques will be used to determine the mean, integrated age of groundwater samples. The widespread use of regulated chemicals has occurred during the last 50 to 60 years (following World War II). Therefore, groundwater that has recharged during the past 50 years will be considered more susceptible to contamination from various land-use activities. In addition, low-level VOC analysis will be used to identify those public supply wells already impacted by certain contaminating activities, but which are still below action levels. The assessment is designed to sample the approximately 16,000 public supply wells statewide, starting with three focus areas: Sacramento Valley, Livermore Valley, and Orange County. Sampling began in September 2000 and will continue for the next several years over the entire state, depending on the availability of funding.

INTRODUCTION

The California Legislature and Governor, as well as private citizens, have become increasingly concerned about the recent public supply well closures due to the detection of chemicals, such as MTBE from gasoline and various solvents from industrial sources. More specifically, groundwater contamination from MTBE alone, has caused closure of municipal public supply wells in Santa Monica, South Lake Tahoe, Sacramento, Santa Clara, and many other areas. As a result of the increased awareness toward groundwater quality, the Supplemental Report of the 1999 Budget Act required the SWRCB to develop a comprehensive ambient groundwater monitoring plan. To meet this mandate, the SWRCB created the Ambient Groundwater Monitoring and Assessment (GAMA) Program. Under the GAMA Program, with assistance from the U.S. Geological Survey (USGS) and Lawrence Livermore National Laboratory, the SWRCB is implementing the California Aquifer Susceptibility (CAS) assessment.

The CAS assessment will use tritium/helium-3 ($^3\text{H}/^3\text{He}$) analyses to determine the “mean, integrated age” of groundwater samples collected from public supply wells. Groundwater age provides information on groundwater flow and relative susceptibility of the groundwater to potentially contaminating land-use activities. Since the production and widespread use of most chemicals has occurred since World War II, younger or more recently recharged groundwater (age <50 years) is generally more susceptible to contamination. Conversely, the absence of ^3H indicates an older groundwater age (>50 years) and characterizes a public supply well as less susceptible to potentially contaminating activities. In addition, the CAS assessment will also use low-level VOC analyses to identify public supply wells that are already impacted by potentially contaminating activities, but are below the action levels. This may serve as an early warning system for potential public supply well closures. Both the age-dating techniques and the

low-level VOC analyses will provide valuable information to aid in the assessment of California aquifer susceptibility.

GROUNDWATER AGE-DATING TECHNIQUES

When water recharges an aquifer, it carries with it the chemical signature of the atmosphere from which it was derived. Due to anthropogenic activities, the atmospheric concentration of constituents such as tritium (^3H) has changed over time. The concentration of ^3H in groundwater reflects the atmospheric concentration of ^3H at the time of recharge when the water was isolated from the atmosphere. The sampling and analytical methods for the $^3\text{H}/^3\text{He}$ technique used to determine the age of groundwater are briefly described below in Table 1.

Table 1. Sampling and analytical methods for $^3\text{H}/^3\text{He}$ groundwater age dating technique.

Groundwater Age-Dating Technique	Sampling Method	Analytical Method
Tritium/Helium-3 ($^3\text{H}/^3\text{He}$)	<i>Tritium:</i> Samples are collected in 500 ml glass bottles with polypropylene plug seal cap.	Mass spectrometry by the helium ingrowth method.
	<i>Helium:</i> Samples are collected in special copper tubes fitted with stainless steel pinch-off clamps.	Mass spectrometry measures $^3\text{He}/^4\text{He}$.

Tritium/Helium-3

Tritium (^3H) is the radioactive isotope of hydrogen; it has a half-life of 12.43 years (International Atomic Energy Agency, 1981) and is an excellent indicator of groundwater recharged since 1952 (Clark and Fritz, 1997). The principal source of ^3H is the atmospheric testing of thermonuclear weapons, however tritium is also produced naturally by cosmic rays in the earth's atmosphere. The standard unit of measure for ^3H is a tritium unit (TU), which is equivalent to one ^3H atom per 10^{18} atoms of hydrogen (Clark and Fritz, 1997). Tritium content in precipitation closely resembles nuclear testing during the 1950s and 1960s with a maximum concentration, known as the "bomb peak" occurring in 1963. Atmospheric concentrations have gradually declined since 1963, and present-day groundwater typically contains from <1 to 10 TU (Clark and Fritz, 1997).

Tritium occurs as part of the water molecule and helium (^3He) is an inert gas. Natural sources of ^3He include the Earth's mantle and atmosphere, fluid inclusions within rocks, and excess air entrained in groundwater during recharge (Schlosser, 1992). The $^3\text{H}/^3\text{He}$ groundwater age-dating technique is based on the radioactive decay of ^3H to ^3He . This method separates the amount of ^3He derived from ^3H (tritogenic ^3He) from the amount of ^3He derived from natural sources. Simultaneous measurement of ^3H and its daughter product ^3He enhances the age-dating techniques because it permits reconstruction of the initial tritium concentration. The age determined from a groundwater sample is the mean age of the tritium in the water. Groundwater age estimates using the $^3\text{H}/^3\text{He}$ method can be extremely accurate for groundwater containing high ^3H concentrations.

LOW-LEVEL VOC ANALYSES

Currently, most VOC action levels are in the parts per billion (ppb) range. Thus, typical VOC analytical detection limits are also at the ppb level. The CAS assessment will analyze VOCs in groundwater in the parts per trillion (ppt) range. This level of analysis will identify groundwater that is already impacted by potentially contaminating activities, but which still remain below action levels. General constituents to be sampled by the USGS and LLNL for low-level VOC analysis are shown in Tables 2 and 3. Public supply wells will be sampled for constituents shown in either Table 2 or 3, based upon previous research in the area conducted by the USGS and LLNL. The USGS constituent list (Table 3) is based upon constituents monitored as part of the existing USGS National Water Quality Assessment (NAWQA) Program. The LLNL constituent list (Table 2) is based upon a specialized low-level analysis for a specific group of constituents commonly found to impact groundwater. Additional constituents may be chosen based upon specific information regarding regional aquifer susceptibility or land use. For example, groundwater from public supply wells in the Central Valley area may be sampled and analyzed for Dibromo-3-chloropropane (DBCP), due to intense agricultural activities and previous water quality impacts resulting from the use of this chemical in fertilizers. Also shown in Tables 2 and 3 are the maximum contaminant levels (MCL) in ppb, the California detection limits for purposes of reporting (DLR) in ppb and the low-level detection limit (LLDL) in ppb for each constituent.

Table 2. General constituents to be sampled for low-level VOC analysis by LLNL. Also shown are the maximum contaminant levels (MCL), the California detection limits for purposes of reporting (DLR) and the low-level detection limit (LLDL) for each constituent.

Constituent	MCL (ppb)	DLR (ppb)	LLDL (ppb)
Methyl <i>tert</i> -Butyl Ether (MTBE)	5	3.0	.005
Benzene	1	0.5	.005
Toluene	150	0.5	.005
Ethylbenzene	700	0.5	.005
Xylene	1750	0.5	.005
Tetrachloroethylene (PCE)	5	0.5	.015
Trichloroethylene (TCE)	5	0.5	.015
Trihalomethanes (THMs), Chloroform	(Total THMs)	0.5	.015
Bromodichloromethane	100	0.5	.015
Chlorodibromomethane		0.5	.015
Dibromo-3-chloropropane (DBCP)*	.2	.01	.020

* DBCP may be sampled in the Central Valley area due to intense agricultural activities.

Table 3. General constituents to be sampled for low-level VOC analysis by USGS. Also shown are the maximum contaminant levels (MCL), the California detection limits for purposes of reporting (DLR) and the low-level detection limit (LLDL) for each constituent.

Constituent	MCL (ppb)	DLR (ppb)	LLDL (ppb)
Halogenated Alkanes			
1,1,1,2-Tetrachloroethane	NA	0.5	.030
1,1,1-Trichloroethane	200	0.5	.032
1,1,2,2-Tetrachloroethane	1	0.5	.090
1,1,2-Trichloro-1,2,2-trifluoroethane	1200	10	.060

1,1,2-Trichloroethane	5	0.5	.060
1,1-Dichloroethane	5	0.5	.066
1,2,3-Trichloropropane	NA	0.5	.160
1,2-Dibromo-3-chloropropane (DBCP)	0.2	.01	.210
1,2-Dibromoethane (EDB)	0.05	.02	.036
1,2-Dichloroethane	0.5	0.5	.130
1,2-Dichloropropane	5	0.5	.068
1,3-Dichloropropane	NA	0.5	.120
2,2-Dichloropropane	NA	0.5	.050
Bromochloromethane	NA	0.5	.044
Bromomethane	NA	0.5	.260
Chloroethane	NA	0.5	.120
Chloromethane (Methyl chloride)	NA	0.5	.500
Dibromomethane	N/A	0.5	.050
Dichlorodifluoromethane (CFC 12)	NA	1	.270
Dichloromethane (Methylene chloride)	5	0.5	.380
Hexachloroethane	NA	NA	.190
Iodomethane (Methyl Iodide)	NA	NA	.120
Tetrachloromethane (Carbon tetrachloride)	1	0.5	.060
Trichlorofluoromethane (CFC 11)	150	5	.090
Trichloromethane (Chloroform)	(Total THMs) 100	0.5	.052
Tribromomethane (Bromoform)		0.5	.060
Chlorodibromomethane		0.5	.180
Bromodichloromethane		0.5	.048
Halogenated Alkenes			
1,1-Dichloroethene	6	0.5	.040
1,1-Dichloropropene	NA	NA	.026
3-Chloro-1-propene (Allyl chloride)	NA	NA	.200
Bromoethene (Vinyl bromide)	NA	NA	.100
Chloroethene (Vinyl chloride)	0.5	0.5	.110
Hexachlorobutadiene	NA	NA	.140
Tetrachloroethene (Tetrachloroethylene)	5	0.5	.100
Trichloroethene	5	0.5	.038
cis-1,2-Dichloroethene	6	0.5	.038
cis -1,3-Dichloropropene	0.5	0.5	.090
trans -1,2-Dichloroethene	10	0.5	.032
trans -1,3-Dichloropropene	0.5	NA	.090
trans-1,4-Dichloro-2-butene	NA	NA	.700
Aromatic Hydrocarbons			
Benzene	1	0.5	.035
Naphthalene	NA	0.5	.250
Styrene	100	0.5	.042
Alkyl Benzenes			
1,2,3,4-Tetramethylbenzene	NA	NA	.230
1,2,3,5-Tetramethylbenzene	NA	NA	.200
1,2,3-Trimethylbenzene	NA	NA	.120

1,2,4-Trimethylbenzene	NA	0.5	.056
1,3,5-Trimethylbenzene	NA	0.5	.044
1,2-Dimethylbenzene (ortho-Xylene)	Single isomer or	NA	.038
1,3-Dimethylbenzene (meta-Xylene)	Sum of isomers	NA	.060
1,4-Dimethylbenzene (para-Xylene)	1750	NA	.060
2-Ethyltoluene (o -Ethyl toluene)	NA	NA	.060
Ethylbenzene	700	0.5	.030
Isopropylbenzene	NA	0.5	.032
Methylbenzene (Toluene)	150	0.5	.050
n-Butylbenzene	NA	0.5	.190
n-Propylbenzene	NA	0.5	.042
p-Isopropyltoluene	NA	0.5	.070
sec-Butylbenzene	NA	0.5	.032
tert-Butylbenzene	NA	0.5	.060
Halogenated Aromatics			
1,2,3-Trichlorobenzene	NA	0.5	.270
1,2,4-Trichlorobenzene	70	0.5	.190
1,2-Dichlorobenzene	600	0.5	.048
1,3-Dichlorobenzene	NA	0.5	.054
1,4-Dichlorobenzene	5	0.5	.050
2-Chlorotoluene	NA	0.5	.042
4-Chlorotoluene	NA	0.5	.060
Bromobenzene	NA	0.5	.036
Chlorobenzene	70	0.5	.028
Ethers and other Oxygenated Compounds			
2-Butanone	NA	NA	1.6
2-Hexanone	NA	NA	.700
4-Methyl-2-pentanone (MIBK)	NA	5	.370
Acetone	NA	NA	7
Diethyl ether	NA	NA	.170
Disopropyl ether (DIPE)	NA	NA	.100
Ethyl tert-butyl ether (ETBE)	NA	3	.054
Methyl tert-butyl ether (MTBE)	5	3	.170
Tetrahydrofuran	NA	NA	2.2
tert-Amyl methyl ether (TAME)	NA	3	.110
Others			
2-Propenenitrile (Acrylonitrile)	NA	NA	1.2
Carbon disulfide	NA	NA	.070
Ethyl methacrylate	NA	NA	.180
Methyl acrylate	NA	NA	1.4
Methyl acrylonitrile	NA	NA	.600
Methyl methacrylate	NA	NA	.350

NA = not available

CALIFORNIA'S REGIONAL AQUIFER SYSTEMS

Groundwater flow to wells is controlled by factors that are unique to the complex hydrogeologic settings across California. The complexity of California hydrogeology is driven by the pronounced physiographic and climatic contrasts of the state. In 1980, DWR identified 357 individual groundwater basins in California. These basins were identified on the basis of geological and hydrological conditions, and in some cases political boundaries. Although each individual basin is unique, in general they can be classified as part of five principal aquifers, four of which consist primarily of basin-fill deposits. The four basin-fill aquifers are the Basin and Range aquifers, the Central Valley aquifer system, the Coastal Basins aquifers, and the northern California basin-fill aquifers. The fifth major aquifer is the northern California volcanic-rock aquifers.

The Basin and Range aquifers are located in an area that comprises most of the southern California desert. The water-yielding materials in this area are in valleys and basins, and consist primarily of unconsolidated alluvial-fan deposits, although locally flood plain and lacustrine (lake) beach deposits may yield water to wells. Also, the consolidated volcanic and carbonate rocks that underlie the unconsolidated alluvium are a source of water if the consolidated rocks are sufficiently fractured or have solution openings. Many of these valleys and basins are internally drained; that is, water from precipitation that falls within the basin recharges the aquifer and ultimately discharges to the land surface and evaporates within the basin. Groundwater is generally under unconfined, or water-table, conditions at the margins of the basins, but as the unconsolidated deposits become finer grained toward the centers of the basins, the water becomes confined.

The Central Valley aquifer system occupies most of a large basin in central California between the Sierra Nevada and the Coast Range Mountains. The basin contains a single, large, basin-fill aquifer system, the largest such system in the Nation. Although the valley is filled with tens of thousands of feet of unconsolidated sediments, most of the fresh groundwater is at depths of less than 2,500 feet. Groundwater in the valley is under unconfined to confined (artesian) conditions, primarily depending on depth; most of the shallow groundwater is unconfined.

The Coastal Basins aquifers occupy a number of basins in coastal areas from northern to southern California. These basins have similar morphology and a Mediterranean climate. All are in structural depressions formed by folding and faulting, all are filled with marine and alluvial sediments, and all are drained by streams that contain water at least part of the year. Groundwater in the basins is under unconfined to confined conditions, and two or more vertically sequential aquifers can be present in a basin, separated by confining units that consist of fine-grained sediments

The most productive and highly-utilized aquifers in interior northern California are the northern California basin-fill aquifers. These aquifers are in unconsolidated alluvial sediments. The northern California volcanic-rock aquifers consist of volcanic rocks that yield water primarily from fractures and locally from inter-granular spaces in porous tuffs.

AQUIFER SUSCEPTIBILITY DETERMINATIONS

Evaluating the susceptibility of groundwater requires thorough knowledge of the hydrogeologic setting. Thus, only public supply wells of known location, depth of water bearing zones, and well construction will be sampled. In addition, prior to sampling, well information necessary to ensure a comprehensive assessment will be collected (including well yield information, water level data, water quality data, geophysical log data, and aquifer test data).

Subsequent to data collection and analysis, the susceptibility of the water supply to potentially contaminating activities will be evaluated. The presence of ^3H indicates that water that was recharged less than 50 years ago is being utilized as a drinking water source, and characterizes a well as potentially susceptible to contamination. The absence of ^3H characterizes older groundwater that was recharged more than 50 years ago and, thus is less susceptible to contamination. The low-level VOC analyses will identify which public supply wells are already impacted by potentially contaminating activities.

DATA MANAGEMENT AND REPORTING

Groundwater quality, age-dating, and hydrogeologic data collected as part of the CAS assessment will be managed utilizing the Geographic Environmental Information Management System (GEIMS)/GeoTracker system. The GEIMS database, designed by LLNL under the direction of the SWRCB, has the capability to store and manage extensive data sets associated with contaminant sources, water quality data, water well, and infrastructure data needed for a comprehensive ambient groundwater quality monitoring program. In addition, GEIMS data can be displayed and analyzed via an Internet-accessible GIS system, known as GeoTracker.

In accordance with federal regulations, DHS requires public water systems to sample their sources and have the samples analyzed for inorganic and organic substances in order to determine compliance with drinking water standards (MCLs). The water supplier must notify DHS and the public when a primary or secondary MCL has been violated. In addition, DHS has established a list of detection limits for purposes of reporting (DLRs) of regulated and commonly reported chemicals. The DLR is the level at which DHS is confident about the quantification of the chemical's presence. Both the MCLs and DLRs for constituents to be sampled as part of the CAS assessment are identified in Tables 2 and 3.

BENEFITS OF THE CALIFORNIA AQUIFER SUSCEPTIBILITY ASSESSMENT

California's hydrogeologic diversity provides for a unique opportunity to conduct an aquifer susceptibility assessment. The CAS assessment will evaluate the use of groundwater dating techniques and low-level VOC analyses in determining aquifer susceptibility over a wide range of hydrogeologic environments.

The findings of the CAS assessment will be used by the SWRCB to identify public supply wells which are most susceptible to contamination, as well as those public supply wells which are already impacted but are still below action levels. This determination will enhance the State's efforts to focus its groundwater protection resources on the groundwater that is the most vulnerable to contamination and will evaluate the need for future groundwater investigations. In addition, the CAS assessment will provide valuable information to the local water agencies and aid them in their efforts toward individual well protection and sustainable groundwater resources management.

The CAS assessment allows for the overall evaluation of groundwater being used as a drinking water source, without the need for construction of additional wells. In addition, the assessment provides for a thorough evaluation of information and data associated with each public supply well and will aid in the identification of water quality impacts or increased susceptibility resulting from improper well construction.

The CAS assessment supports the DHS Source Water Assessment Program (SWAP) and facilitates ongoing, effective communication and coordination among the various groundwater resource agencies (e.g., SWRCB, RWQCBs, DHS, DWR and various local water agencies).

SIMILAR PROGRAMS IN OTHER STATES

Various other states have similar programs to investigate aquifer susceptibility. For example, the state of Minnesota Department of Natural Resources is utilizing groundwater chemistry data and age-dating techniques to estimate groundwater sensitivity to pollution. In addition, the Virginia Department of Health (with assistance from the USGS) has developed the Virginia Aquifer Susceptibility (VAS) Study in support of Virginia's Source Water Assessment Program (SWAP). The VAS Study uses atmospheric tracers (such as chlorofluorocarbons, tritium, and carbon-14) that are commonly present in groundwater to determine the groundwater age. Similar to the CAS Assessment, the VAS Study is based on the idea that a young groundwater age (<50 years) indicates greater susceptibility to near-surface contamination. Although other states are using age-dating techniques to investigate groundwater susceptibility, it appears that California is the only state that is also using low-level VOC analyses.

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