# Land-use conversion and its potential impact on stream/aquifer hydraulics and perchlorate distribution in Simi Valley, California

By: M. Ali Tabidian, Ph.D. October 2006

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# Land-use conversion and its potential impact on stream/aquifer hydraulics and perchlorate distribution in Simi Valley, California<sup>1</sup>

#### M. Ali Tabidian, Ph.D.

#### <u>Abstract</u>

Temporal changes in groundwater- and land-use along Arroyo Simi in Simi Valley, Ventura County, California occurring since the late 1800s, caused a reversal of the stream/aquifer hydraulics by the mid-1900s. Groundwater levels dropped by over one hundred feet in some areas, local stream baseflows (e.g., seeps and springs) ceased flowing and Arroyo Simi became an influent stream.

Groundwater depletion and degradation accompanying fast urbanization of the area significantly reduced its availability, requiring importation of large quantities of water. By the late 1970s, water importation allowed the local groundwater regime to regain its pre-development steady-state position as stream/aquifer hydraulics was reversed. In the western end of the valley, high groundwater levels began interfering with development. To manage elevated groundwater levels and minimize their impact on structures, a dewatering system composed of five pumping wells and an array of observation wells was installed.

Several local water quality issues have emerged as a result of agricultural and ranching activities, mostly up to the 1950s, and later as a result of industrial activities and fast urbanization. In particular, nonpoint source water pollution and the recent discovery of perchlorate and other contaminants by various private and governmental agencies in the soils and water resources of Simi Valley and the surrounding hilly areas. This pollution of the surrounding hills and hillsides by perchlorate has warranted temporal and spatial understanding of the local hydrogeologic system and its historical hydraulics and development.

In order to document the spatial distribution and temporal changes of perchlorate in the Simi Valley area, surface water and groundwater samples have been collected at a limited number of locations throughout the Simi Valley area by several public and private agencies. All of the locations on the valley floor where perchlorate has been detected are within a mile of Arroyo Simi. Based on available data, this may be indicative of Arroyo Simi as a source of perchlorate to these areas in contrast to point and diffusive sources

<sup>&</sup>lt;sup>1</sup> Disclaimer: The statements and conclusions in this report are those of the contractor and not necessarily those of the California Environmental Protection Agency. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

(e.g., fertilizer applications and fireworks usage). In water samples obtained from other areas of Ventura County, Tapo Canyon and areas of eastern end of Simi Valley, no perceptible amounts of perchlorate have been detected.

## Introduction

Simi Valley, with a population of over 120,000, is located in southeast Ventura County, CA, about 30 miles northwest of downtown Los Angeles (Figure 1). At present, land use is mostly residential with some small commercial centers spread throughout the city and limited light industries located in the low topographical regions of the valley including the western end of the valley.



Figure 1. Project area. (The map is based on U.S.G.S. 7 1/2 Minute topographical maps).

The western end of the valley floor, with topographical elevations of less than 700 feet, is considered a groundwater discharge area. The bulk of local light industries, the local wastewater treatment plant, a regional sanitary landfill and two recycling centers are located in the western end of the valley and adjacent areas. A major rocket testing/energy-related research facility (Rocketdyne Santa Susana Field Laboratory, SSFL) in operation since the late 1940s, is located south and southeast of the valley (Figure 2) in a groundwater recharge area, with topographical elevations of over 1900 feet at some locations.

In general, local groundwater levels mimic the surface topography of the area. Groundwater from the surrounding mountains and head areas of many alluvial fans on hillsides flows towards the valley floor with a downward component and in a westerly direction. On the valley floor, groundwater flows towards low topographical regions of the central and discharge-zone areas of the western end of the valley. The SSFL is located in a groundwater "recharge zone" with several groundwater and surface drainage system divides. From the divides, groundwater flows in several directions including a north/northwesterly direction with a downward component towards the groundwater discharge regions of the valley floor. Several named and unnamed canyons and streams (e.g., Runkle Canyon, Meier Canyon, Dayton Canyon/Creek, Bell Canyon/Creek, and Woolsey Canyon) (Figure 2) collect runoff from the SSFL and surrounding areas. Dayton Creek, a tributary to Bell Creek, and Bell Creek, drain to the eastward flowing Los Angeles River in the San Fernando Valley. Woolsey Canyon drains the areas on the eastern portions of the SSFL and adjacent areas. Runkle and Meier and other unnamed canyons drain northern and northwestern portions of the SSFL and adjacent areas convey runoff into Arroyo Simi (Figure 2).



Figure 2. Key features and the drainage system of the project area.

Various defense-related activities at the SSFL since the late 1940s including rocket testing, nuclear energy-related research, usage, storage and disposal of various chemicals caused significant contamination of soil/sediment/bedrock, surface- and ground-water by TCE, PCE, heavy metals, radio-nuclides/tritium and perchlorate (ClO<sub>4</sub><sup>-</sup>). Some of those contaminants have migrated to the surrounding areas. For example, it has been estimated that over 1,200,000 gallons of TCE were used for various purposes in over 21,500 rocket tests (excluding commercial tests) conducted at the SSFL between 1954 and 1983. Although "Much of the TCE used in the flushing operations evaporated......" (U.S. Army Corps of Engineers, 1999), over 530,000 gallons of it were

released to the environment, including the soil/sediment/bedrock and groundwater resources of the area. More recently, monitoring under the National Pollutant Discharge Elimination System (NPDES) and numerous other soil and water-related investigations by private and governmental agencies, (e.g., Boeing/Rocketdyne Company, U.S. EPA, and California Department of Toxic Substances Control) revealed perchlorate contamination of surface waters in Dayton Canyon tributaries, which collect runoff from the SSFL, and of soil, surface water and groundwater resources of the SSFL and the surrounding areas.

#### **Historical hydrologic conditions**

From the late 1800s to the 1950s, land use in the Simi Valley area was primarily farming and ranching. Local water resources, including groundwater reservoirs, water from Arroyo Simi and local runoff collected in small ponds and reservoirs, were utilized for irrigation, domestic and stock purposes. Pumping of groundwater in excess of recharge caused local groundwater levels to drop by over one hundred feet in many locations, stream/aquifer hydraulics was reversed, and Arroyo Simi became an influent stream. Since the 1960s, due to urbanization, the population of the area has increased drastically (Figure 3) and a number of light industries and small commercial centers have been established.



Figure 3. Simi Valley population growth. (Data source: Simi Valley Historical Society and Museum; City of Simi Valley; Ventura County Public Works Agency; Miller, 1965; Cameron, 1963; California Department of Finance).

Due to the depletion and quality degradation of local groundwater resources, water was imported to the valley, initially from the Colorado River through the Colorado River Aqueduct system (from the early 1960s to early 1970s) and later from the early 1970s to present from northern California from the California State Water Project (California Aqueduct). The imported water has been distributed to users by a private company (Golden State Water Company, formerly Southern California Water Company, which blends imported water with local groundwater) and the City of Simi Valley (Ventura County Waterworks District No. 8).

Groundwater levels regained their high, pre-development steady-state conditions as a result of water importation and significant reductions in utilization of local water resources, in tandem with urbanization of the area. The rise in groundwater levels has created engineering problems with man-made structures including residential units and commercial centers at the western end of the valley (Leighton and Associates, 1985, 1988). A dewatering system was developed to remedy these problems. At present, the dewatering system is composed of five active dewatering wells, with a total discharge of about 2000 gallons per minute (City of Simi Valley, personal communications, 2003), and an array of observation wells to monitor the effectiveness of the dewatering system.

The dewatering system has reduced the damage potential to residential and other properties significantly. The discharged water from the dewatering project has not been utilized due to high total dissolved solids (TDS of about 2000 mg/L) and other water quality-related issues in the area. More recently, perchlorate has been discovered in groundwater resources of the dewatering project areas. At the present, the dewatering project water is discharged into Arroyo Simi, which percolates through the stream-bed sediments and re-enters the local groundwater reservoir several miles downstream from the discharging areas and/or ultimately enters the Pacific Ocean during the rainy season.

Several point-source and nonpoint-source water quality problems resulting from agricultural and ranching activities from the late 1800s to mid-1900s, activities at the SSFL since the late 1940s, and the subsequent urbanization of Simi Valley have been documented. The occurrence of nitrate, chloride (Tersibashian, 2001), phosphate, perchlorate, TCE and other contaminants in the water resources of Simi Valley and the SSFL have emerged during more recent years, warranting further study of the temporal and spatial changes in the hydraulics of the area.

The main thrust of this study is to analyze the temporal and spatial changes in the groundwater and stream/aquifer hydraulics of Arroyo Simi as related to local land-use conversions, potential contamination of local groundwater resources by Arroyo Simi's waters, and interference of high groundwater levels with man-made structures including residential units.

To meet the stated objectives, the physical system characteristics, including the geology and hydraulics of the area, are defined by investigation and documentation of historical water-related activities, changes in surface and groundwater levels, and a detailed examination of over 200 geologic logs.

## <u>General geologic and hydrogeologic settings</u> <u>Bedrock units</u>

The major bedrock units making up the hills and mountains bordering Simi Valley and the SSFL areas (Chatsworth Formation, Santa Susana Formation, Sespe Formation, and Conejo Volcanics) are mostly fractured clastic sedimentary rocks (marine and non-marine conglomerate, sandstone, siltstone, shale, mudstone) and igneous rocks of Cretaceous and Tertiary age (Irvine, 1991; Dibblee, 1992). The SSFL "is located on the south flank of an east-west striking and westward plunging syncline which passes through the central part of Simi Valley."(Montgomery Watson, April 2000).

Hydrogeologic characteristics of the area's aquifer systems are strongly anisotropic and heterogeneous (horizontally and vertically). The heterogeneity is caused by lithologic variations that reflect the complex depositional environment of sedimentary rocks, as well as subsequent deformation and tectonic activities.

In addition to temporal and spatial changes in depositional systems and changes in strength and position of the fluvial systems; faulting, fracturing, shearing and formation of plunging folds including synclines; development of unconformities and "channeling" along the geologic contacts and formation of graded beds and sole marks; and marine regressional and transgressional activities are among the factors that have contributed to the heterogeneity, anisotropy and complexity of the local hydrogeologic systems and the bedrock units (Kew, 1924; Link et. al., 1981; Link, 1981; Hanson, 1981; Parker, 1985; Squires and Filewicz, Editors, 1983; Irvine, 1991; Holt, 1991; MESA<sup>3</sup>, Inc., 1995; Hitchcock et al., 1999).

The overall bulk hydraulic conductivity and storage coefficient of the sandstone units of the area are estimated to be  $1.3 \times 10^{-5}$  cm/sec and 0.00025- 0.0053 respectively, based on numerous aquifer tests at the SSFL. Haley & Aldrich, Inc. (2001) conclude that "The fracture network imparts about an order of magnitude increase in hydraulic conductivity to bedrock, on average, over that of the matrix" and that "The fractures at SSFL are small, systematic and interconnected" with "frequent" and "systematic fractures" and fractures have apertures of up to 300 micrometers (Montgomery Watson, 2000).

The Chatsworth Formation is over 1,800 meters thick and is composed mostly of brittle sedimentary rocks. It has further been described as a "deep-sea fan complex" that is "sand-rich", which is composed of mostly silicate minerals, with minor amounts of mudstone and up to 3 percent clay and iron oxides and "carbonate cement makes up to 25 percent of the total" (Link et al., 1981; Link, 1981; Parker, 1985). High yielding localized conduits with a dual porosity system have been developed as a result of fracturing, shearing, faulting, folding and chemical weathering due to the abundance of brittle sandstone and mudstone units and the bedrock units with calcareous cementation. In addition to the aforementioned factors that have contributed to formation of postdepositional porosity (secondary porosity) "....a mean matrix porosity of 13%....." has been reported (Sterling et al., 2005). Fractures and fractured zones play a major role in local ground water flow (Sterling et al., 2005). As a result they may play a primary role in solute movement. It has been stated that "an exceptional well in Cretaceous sandstone is reported to yield 1,200 gallons per minute, but most of the wells in the older rocks yield about 100 gallons per minute." (California State Water Resources Board, 1953). Taking advantage of these high-yielding zones at the SSFL (Lab), it has been stated that

"at, and near the Lab, production water wells are often placed near faults because fault zones frequently conduct groundwater better than the surrounding bedrock and the well yield is greater." (Los Angeles Regional Water Quality Control Board files).

For other areas, it has been stated that fault zones developed in crystalline rocks "....may dominate the flow characteristics of a region" and "...important potential aquifers can occur in the more highly fractured crystalline rocks above these fault planes, while the more ductile rocks of the fault planes may behave as flow barriers leading to the possibility of compartmentalization of aquifers...." (Seaton and Burbey, 2005). While it has been asserted that fault zones in the SSFL area, with respect to groundwater flow, behave as aquitards due to the presence of fine-grained gouge (Montgomery Watson Harza, February 2003), as a result of a three-dimensional investigation of Chatsworth and other rock formations, it has been concluded that faulted and eroded zones in some areas become more "prominent at a depth of about 700 ft." and they may "....act as contaminant pathways,...." (Adams and Bainer, publication date unknown). In areas where fracturing is wide and extensive and various fracture systems are interconnected, the results of video logging reveal fast flowing groundwater. Higher-yielding water wells have been developed in such formations in the past. In a field investigation and through image logging of fractured sandstones of a TCE impacted area at the SSFL, it has been demonstrated ".....that the contamination effects related to hydraulic cross-connection can be severe and persistent over many years in sedimentary rocks....." and revealed ".....intersections of bedding-parallel fractures and moderately dipping or steeply dipping fractures." (Sterling et al., 2005).

The detection of several contaminants including TCE in a well (OS-14), in the undeveloped southern areas of the SSFL, has lead researchers to postulate that "..., the finding of chemical contamination at OS-14 suggests possible migration of chemicals in fracture flow from the SSFL." and ".....the possibility of deep fracture flow presents the potential for substances in ground water to migrate long distances......" (Agency for Toxic Substances and Disease Registry, 1999). In addition to geologic features related to tectonic activities (e.g., folds, faults and shear zones) and chemical weathering of the calcareous sedimentary rocks and formation of dissolutional cavities, temporal and spatial variations in marine and non-marine depositional systems (e.g., rivers, alluvial fans), which can provide pathways for contaminant migration, have further influenced the hydrogeologic characteristics and complexity of the bedrock aquifer system in the area.

#### Unconsolidated deposits

The lithology and geology of the source-rocks, stream strength and characteristics, topography, tectonic activities including rock displacements along the fault zones (Parker, 1985; Irvine, 1991; Holt, 1991; Squires, 1997; Evensen, 1997; Hitchcock et. al., 1999), subsurface shallow bedrock unit topography and depositional systems, including multiple alluvial fans, are among the dominant factors that have directly influenced variations in thickness, texture and composition of the unconsolidated material, the saturated sand and gravel thickness, the aquifer types, their hydraulics and degree of confinement and the strength of the stream/aquifer interactions.

In the areas where the bedrock-unit elevations are high and in turn the thickness of the overlying saturated sand and gravel is thin, the groundwater hydraulics have been dominated by high bedrock-unit characteristics. For example, unusual anomalies in gradients and development of sub-basin hydrologic systems are "attributed to a buried bedrock ridge, breached near the south end, that confines and restricts the natural westward flow from the east basin into the main basin." (Leighton and Associates, 1972).

The south-southwesterly flowing Arroyo del Tapo, a major tributary to Arroyo Simi is located on the southern slopes of Big Mountain (Figure 2) in the north and northcentral portions of the valley and has contributed a significant amount of relatively "clean" and better sorted sand and gravel deposits (alluvial fans) to the valley floor and stream-bed deposits. However, Runkle and Meier canyons, located on the northern flanks of Simi Hills near the SSFL on the south and southeast portions of the valley (Figure 2) have provided limited amounts of sediment load with a lower degree of sorting. As a result, on the hillsides and valley floor in general and along the course of Arroyo Simi in particular, the hydrogeologic setting including the thickness and textural characteristics of sand and gravel deposits are highly variable. Along the central and western portions of Arroyo Simi where the stream-bed deposits are rich with better sorted sand and gravel contributed by the Arroyo del Tapo the potential for stream and aquifer interactions (water and contaminant losses and gains) are high compared to other areas of Arroyo Simi, where the bedrock units are exposed and/or stream-bed deposits are composed of limited and poorly sorted alluvium.

The valley floor, as well as areas adjacent to local canyons and creeks, and the lower portions of the hillsides are composed of mostly unconsolidated (e.g., alluvium and alluvial fans and colluvial deposits) to semi-consolidated deposits. These deposits, including the many associated alluvial fans (Hitchcock et al., 1999), are generated through the weathering of sedimentary and igneous rocks associated with the hills and mountains surrounding the valley (primarily Big Mountain on the north and Simi Hills on the south (Figure 2). Examination of over 200 geologic and irrigation well logs shows that the thickness and composition of the unconsolidated material, including the saturated sand and gravel, is highly variable spatially throughout the valley. On the flanks of the surrounding mountains and on the valley floor itself, in the areas where the bedrock elevations are high (California Department of Water Resources, 1968) and/or exposed, the thickness of unconsolidated material is thin to non-existent. At many locations in the northern and north-central portions of the valley floor, where Arroyo del Tapo joins Arroyo Simi (Figure 2), unconsolidated material thickens to over 400 feet with an extensive amount of saturated sand and gravel (over 150 feet). However, at numerous locations in the southern portions of the valley floor and on the northern flanks of Simi Hills near the SSFL, the thickness of the unconsolidated material is between 150 and 300 feet, with much less saturated sand and gravel compared to the north and north central portions of the valley. As a result, the present active wells and the most historical productive wells were developed in the unconsolidated material in areas with over 150 feet of saturated sand and gravel in the alluvial fan bodies in the north central parts of the valley floor. Near these sections of Arroyo Simi, due to the availability of better sorted and more extensive sand and gravel deposits, the stream/aquifer interactions are much stronger.

Stream/aquifer interactions are weak along the course of Arroyo Simi where bedrock units with no or low secondary porosities are near the surface or exposed and sand and gravel deposits are limited. In particular, along Arroyo Simi near the central portions of the valley floor in at least one locality, bedrock units are exposed. In this specific area and in similar areas (e.g., eastern portions of Arroyo Simi, Meier and Runkle canyons) the stream-bed materials are much less conductive compared to adjacent areas. Here the stream-bed sediments are composed of poorly sorted alluvium. Hence, stream losses and gains are not likely as significant as in the central and western portions of Arroyo Simi.

#### **Regional recharge and discharge**

Recharge and infiltration rates at the SSFL, where average annual precipitation is just over 18 inches per year, have been estimated in the range of 1 to 20 percent and 11 to 44 percent respectively, attained using different methods for various time periods (Montgomery Watson Harza (MWH), December 2003).

Groundwater recharge occurs in exposed fractured rocks in the mountainous terrain of the SSFL and in alluvial fan heads on the mountain flanks, whereas groundwater discharge occurs in the central parts of the valley floor specifically the western end of the valley floor. In mountainous recharge zone areas, in general, the deeper the well-screen intervals are, the lower the groundwater levels in those wells (Table 1), which indicates a downward hydraulic gradient and confirms the area as a recharge zone. However, contradictory to this general rule, the heterogeneity of the area and the erratic nature of the rock fractures provides exceptions to this general downward movement of groundwater on a small spatial scale as documented by Sterling et al. (2005). Locally, in addition to the presence of flowing wells (wells with groundwater levels above the ground surface) it has been concluded that in some areas "...the magnitude of the vertical gradient is small" and in others vertical hydraulic gradients are significant (MWH, February 2003). Groundwater recharge from rainfall infiltration and percolation can occur in a relatively short time period. Some groundwater hydrographs for the SSFL wells show higher groundwater levels in 1999, and likely reflect the fast recharge rates from unusually high precipitations in 1998 and 1999.

Borehole Depth	Measuring Point Elevation	Depth to Groundwater Level
(Feet)	(Feet)	(Feet)
75	1768.7	30
100	1806.3	46
125	1836.3	107
125	1824.3	115
127	1819.7	≤ 120
135	1853.1	100
150	1810.9	125
150	1841.7	126
150	1809.9	125 ±
152	1817.7	~120
160	1880.4	138
160	1840.3	~145
175	1945.0	-

Table 1. Total well depth and depth to groundwater levels for select monitoring wells developed in aquifers of the SSFL in 1989. The wells are classified as "open hole" (Source of data: Ventura County and LARWQCB files).

175	1810.8	120
175	1867.0	140 ±
220	1809.0	≥110
240	1839.5	≥240
440	1853.4	400 ±
440	1836.4	440 ±

In November 2003, groundwater levels ranged from above ground surface to over 500 feet below the ground surface while groundwater elevations ranged from 1314 to 1898 feet above the mean sea level at the SSFL and adjacent highland areas (Haley & Aldrich, Inc., 2004). Groundwater levels and their seasonal fluctuations are highly variable in wells developed in bedrock units and also in unconsolidated deposits due to groundwater pumpage and seasonal changes in recharge rates from precipitation. Other factors affecting groundwater levels include aquifer characteristics, depth to groundwater levels, possibly seasonal changes in hydrology of local ponds and reservoirs, and the degree of aquifer confinement. In some areas of the SSFL, annual groundwater level fluctuations are in the tens of feet and respond relatively quick to rainfall events as reflected in groundwater hydrographs.

There are a number of springs and flowing wells associated with the bedrock units on hillsides surrounding the SSFL. The wells near Meier Canyon remain flowing (Figure 4) are in historical discordance in their groundwater level fluctuations as compared to groundwater fluctuations in wells developed in valley floor Pleistocene deposits (Figure 5).



Figure 4. South central-southeast (SSFL) hydrogeologic setting of the southeastern parts of the Simi Valley area.

This discordance in historical as well as recent observations in groundwater fluctuations is a reflection of the heterogeneity, fracture-zone continuity/discontinuity, weak interconnectivity between the valley floor Pleistocene deposits and the SSFL bedrock units and groundwater hydraulic gradient anomalies of the bedrock units (e.g., Chatsworth Formation). The recent inconsistency in observed temporal changes in the concentration of perchlorate in the area (discussed later) may be as a result of the aforementioned temporal and spatial changes in the hydraulics of recharge zones and resultant variations and fluctuations in local groundwater flows and groundwater levels.



Figure 5. Northwest-south central hydrogeologic setting of the Simi Valley area.

Montgomery Watson Harza (February 2003) stated that "The collective volumetric discharge of groundwater from seeps and springs is believed to represent a significant portion of the total inflow into the groundwater system beneath the SSFL". Therefore, on-site contaminated groundwater can potentially move towards local hillsides and valley floors through advection, and contaminants may episodically emerge on hillsides through intermittent seeps and springs. Especially in the absence of clay minerals, contaminants like perchlorate may diffuse into porous rock matrix over local concentration gradients. However, transport by advection is likely the dominant mode of contaminant movement. Although the concentration of perchlorate may decrease due to diffusion and down-gradient dilution, the process of molecular diffusion will not slow or stop the movement or spread of contaminants, especially the non-reactive and conservative anions such as perchlorate in higher conductivity and extensive preferential flow zones like those in fractured and sheared rocks of the Chatsworth Formation.

In contrast to the SSFL areas, the Simi Valley floor, particularly the western part, have features indicative of regional discharge zones: the groundwater hydraulic gradient has an upward component where there are several confining to semi-confining layers, the Total Dissolved Solids for groundwater are high (up to about 2000 mg/L), and there are some seeps, springs and flowing wells in the area. The western end of the valley floor has at least two distinctive aquifer systems, an upper unconfined system and a lower aquifer system composed of several geologic units that are under various degrees of confined to semi-confined conditions. The depth to water table for the upper saturated system is shallow, whereas groundwater levels in the lower confined aquifer system can rise to over ten feet above the ground surface (Table 2), contributing to the formation of seeps, springs and swampy areas depicted on a very early hand-drawn map of the area (Figure 4). Further, as a result of confined conditions in the western end of the valley, flowing wells have been constructed in the area since the early 1900s.



# Figure 6 Swampy areas of western end of Simi Valley depicted on a very early hand drawn map of the area. (Simi Valley Historical Society and Museum files).

Seeps, springs and shallow groundwater levels and constriction of westerly flowing groundwater in the western end of the valley enhance the potential for salts and contaminants to accumulate within the soil profile and root-zone, especially during dry seasons and prolonged drought periods. The extent of historical as well as more recent salt/contaminant (e.g., ordinary salt, perchlorate compounds) concentration in the area's soil profile and their potential impact on the local ecological and biological systems, is unknown.

Valley (Source of data: City of Simi Valley files).												
Observation	First&Ayhens	Bonita&Madera	Cochran&First	Los	North	Sinaloa&Vorale						
Well Location	-			Angeles	End							
				&Madera	Shasta							
					Way							
Land Surface	769	728	827	721	739	757						
Elevation,												
Feet												
Shallow												
Aquifer												
Groundwater												
Levels	765.6	723.5	Dry	715.9	736.6	752.9						

Table 2. Mo	thly average groundwater level elevations (feet) for observation
wells develop	ed in shallow and deep aquifer units in the western end of Simi
Valley (Sour	e of data: City of Simi Valley files).

March 1998	762.3	720.9	Dry	713.5	736.5	747.4
August 1998						
Deep Aquifer						
Groundwater						
Levels						
March 1998	772.4	727.4	807.2	727.3	748.3	744.7
August 1998	773.6	725.9	809.4	732.9	754.5	748.3

#### Stream/aquifer hydraulics

Arroyo Simi and its associated tributaries and canyons (e.g., Arroyo del Tapo, Meier and Runkle canyons) (Figure 2) drain the valley and the surrounding hills and mountains including the northern, western and adjoining areas of the SSFL. Groundwater through seeps and springs, interflow, discharge from several dewatering wells, and runoff waters that enter Arroyo Simi and its tributaries ultimately flows in a westerly-southwesterly direction towards the Pacific Ocean (Arroyo-Simi's stream-bed elevations are over 1100 feet at the eastern end of the valley and less than 700 feet at the western end). In the western end of the valley, the local wastewater treatment plant discharges its treated wastewater to Arroyo Simi at a rate of about 10 million gallons per day. Further downstream, at low flow rates and during the dry periods, the westsouthwesterly flow in Arroyo Simi may reduce or disappear by evaporation and infiltration through the stream-bed sediments and in rainy seasons, Arroyo Simi's water may ultimately enter the Pacific Ocean.

Although during pre-groundwater utilization periods (pre early 1900s) and at present, the western and other portions of Arroyo Simi itself and tributaries such as Arroyo del Tapo can be classified as perennial effluent streams, other smaller tributaries and canyons such as Meier and Runkle canyons are intermittent and ephemeral. In addition to surface runoff generated from precipitation, irrigation return flow and urban runoff, these intermittent and ephemeral creeks and canyons can potentially gain water from industrial-related activities, groundwater seeps and springs, flowing wells and through interflow from bedrock units, especially after major rainfall events. The flux associated with the aforementioned is not high enough or long enough to sustain a continuous flow, especially during dry months and prolonged drought periods due to low groundwater levels.

Stream-bed deposits associated with the central and western portions of Arroyo Simi and the tributaries draining northern portions of the valley, such as Arroyo del Tapo, are composed of relatively better sorted and more extensive sand and gravel deposits compared to tributaries draining the southern portions of the valley, including Meier and Runkle canyons, which drain the SSFL and surrounding areas. Sediments associated with these canyons are composed of limited amounts of poorly sorted deposits with a greater median grain size diameter.

Although there are strong temporal changes and spatial variations in stream/canyon-bed and flood-plain deposits, grain-size distribution analysis of 11 samples obtained from select locations along the local streams and canyons show that uniformity coefficient values for samples obtained from the western potions of Arroyo Simi and Arroyo del Tapo are less than 4.4 (Table 3), while they are higher for samples obtained from the southern canyons such as Runkle. As a result, water losses through sandy/gravelly areas of Arroyo Simi, with a major head difference between stream stage and groundwater levels, must have been significant during the 1950s and 1960s when, as a result of extensive groundwater pumpage, groundwater levels were at their historically lowest positions (Figures 5, 7, 8, 9).

 Table 3. Stream/canyon sediment-bed sorting characteristics for select locations.

Stream/Canyon	Number of	Average Median	Average Uniformity

	Samples	Particle Size, mm	Coefficient
Lower Portions of Tapo Canyon	3	1.1	4.4
Middle Portions of Runkle	2	2.1	12.2
Canyon			
Western Portions of Arroyo Simi	6	0.9	3.4
in Simi Valley			

Increased groundwater pumpage from the early 1900s to 1960s and a continuous decline in groundwater levels at a rate of about 4 feet per year in some areas of the valley in the 1920s and 1930s (Bagnall, 1938), caused local stream/aquifer hydraulics to reverse and subsequently effluent streams became influent (Figures 5, 7, 8, 9). Groundwater levels continued to decline until the 1960s, which in turn contributed to further stream losses during this period.



Figure 7. North-south hydrogeologic setting of the western end of the Simi Valley.



Figure 8. North-south hydrogeologic setting of the western area of the Simi Valley about one mile east of Figure 5 and 0.25 miles west of Arroyo Simi and Runkle Canyon confluence.



Figure 9. North-south hydrogeologic setting of the central area of Simi Valley just to the west of and along Tapo Canyon Road.

Groundwater levels compiled in Figure 10 are based on static groundwater levels of the late 1950s and the early 1960s, and depict general static groundwater levels at their lowest positions as compared to stream-bed elevations. Groundwater levels were much lower than the stream bed/stage, even at areas located more than a mile from the course

of Arroyo Simi; as a result, a significant quantity of stream water from surface runoff and associated dissolved chemicals and contaminants must have entered the depleted local groundwater reservoirs in the late agricultural eras (1950s and 1960s) of the valley and prior to more recent urbanization. Due to the temporal and spatial variability and lack of historical data, the quantity of water and contaminant losses from Arroyo Simi in the 1950s and 1960s to local aquifer units and in turn the quality of domestic water supplies is unknown.



Figure 10. Static groundwater levels of the late 1950s and the early 1960s (black color numbers) as compared to stream-bed elevations (blue color numbers).

Since the early 1960s, the availability of virgin and agricultural land has been steadily decreasing as a result of urbanization and has also continuously diminished the opportunity for infiltration. However, due to water importation to the area, from the Colorado River from 1963 to 1973 and from the State Water Project from the early 1970s to present, available water for infiltration and in turn aquifer recharge has increased. In addition to water importation to the valley and urbanization, local groundwater pumpage was reduced significantly during this period. As a result, local groundwater levels started to recover (Leighton and Associates, 1972, 1985, 1988) to their pre-farming/ranching steady-state positions by the 1970s (Figure 11). As a result, portions of Arroyo Simi, including a portion in the western end of the valley became a gaining stream once again.

During the groundwater recovery period (1960s to 1970s), and fast rate of development of the area, hundreds of wells (irrigation and domestic) were abandoned, some of them improperly (Leighton and Associates, 1985and 1988). By the 1970s, groundwater potentials regained their pre-development levels and seeps and springs began to reappear. As a result, not only did stream baseflow rates through seeps and springs increase, but extensive urbanization and improper abandonment of some water wells in the area caused high groundwater levels to interfere with man-made structures including residential and commercial units. As discussed above, in order to minimize the negative impact of high groundwater levels on man-made structures, the City of Simi Valley has developed a dewatering system to lower these groundwater levels.



Figure 11. Groundwater elevations in feet for spring-season measurements. Map location of the measurement site is T2N/R18W-8C2. Land surface elevation at the monitoring location is 746.4 feet. (Modified from Ventura County Public Works Agency, Flood Control and Water Resources Department, 1986.)

#### Water usage and groundwater level changes

An early hand-drawn map of the valley and surrounding areas (Figure 4) shows the location of seeps and groundwater-fed swampy areas as well as a ranch house. From this map, there is no indication of any water wells associated with the ranch house. It has been reported that early settlers used surface water and water from seeps and springs for various purposes, including domestic use and watering cattle. Several dry land crops were raised and irrigation with spring and stream waters were used on smaller farms and gardens during the late 1800s and early 1900s (Schuyler, 1904; Austin, 1928; Bagnall, 1938; Haig, 1975).

As settlement of the valley progressed, demand for water increased due to agricultural and ranching activities and in turn this higher demand augmented by multiple dry years in the late 1800s were the primary factors that contributed to the construction of the very first artesian flowing water wells around 1887 or 1888 (Bagnall, 1938). It has been stated that "During the nineties (1890s) every farm had a dug well with a windmill and some kind of a tank and water-trough for storage to provide water for the stock and vegetable gardens" and "By 1905, a drilled well was a necessity." (Cameron, 1963).

From the early 1900s through the 1930s, although surface waters were still utilized, the role of groundwater became more important in raising several types of irrigated crops (Austin, 1928; Cameron, 1963; Haig, 1975), and groundwater levels started to decline at a rate of several feet per year in some parts of the valley (Bagnall, 1938). During this period and up through the 1950s, highly valued crops such as fruits and nuts became abundant. Orchard well construction expanded and the usage of local groundwater resources accelerated. Over a dozen private water companies were organized, several hundred wells were drilled and the local groundwater reservoirs were extensively utilized. As a result, groundwater levels dropped significantly throughout the valley and springs ceased flowing. In some areas, groundwater levels dropped by over one hundred feet (Figure 11). Troxel (1957) found that prior to the 1960s, land use in the valley was mostly irrigated agricultural; consequently, groundwater levels declined by over 75 feet between 1929 and 1951 in numerous areas of the valley.

In addition to the use of groundwater resources during this period and prior to importation of surface water to the valley, which began in 1963 (California Department of Water Resources, 1965), surface waters stored in small ponds and reservoirs were still utilized and spreading grounds and flood control detention ponds were used to capture surface runoff to enhance the groundwater reservoir's recharge rates. The location of some of these reservoirs, including one along Meier Canyon near the SSFL and another one in Runkle Canyon, are still evident on topographical maps published by the U.S. Geological Survey.

Local surface water and groundwater were the two primary sources of water until 1963. As local groundwater levels declined, groundwater reservoirs were depleted and the quality of water degraded, water was imported to the valley to supply the rapid urbanization and increased population. Based on available data for water importation (Figure 12) per capita water importation averaged about 193 gallons per day between 1970 and 2001.



#### Figure 12. Yearly water imports (in acre-feet) to Simi Valley by Calleguas Municipal Water District. (Data source: Calleguas Municipal Water District of Ventura County)

Surface water was initially imported to the valley from the Colorado River through the Colorado River Aqueduct system in 1963 (California Department of Water Resources, 1965; personal communication with Southern California Water Company personnel, 2004) and since the early 1970s from Northern California through the State Water Project (California Aqueduct). Before water importation and distribution, Calleguas Municipal Water District of Ventura County (CWD), a local water district, ".....depended on pumping from overdrafted ground water basins to provide water service to a rapidly developing urban area." (California Department of Water Resources, 1965). Imported water, including that from the Colorado River, was mostly used for domestic purposes. As the area became urbanized, it was not economical for the Colorado River waters to be used for orchard irrigation (personal communication with Michael Kuhn, April 2004).

At present, for domestic and industrial purposes, CWD imports water to the valley from the State Water Project (California Aqueduct) through the Metropolitan Water District of Southern California. In the valley, the imported water is distributed to users by the City of Simi Valley (Ventura County Waterworks District Number 8) and Golden State Water Company (GSWC), formerly Southern California Water Company. The Ventura County Waterworks District Number 8 water distribution system covers mostly areas in the northeast, north central and western portions of Simi Valley while the GSWC provides water to users located in the east, central and south central regions of the valley.

In addition to imported water, local groundwater resources are still being utilized for irrigation and domestic purposes. Recent usage of local groundwater by the city for irrigation purposes, and a local community (Trade Winds Mobile Park) and the GSWC for domestic purposes has been documented. However, there is no data available on the extent of groundwater extraction in the area by individual home or property owners through domestic and/or stock wells during either the historical agricultural era or in more recent years.

Based on information provided by the California Department of Health Services, Ventura County Waterworks District No. 8-Simi Valley has three wells, two of which have been designated as standby wells and the other named inactive. The District extracted over 850 million gallons of groundwater from the local aquifer system between 1994 and 2001. The water extracted from these wells was used for irrigation purposes and, according to the California Department of Health Services; none of this water was introduced to the domestic system for at least the past five years.

Since the early 1960s, the GSWC has supplemented the distribution of imported water with local groundwater. Recent data (1994-2003) obtained from the California Department of Health Services and County of Ventura shows variations from year to year. The average annual local groundwater pumped and the average annual imported water distributed was 207 and 2,302 million gallons respectively. Available data shows that the population serviced by water from the GSWC in Simi Valley has ranged from 29,200 to 44,800 during the most recent years.

The GSWC may have operated other wells in the past in other parts of the valley and possibly blended local groundwater resources with imported Colorado River or the State Water Project waters. In more recent years the agency has mixed groundwater resources extracted from two wells with imported State Water Project waters before its distribution to users. These two wells are "Sycamore Well 03", which is over 600 feet deep and was constructed in 1962, and "Niles Well 01". Both wells were developed in sediments associated with a major alluvial fan located in north central and central Simi Valley.

The aforementioned wells are located near areas where perchlorate in groundwater resources has been detected (discussed later) at concentrations of up to about 15 ppb (Department of Toxic Substances Control, April 2003). As a result, local residents have become concerned about their level of exposure to contaminants and the quality of their tap water due to this recent discovery of perchlorate and radio-nuclides with concentrations above the MCL (California Department of Water Resources, 2003) in groundwater resources of the valley since the late 1990s. As a result, the GSWC has increased its groundwater quality and perchlorate monitoring over the past several years.

More recently, in groundwater samples obtained from the aforementioned wells, perchlorate and trichloroethylene, with concentrations of less than Maximum Contaminant Limit and Detection Limit but equal to or greater than "trigger" levels, have been reported (California Department of Health Services files). Also, based on historical groundwater quality data, groundwater resources of the Quaternary deposits of the Simi Valley area have been classified as calcium sulfate to calcium-sodium sulfate (California Department of Water Resources, 1959 in California Department of Water Resources, 2003). Three of the four public supply wells sampled for radiological activities have reported concentrations above the MCL (California Department of Water Resources, 2003). As a result, the development of a groundwater monitoring system and continuous monitoring of the groundwater resources of the area is warranted.

Trade Winds Mobile Park, a mobile home community which was formed in 1959, has utilized local groundwater resources until recent years. According to the latest records obtained from the Ventura County Public Works Agency and California

Department of Health Services, the entire community's source of water was local groundwater, which was served through 100 connections to a population of about 130 people. In recent years, up to four wells located near the course of Arroyo Simi were utilized. The water quality of these wells, due to their close proximity to the stream, was likely impacted by Arroyo Simi's water quality at time periods when groundwater levels were much lower than the river bed. Groundwater quality data pertaining to the aforementioned wells show that in addition to a relatively high TDS, gross alpha measurements ranged up to 35 Pci/L with a gross alpha counting error of 8 PCi/L and manganese concentrations of up to 350  $\mu$  g/L. The community has recently discontinued use of these wells.

At the SSFL, seventeen wells were developed in the Chatsworth Formation by 1963, but only six were productive enough (collectively up to a maximum rate of 400 gpm) to be used for domestic and industrial purposes (Montgomery Watson, 2000). Water has been imported to the SSFL since the 1960s due to declining water levels and deterioration of water quality. The imported and pumped waters were used for industrial (Agency for Toxic Substances and Disease Registry, 1999) and/or domestic purposes. Although human consumption of local groundwater resources has been discontinued (U.S. Department of Energy Community Meeting in Simi Valley, June 2004), local groundwater extraction on average has been about 250 gpm for industrial purposes and water importation has continued "at an annualized average rate ranging from about 50 to 130 gpm,…" (Montgomery Watson, 2000).

#### **Impact of land-use on Arroyo Simi**

Arroyo Simi receives water from urban runoff, discharge from industrialized sites (e.g., the SSFL), treated urban sewage (about 10 million gallons per day), groundwater from the dewatering project (about 2000 gallons per minute), and runoff generated from precipitation. The average annual precipitation ranges from more than 18 inches at high elevation areas such as the SSFL (Haley & Aldrich, Inc., 2004) to about 13 inches on the valley floor (Figure 13). Analysis of historical precipitation data (1948-2003) for the valley-floor area shows that the wettest month is February and the driest month is July with monthly average precipitations of 3.27 and 0.02 inches respectively.



Figure 13. Annual total precipitation in Simi Valley floor areas in inches. (Data source: Ventura County Public Works Agency.) (Note: 1948-1970 data were collected in an area with a surface elevation of 760 feet and in 1971 the monitoring station was moved to another area with a surface elevation of 1075 feet.)

Analysis of rainfall-runoff data (Table 4) shows that less than 5% of annual rainfall in Arroyo Simi drainage basin exited the valley as stream discharge in the period 1953-1965. Later urbanization greatly reduced infiltration rates increasing stream discharge to more than 19% of rainfall.

ior the	perious	5110 w II, and	i as percen	tage of the	periou s a	verage ann	uai						
precipitatio	precipitation. (Sources of data: Ventura County and USGS files/data banks).												
Period	1953-1955	1956-1960	1961-1965	1966-1970	1971-1975	1976-1980	1981-1985	1986-1990	199				
Avg. Annual	167.6	964.6	2426	6215	2947	10573	8504	6013	1				
Discharge													
(ac-ft)													
Avg. Annual	9.9	13.2	12.9	15.9	10.9	19.8	16.7	11.3					
precipitation													
(inches)													
Avg. Annual	0.04	0.26	0.64	1.65	0.78	2.81	2.26	1.60					
Discharge													
(inches)													
Discharge as	0.36%	1.36%	3.67	9.06	6.63	12.37	11.86	15.82					
% of annual													
precipitation													

Table 4. Arroyo Simi's average annual discharge (in acre-feet and inches)for theperiods shown, and as percentage of the period's average annualprecipitation.(Sources of data: Ventura County and USGS files/data banks)

From the late 1800s through the early 1960s, land use in the area was primarily agricultural. As discussed earlier, local groundwater supplies, captured runoff water, and water from streams including Arroyo Simi and Arroyo del Tapo were used for irrigation and other purposes. Capturing and utilizing local surface waters, augmented by the disappearance of seeps and springs as a result of major drops in groundwater levels throughout the valley, contributed to total cessation of Arroyo Simi's discharge during dry months, monitored at the western end of the valley at Madera Road (Figure 14).



Figure 14. Annual total discharge for Arroyo Simi in acre-feet.Measurementswere taken at Madera Road bridge. (Data source: VenturaCounty Public WorksAgency and U.S. Geological Survey, Sacramento.)

Discharge rates of Arroyo Simi have increased drastically as a result of major reductions in groundwater usage and the capture and utilization of surface water resources, in tandem with the fast urbanization of the valley and the reduction of infiltration rates from the 1960s onwards. Additionally, importation of water to the valley, the reappearance of seeps and springs as a result of stream/aquifer hydraulic gradient reversal due to groundwater level recovery, addition of waters from the dewatering project and the local wastewater treatment plant have also contributed to higher stream discharge rates. All of these factors have contributed to higher discharge rate is urbanization, which has decreased infiltration and increased runoff rates.

#### Groundwater dewatering system

The historical groundwater level fluctuations in the valley are reflected in Figure 11. As discussed above, from the early 1900s to the early 1960s, the aquifer system was under overdraft conditions and groundwater levels dropped continuously. However, as the valley urbanized, water was imported to the valley and the existing wells destroyed, groundwater levels reached their predevelopment steady-state positions by the 1970s. In the western end of the valley, where groundwater levels were near or above the ground surface, groundwater began to impact the residential and commercial buildings and other man-made structures such as public utility lines (Leighton and Associates, 1972, 1985, 1988).

In order to remedy the high groundwater-related problems in groundwater discharge zone areas in the western end of the valley, the Simi Valley County Sanitation District developed a dewatering system. Through the dewatering system, which at the present is composed of 5 dewatering wells, a flowing well and an array of observation wells, the Simi Valley County Sanitation District continuously discharges about 2000 gallons of groundwater per minute into Arroyo Simi and its tributaries.

The system is effective for a majority of the impacted areas. However, as dewatering wells become less efficient and/or become nonfunctional and in unusually wet years groundwater may reach the ground surface or even surpass the ground surface and interfere with man-made structures. Additionally, as groundwater seeps upward to the surface and undergoes evapotranspiration, dissolved ions and contaminants such as perchlorate may become further concentrated in soils of the area. As a result, saturated soil profile, wet ground surfaces and the potential for accumulation of contaminants in the soil profile have created various environmental, health and economical concerns such as utilization of groundwater.

Utilization of groundwater generated through the dewatering project has not been considered seriously in the past due to a high TDS of about 2000 mg/L and the availability of better quality imported water. As discussed above, the western end of Simi is considered a groundwater discharge zone with a high TDS. However, in the central regions of Simi Valley, TDS of groundwater resources decreases to less than 1000 mg/L. Hydrogeologic observations predict that in high precipitation areas where low TDS rainfall water infiltrates the soil profile and percolates through the deeper geologic units towards bedrock units, TDS of percolating water increases with depth. The TDS of younger groundwater in shallower geologic units (Pleistocene deposits and the weathered

bedrock units) of the SSFL is much higher, compared to the TDS of groundwater samples obtained from the deeper bedrock units (Chatsworth Formation) (Table 5). While over 84% of select groundwater samples obtained from the shallow aquifer units indicate a TDS of over 750 mg/L, over 90% of groundwater samples obtained from deep aquifer units reveal TDS values of less than 750 mg/L. Since the SSFL is located in a recharge zone, the TDS of deeper groundwater may increase with time where shallow and deep hydrogeologic units are interconnected. Despite higher average TDS values of the shallower aquifers at the SSFL, the average TDS values of groundwater samples, obtained from wells developed in aquifers of "discharge zones" of the western end of Simi Valley, are even higher (Table 1) compared to water resources at the SSFL.

In more recent years, due to a higher demand for water and more aggressive water conservation practices by local public agencies a blending of the dewatering project water with imported water has been considered. However, in addition to high concentrations of naturally occurring ions (TDS of up to about 2000 mg/L) such as sulfate (up to about 900 mg/L), and manganese (up to 350  $\mu$  g/L), the recent discovery of perchlorate by Calleguas Water District of Ventura County and the California Department of Toxic Substances, with concentrations of up to 19.28 ppb, has further limited the usefulness of groundwater resources of the valley in general and the dewatering project area in particular.

Table 5. Total dissolved solids (TDS) for groundwater samples obtainedfromshallow (Pleistocene deposits and shallow weathered bedrock units) anddeep(bedrock) aquifer units of the SSFL and the western end of Simi Valley(dewateringareas) aquifer units. (Source of data: Haley & Aldrich, Inc., May2003 andFebruary 2004; and various City of Simi Valley and Ventura Countyhydrogeologicfiles)

	Number of	Average	Minimum	Maximum	<750	750-1500	>1500
	Samples	TDS mg/L	TDS	TDS	mg/L	mg/L	mg/L
			mg/L	mg/L			
<b>Shallow Aquifer</b>	38	1154	485	7475	15.8%	76.3%	7.9%
Units of the							
SSFL							
Deep Aquifer	71	615	150	1500	90.1%	9.9%	0.0%
Units of the							
SSFL							
Western End of	57	1308	614	2498	7.0%	59.7%	33.3%
Simi Valley							
<b>Aquifer Units</b>							

### <u>Perchlorate contamination of soils and waters</u> <u>SSFL and immediate surroundings</u>

Perchlorate and other contaminants have been detected in soils, surface- and ground-water resources of the SSFL and surrounding areas. Characterization of the contamination is based on hundreds of soil and water samples collected and analyzed by the U.S. EPA, CA EPA, Boeing/Rocketdyne Company, Calleguas Water District of

Ventura County, Golden State Water Company and other agencies since 1997 (Montgomery Watson Harza, November 2003; LARWQCB, Department of Toxic Substances Control and City of Simi Valley files). As a result of this extensive sampling program, perchlorate and other contaminants have been detected in soils, surface- and ground- water resources of the SSFL and the surrounding areas including surface waters of the SSFL entering local drainage systems, in the Brandies Bardin Institute groundwater resources, in Meier and Runkle canyons, in Dayton Creek/Canyon areas and in the groundwater resources of Simi Valley.

High perchlorate concentrations have been detected in soil and water resources of the SSFL in areas near the past usage/storage/disposal areas. Lower perchlorate concentrations have been detected in soils and stream/canyon-bed sediments of the areas surrounding the SSFL and groundwater resources of the Simi Valley floor area.

Within the domain of the SSFL, perchlorate concentrations have been detected of up to130,669  $\mu$  g/kg in concrete samples, 71,290  $\mu$  g/kg in soil samples, 23,000  $\mu$  g/L in soil leachate samples, 630  $\mu$  g/L in surface water, 512  $\mu$  g/L in shallow groundwater, 750  $\mu$  g/L in deeper wells developed in the Chatsworth Formation, and 1,600  $\mu$  g/L in a groundwater sample obtained from a short-interval specific zone of the Chatsworth Formation. Low perchlorate concentrations near the detection limits (4  $\mu$  g/L and 5  $\mu$  g/L) have also been recorded in water samples obtained from two offsite wells (Montgomery Watson Harza, February 2003 and June 2003; LARWQCB files).

As discussed previously, the SSFL is located in high elevation regions of the Simi Hills area and encompasses the upper portions of several drainage basins. As a result, surface water flows in several directions from the SSFL highlands towards the local valley floors (Simi Valley and the San Fernando Valley) and other lowland areas (Figure 2). It has been stated that ".....storm water that may have contained perchlorate from the northern portion of the Building 359 RFI site was discharged into the headwaters of the Northern Drainage." (MWH, August 2003).

Streams and canyons (e.g., Dayton, Bell, Meier and Runkle creeks/canyons) are capable of transporting contaminants, including perchlorate and perchlorate compounds assimilated in sediments and concrete, not only as dissolved load but also as bed load and suspended load. As a general rule, during a major rainfall event in the areas with steep stream/canyon gradient (e.g., upper portions of the local valleys and creeks) generated runoff water is capable of transporting contaminants downstream quickly as dissolved, suspended and bed loads. Further down stream/canyon, as the gradient of streams and canyons decreases and near the confluence of tributaries, there is a tendency for deposition of bed load and suspended load as water velocity decreases. As a result, deposited particles with assimilated contaminants may become a source of soil/water contamination to their surrounding locals.

Locally, in addition to sediment deposition, contaminated stream waters may collect or pool in low land areas and undergo evaporation. As a result, contaminants as well as other chemical compounds may concentrate and deposit in the areas where streams are less energetic and stream water pools and water evaporates. The concentration of contaminants in pooled waters and streambed sediments may get diluted to even less than detection limits and/or transported further downstream due to intensive rainfall and runoff events as it was observed in Dayton Canyon in 2005 and in early 2006 (Allwest Remediation, Inc., 2005; Department of Toxic Substances Control files and handouts at local meetings, 2006). Fast spatial and temporal changes in hydraulics, geometry, geology and hydrologic conditions of the local canyons and streams, can lead to drastic spatial changes in transportation and deposition of contaminated sediments. The aforementioned mechanism of solute movement may have played a dominant role in the sporadic detection of perchlorate (Allwest Remediation, Inc., 2005) in sediments of Dayton Creek.

Infiltrated water at the SSFL percolating through the soil profile as well as other sediments and rocks may enter the saturated zone or appear on hillsides and surrounding canyons as interflows, seeps, springs and artesian flowing wells. Surface runoff, interflows, seeps, springs and/or artesian flowing wells can potentially contribute to the spread of naturally occurring chemicals and contaminants.

In 1998, perchlorate with a concentration of 4.26 ppb was detected in a water sample that was obtained from outfall 006, which is located to the north of the Former Sodium Disposal Facility (FSDF) in area IV (LARWQCB files). In soils and groundwaters of the FSDF area, perchlorate has been detected and subsequently the area's soils were excavated in 2000 (Montgomery Watson Harza, February 2004). Additionally, north of area IV along Meier Canyon, perchlorate with a concentration of 4.6  $\mu$  g/L was detected in a near ground surface sediment sample that was collected and analyzed by the Department of Toxic Substances Control in 2002 (Department of Toxic Substances Control, April and September 2003).

The extent of perchlorate and perchlorate compounds that may have been historically dispersed to the surrounding areas from the SSFL through soil erosion by wind and surface runoff is unknown. Some investigators believe that perchlorate contamination is limited in lateral and vertical extent to distances no greater than a few thousand feet from its source. However, surface runoff water is capable of transporting perchlorate and other contaminants to much greater distances in short time periods as it has been stated that perchlorate and perchlorate compounds have been disposed of at and near the ground surface at the SSFL (Montgomery Watson Harza, August 2003).

During more recent years (Montgomery Watson Harza, August 2003), in order to minimize or eliminate contamination of the areas surrounding the SSFL by contaminated runoff water generated at the SSFL, as required by the National Pollutant Discharge Elimination System program (NPDES), a monitoring system has been developed and the SSFL's "outgoing" surface water has been monitored for various contaminants and since 1998 for perchlorate repeatedly at eight outfalls. In addition to mercury, copper and other contaminants exceeding their permissible limits at times (e.g., October and December 2004, LARWQCB files) perchlorate has been detected in some "outgoing" waters. The highest concentration of perchlorate detected was 35.1  $\mu$  g/L at the Happy Valley monitoring station; waters entering Meier Canyon contained a perchlorate concentration of 4.26  $\mu$  g/L (LARWQCB files).

Based on limited perchlorate data collected under the NPDES program during recent years, it appears that perchlorate concentrations in runoff waters leaving the site have been decreasing, particularly at the Happy Valley Outfall where the NPDES monitoring station is located (Table 6). However, the status of past temporal changes of stream load with respect to assimilated contaminants is not known.

Table 6. Perchlorate concentrations for water samples with higher than detectionlimit concentrations obtained from the Happy Valley Outfall station (Source ofdata: Los Angeles Regional Water Quality Control Board Files).

Sampling	3/98	5/98	5/98	5/98	5/98	2/00	3/00	3/00	3/00	4/00	1/01	2/01	2/01	3/01	3/01	3/01	3/01	2/03	2/03	3/03
Date																				
Perchlorate	20	35.1	22	28.3	8.24	16	13	17	8.2	9.4	8	5.5	4.2	5.3	4.9	5.2	4.8	4.7	12	5.3
Concentration																				
( $\mu$ g/L)																				

Historical perchlorate concentrations in soils and waters of the area were likely higher than those at present day. Factors that may have contributed to perchlorate concentration dilutions and reductions in general and shallower groundwater depths in particular are remedial activities such as source elimination in Happy Valley and the Former Sodium Disposal Facility (FSDF) areas. Also decreased perchlorate usage, dilution of contaminated waters by infiltrated water from precipitation and imported water, rainfall and runoff distribution and intensity, and changes in monitoring or sampling locations, are among factors that may have contributed to this decrease in concentrations. For example, Montgomery Watson Harza (November 2003) indicates that "Historically, perchlorate was detected in soil that was subsequently excavated as part of the FSDFIM during 2000; perchlorate was not detected in the remaining soils/bedrock at the FSDF." As discussed before, the SSFL area is located in high elevation regions of the Simi Hills and is considered a regional groundwater recharge zone. Although there have been major historical changes in the groundwater hydraulics of the area, it encompasses several groundwater divides. As a result, contaminated groundwater of the area can potentially flow in several directions toward local valley floors and lowland areas, including groundwater discharge zones and could appear as seeps, springs, and flowing (artesian) wells on hillsides and surrounding valley floors.

Perchlorate and nitrosodimethylamine (a byproduct of liquid rocket fuel) have been detected at several locations near the SSFL although some are putative as to detection or source (Department of Toxic Substances Control, 2004; Montgomery Watson Harza, August 2003; LARWQCB files). Perchlorate with a concentration of 28ppb was detected in a water sample obtained from a flowing well less than 2 miles south of the SSFL boundary and Bell Creek in Ahmanson Ranch; perchlorate with concentrations up to 150  $\mu$  g/L, in samples from a flowing well located about one mile north of the SSFL at the Brandeis Bardin Institute (Montgomery Watson Harza, August 2003); perchlorate with concentrations up to 62,000 mg/kg in Dayton Canyon stream-bed sediments obtained from areas about one mile east of the SSFL's eastern boundary (Allwest Remediation, Inc., 2005) and perchlorate concentrations up to 60  $\mu$  g/kg in sediment-groundwater samples located about 0.5 miles west/northwest of the SSFL boundary (Miller Brooks Environmental, Inc., May 2003 and September 2003).

Subsequent testing for perchlorate in groundwater samples obtained from the aforementioned locations, did not detect perchlorate in some areas and more site-specific investigation and data collection is required to confirm the presence or absence of perchlorate and other contaminants and their potential association with the SSFL activities. For example, there are several faults and shear zones that cross the SSFL and the surrounding areas (Dibblee, 1992). For the most part, these structures are not well-

characterized, and their effect on the fate and transport of perchlorate has not been fully understood.

As discussed above, although the most extensively perchlorate-contaminated areas are located where usage, storage, disposal, and destruction of perchlorate/perchlorate compounds were the most intensive, there are strong spatial (lateral and vertical) and temporal changes in concentrations of perchlorate on-site within the SSFL domain itself and offsite on hillsides and valley floor areas. Temporal fluctuations in perchlorate concentrations of at least two orders of magnitude have been observed in groundwater samples obtained from wells developed in the Chatsworth Formation near the contaminant-source areas of the SSFL. One of the most challenging issues in areas such as the Brandeis Bardin Institute and Ahmanson Ranch, which need long-term short interval sampling, is to further explore the mechanism and reasons for erratic and drastic temporal changes in perchlorate concentrations.

Short-term temporal or spatial changes in surface water and groundwater hydraulics including major seasonal changes in water levels in streams, ponds, and groundwater reservoirs are among the factors that may have influenced the spatial and temporal distribution and fluctuations of perchlorate concentrations in the area. Remedial activities and related processes (Montgomery Watson Harza, February 2003) may have also influenced these erratic temporal changes. Based on available data collected by various agencies (LARWQCB files), no long term regional temporal trends in perchlorate concentrations can be deciphered. In some areas, fluctuations in perchlorate concentrations range from hundreds of ppb to non-detectable levels and back to hundreds of ppb, while in other areas fluctuations have not been as drastic.

Heterogeneity and anisotropy of the aquifer system dominantly impact the movement and spread of perchlorate and other contaminants in the area. While perchlorate has been detected in water samples obtained from shallow wells (less than 120 feet deep) developed in areas where perchlorate has been used, destroyed and/or stored, it has not been detected in a 2300-foot deep pumping well located only about 1000 feet away (Montgomery Watson Harza, February 2003). The lack of the detection of perchlorate at such a short distance away is not necessarily a confirmation of the lack of perchlorate movement in the area. Such observations could be due to contaminant dilution, small vertical hydraulic gradient (Montgomery Watson Harza, February 2003) and/or heterogeneity and anisotropy of the local hydrogeologic system including erratic fracture patterns in the rocks.

Recent lithologic and video camera logging conducted in the area (Haley & Aldrich, Inc., May 2003) have revealed fractures with openings of up to 1/8 of an inch in deeper rocks. Also, a significant amount of claystone and calcareous rocks exist in the impacted areas and the continuity of the fractures in brittle rocks and solution cavities in calcareous rocks are not known. The presence or lack of clay minerals with available negative charges and their influence on perchlorate's fate and transport are also unknown.

Montgomery Watson Harza (February 2003) concluded that "detected perchlorate concentrations in Chatsworth Formation groundwater are similar to or higher than concentrations in near-surface groundwater." The detected perchlorate in aquifer units must have traveled through the soil profile and the unsaturated zone, before reaching the deeper Chatsworth Formation units. Therefore, it is likely that the perchlorate concentrations of shallower soil and saturated zone units were higher in the past and

molecular diffusion has not been effective enough to stop or slow down the transport and spread of perchlorate toward the deeper aquifer units.

## <u>Perchlorate contamination of soils and waters</u> <u>Simi Valley floor</u>

Perchlorate was discovered in a groundwater sample obtained from the dewatering project area in the western end of Simi Valley. Following this discovery and to define the extent of groundwater contamination by perchlorate, water samples from existing shallow monitoring wells at several local gas stations, other dewatering wells and the associated monitoring wells, and groundwater production wells screened in unconsolidated deposits were tested. Groundwater samples were also collected from the seep areas in the western end of the valley by various agencies. Several surface water and soil samples from local streams and canyons also were analyzed for perchlorate. Many of these samples were specifically collected to define the temporal changes and the spatial extent of perchlorate contaminations in soils and waters of the valley.

The results of these measurements show that the spatial distribution and concentration of perchlorate are highly variable. Concentrations of perchlorate in groundwater samples were up to about 19  $\mu$  g/L (LARWQCB files) and up to 4.8  $\mu$  g/L in samples from the groundwater seep areas within the residential areas of the western end of Simi Valley. No perchlorate has been detected in surface water samples obtained from Arroyo Simi and its tributaries. On the valley floor itself, most of the sampling sites with detectable perchlorate levels are within a short distance from Arroyo Simi and almost all of them are confined to a narrow zone within approximately one mile from the course of Arroyo Simi and west of Stearns Street. With the exception of the SSFL and its immediate perimeter, no perchlorate has been detected in water samples from the areas east of Stearns Street or in the areas outside of this one-mile zone from the river. In addition, based on limited samples, no perchlorate has been detected in surface water samples collected from the valley floor area and along the course of Arroyo Simi itself and its northern tributaries.

Within the one mile distance zone, concentrations of detected perchlorate in groundwater samples are highly variable. In addition to the heterogeneous and anisotropic nature of the Pleistocene and Holocene deposits due to temporal and spatial changes in depositional systems, other factors that might influence this variability include historical and seasonal changes in surface water and the groundwater hydraulics of the valley floor area. In contrast to the downward component of groundwater flow in alluvial fan heads on the hills and hillsides, groundwater flow in the areas along the course of Arroyo Simi, particularly the western end of Simi Valley, has an upward flow component from the lower portions of Pleistocene deposits and the area acts as a discharge zone. Upward leakage including bedrock leakage of water has likely diluted the contaminant concentrations that entered the shallower parts of the saturated zone from losing streams and/or from the land surface. In addition, seasonal fluctuations in Arroyo Simi's water levels, a major rise in water levels and the formation of bank storage and its subsequent discharge in unusually wet years and flood periods must have had major historical influences on the distribution and concentration of chemical species in the areas adjacent to Arrovo Simi.

In parts of the SSFL area, groundwater stored in fractured, sheared and faulted bedrock units, are contaminated by perchlorate and other solutes. Although these contaminants may move quickly through such fractured and faulted zones, especially the fault and shear zones which mostly contain modest amounts to no gouge that might impede water transmission (Montgomery Watson, 2000), the extent of such conduits in bedrock formations underlying the Pleistocene/Pliocene rocks of the Simi Valley area is unknown. Due to the lack of monitoring wells dedicated to the unsaturated zone and the sub-Pleistocene/Pliocene bedrock units and most of the area outside the one-mile distance zone, the extent of perchlorate contamination of soil and groundwater resources of these areas is unknown.

The present total amount of perchlorate dissolved in the groundwater resources (both the saturated and the unsaturated zones) of Simi Valley is difficult to estimate. It has been approximated that the Simi Valley Groundwater Basin's storage capacity is about 180,000 acre-feet (California Department of Water Resources, 2003), however the availability of measurements of the perchlorate concentrations for the saturated zone in general and outside the one-mile distance zone in particular is minimal and perchlorate data is unavailable for the unsaturated zone or the bedrock units throughout the valley. Due to a lack of data, the past and present total amount of perchlorate dissolved in the water resources of the Simi Valley area are difficult to estimate.

Past concentration of contaminants in groundwater may have been reduced as valley groundwater levels recovered from overdraft in the 1970s and stream-aquifer hydraulics were reversed. Through natural groundwater discharge (underflow, evapotranspiration, baseflow) and groundwater discharge through the dewatering project, significant amounts of Simi's groundwater in the western end have been removed since the 1970s and replaced by more recent waters from local precipitation and over irrigation. A trend toward lower perchlorate concentrations will likely continue into the future, due to contaminant-source elimination/reduction and further future dilution, assuming no new perchlorate enters the valley. In addition, the impact of the western end of Simi Valley's unconsolidated material with organic content and its potential reduction of perchlorate concentrations historically as well as perchlorate's conversion to other chemical species is not known. Based on a preliminary investigation in Massachusetts, it has been found that even though tap water perchlorate concentrations there ranged from 190 to 943  $\mu$  g/L, the associated septic tank effluents showed nearly complete destruction of perchlorate to concentrations of less than 0.23  $\mu$  g/L (Massachusetts Department of Environmental Protection, 2005).

#### Potential sources of perchlorate

During recent years, with the advancement and refinement of methodology and technology in the detection of contaminants at low concentrations, perchlorate has been found in rain water, residential wastewater and road runoff (Munster et al, 2006), drinking water (Metropolitan Water District of Southern California, 1998; Motzer, 2001; Jackson et al, 2003; Thorne, 2004; Jackson et al, 2005; United States Government Accountability Office, USGAO, 2005; GeoSyntec Consultants, 2005), food supplies (Ellington and Evans, 2000) and even in a variety of tobacco products (Syracuse Research Corporation, 2005), which has threatened the safety of food and drinking water supplies and in turn human health (California Environmental Protection Agency, 2005).

Based on the USGAO's review of 90 health risk studies published since 1998, it has been stated that "For 26 of the 90 studies, the findings indicated that perchlorate had an adverse effect. Eighteen of these studies found adverse effects on development resulting from maternal exposure to perchlorate." (USGAO, 2005). "Children and

developing fetuses may be more likely to be affected by perchlorate than adults because thyroid hormones are essential for normal growth and development." (Syracuse Research Corporation, 2005). The results of other research have further shown that "....after 28 days of exposure to ammonium perchlorate, fish exposed to the two higher levels (10 and 100 mg/L) were developmentally retarded, with a lack of scales and poor pigmentation, and significantly lower wet weight....." (Crane et al., 2005).

The introduction of perchlorate to food and water supplies has been traced to anthropogenic sources and man-made products, which contain manufactured perchlorate compounds (Syracuse Research Corporation, 2005), and in much smaller proportion to naturally occurring compounds in some fertilizers (Chilean nitrate fertilizers) (Urbansky et al, 2001; Jackson et al, 2003). Perchlorate compounds may occur as "a natural mineralogical impurity" or through "in situ generation of perchlorate by electrochemical reactions" (Jackson et al, 2005). Chemical analysis of caliche ores produced in two major production plants in Chile from 1932 to 1967 has revealed an average concentration of 6.3% and 0.03% for nitrate and perchlorate respectively (Ericksen, 1983). It has been reported that 305,614 tons of Chilean Sodium Nitrate fertilizer had been used in California between 1923 and 1960 and "Since 2002, it is estimated that some 75,000 tons of Chilean nitrate fertilizer containing 0.01% perchlorate have been used annually in the U.S.,…." (GeoSyntec Consultants, 2005).

The source of the bulk of perchlorate detected in the environment and food supply is anthropogenic as "....no chemical process acting at temperatures and pressures found at the earth's surface is known to produce perchlorate" and perchlorate occurring in caliche ores of Chile "..... may have been formed by photochemical reactions, perhaps between chlorine and ozone in the atmosphere or at ground level" (Ericksen, 1983).

Since the 1940s, significant amounts of perchlorate compounds (Na, K, NH<sub>4</sub>) have been manufactured for various purposes through methods such as "prolonged electrolysis of hot solutions" and anodic oxidation of the chlorate ion, which can be converted to perchlorate (Nebergall et al, 1976).

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^-$$

In addition to the electrolysis process used in perchlorate compound production, it has been shown that chlorate compounds can be converted to perchlorate compounds through "self-oxidation" and the reaction of chlorates with "strong oxidizing agents" such as ozone (Schumacher, 1960 in Massachusetts Department of Environmental Protection, 2005).

The manufactured perchlorate compounds have been used and/or detected as oxidizing agents in many products, including various military-related explosives, blasting agents for construction, fireworks, matches, safety airbags, road flares, hypochlorite solutions/household bleach and perchloric acid used in industrial activities (Syracuse Research Corporation, 2005; Crane et al. 2005; GeoSyntec Consultants, 2005; Massachusetts Department of Environmental Protection, 2005). Locally, in southeast Ventura County, perchlorate compounds were used for various activities including the manufacture of rocket fuel and were stored and disposed of at the SSFL.

Perchlorate has an aqueous solubility of 217,000 to 220,000 mg/L at 20°C (Motzer, 2001) and can remain in the environment for many decades. Being a negatively charged and conservative ion, perchlorate may not bond to other anions and porous media in environments with available negative charges (clay minerals), if such minerals exist as

finer-grained geologic rocks such as shale and claystone. Perchlorate is a stable ion that can persist in the environment, including moving groundwater, for years. As a result, in areas such as the SSFL, although extensive usage, storage and/or disposal of various chemicals including perchlorate and perchlorate compounds have been reduced significantly or halted totally as a result of major reductions in the amount of rocketengine testing and other related activities, high concentrations of perchlorate and other chemicals have been detected and persisted in the soil and water resources of the area for many years and will likely remain into the future.

Although other putative sources of perchlorate in the soils and water resources of the area have been suggested, the SSFL is the only confirmed industrial area where perchlorate compounds have been used, stored, and disposed of that represents a plausible source for perchlorate contamination in the area. From the 1950s through the early 1990s, perchlorate compounds were used for various purposes including turbine spinners and the development and usage of thousands of igniters, containing about 3 grams of perchlorate each, flare research and production, and solid rocket propellant research and testing and other related operational activities (Montgomery Watson Harza, November 2003 and February 2003).

In addition to the usage of perchlorate compounds, various methods were used to dispose of perchlorate and perchlorate compounds at the SSFL, such as burial or burning activities (Rocketdyne, 1960). Treatment and destruction of perchlorate compounds were more significant in some parts of the SSFL prior to 1971 (Montgomery Watson Harza, February 2003). In 2003, it was reported that the quantity of perchlorate compounds used at the SSFL was limited to the usage of igniters and the storage of about five pounds of magnesium perchlorate (Montgomery Watson Harza, February 2003).

Use, storage, and disposal of hundreds of pounds of perchlorate compounds at the SSFL have been documented, mostly from the 1960s through the early 1990s (MWH, February 2003). Due to temporal changes in the quantity of usage, storage, destruction, and disposal practices of perchlorate and perchlorate compounds and the lack of comprehensive monitoring and documentation of perchlorate-related activities, an accurate historical assessment of perchlorate-relate contamination in the area is impossible.

Perchlorate contamination on the site and in nearby canyons such as Dayton Canyon are demonstrably related to the SSFL activities. Explanations offered (MWH, February 2003 and November 2003; Allwest Remediation, Inc., 2005; LARWQCB files) for potential sources of perchlorate contamination detected in samples obtained from Simi Valley and other nearby areas such as Dayton Canyon include false laboratory readings, fertilizers used on agricultural land and in nurseries, road flares, fireworks, explosives used in construction and mining operations and intentional spread of perchlorate compounds by humans. Available data show that southeast areas of Ventura County and the adjoining areas (e.g., Simi Valley, Dayton Canyon) as the only places with confirmed high concentrations and widespread perchlorate contamination of soil and water resources. In addition, based on a limited number of soil/sediment (stream-bed sediments) and surface water samples, no perchlorate has been detected in the topsoil and surface waters (e.g., Arroyo Simi) of the Simi Valley floor area.

A potential source of perchlorate to the environment has been some more recently manufactured blasting agents. It has been stated that common commercial explosives

and blasting agents that may have been used for industrial purposes in the past (e.g., well development, sand and gravel mining operation and oil industry), do not appear to have contained perchlorate compounds (Dick, 1968). However, in Massachusetts, the highest concentrations of perchlorate contaminations of groundwater and small streams have been attributed to blasting agents with up to 30% ammonium perchlorate that were used at a new municipal building site in 2003 and 2004 and no perchlorate was detected in a nearby quarry, "…which have presumably used a variety of explosive materials for decades." (Massachusetts Department of Environmental Protection, 2005). It is likely that perchlorate is being used in more "recently" manufactured blasting agents.

It also has been stated that natural occurrences and formation of perchlorate compounds occurred in material used in nitrate fertilizer making and road flares as other potential sources of the area's perchlorate contamination. However, there is no published data or any research to confirm that usage of fertilizers and road flares in the area as the sources of perchlorate to the groundwater resources of Simi Valley and the surrounding areas including the recently discovered perchlorate in sediments of Dayton Creek.

Many of the aforementioned products such as fertilizers, blasting agents for constructional activities, fireworks, road safety flares with or without perchlorate compounds, have been used throughout the Ventura County and Simi Valley area. It has been stated that ".... the U.S. imported an estimated 19 million tons of Chilean nitrate...." during the time period of 1909 to 1929 for which detailed information could have been obtained and ".....the use of Chilean nitrate fertilizers has steadily declined since about the 1930s....." (GeoSyntec Consultants, 2005). During the aforementioned time period (1909-1929) the total amounts of fertilizer application in the Simi Valley area was likely minimal by homeowners as the population of the area was low (Figure 3). Even though the Simi Land and Water Company was formed in 1887 and ranching and small-scale agricultural activities started in the 1800s (Cameron, 1963), the local orchard fields (citrus, walnuts, apricots, figs, plums, beets, etc.) and other agricultural activities did not reach their peak capacity, development and productivity until the 1930s and 40s (Cameron, 1963; Havens, 1997).

The population of Simi Valley has been consistently increasing and this increase accelerated in the 1960s and 1970s (Figure 3). As a result, activities such as the application of fertilizers by homeowners and nurseries, fireworks for various occasions, and the usage of road flares have likely increased proportionally to the area's population and automobile increase. Such activities are likely not the sources of perchlorate contamination of the area as no perchlorate has been detected in the limited number of surface water samples collected (Department of Toxic Substances Control, April 2003) throughout the valley floor, near the high road flare and firework usage and mining and tunneling areas.

Although fertilizers have been used all over the valley area and Tapo Canyon by farmers in the past and homeowners at present, perchlorate contamination of valley area is mostly confined to a one mile distance zone along Arroyo Simi and hydraulically and topographically down gradient from the SSFL.

Every year, several major accidents happen on the 118 Freeway near Kuehner Drive (Figure 2) and road flares are used and the largest annual Independence Day fireworks display in the Valley and other fireworks displays for other occasions are conducted at Simi Valley High School annually. There is no data available if any residue from fireworks had been left behind after a firework display and no perchlorate has been detected in limited water samples obtained near these areas. The lack of detection of perchlorate in the surface water and soil samples obtained along Arroyo Simi and its associated tributaries fails to confirm the generation of perchlorate from recent usage of road flares and fireworks in the City, along the 118 Freeway and in up-gradient areas of Arroyo Simi, which is directly impacted by runoff water from a portion of the 118 Freeway, where on an annual basis, several major accidents occur and road flares are known to be used (personal observation). However, in other areas of the U.S. the association of perchlorate in groundwater resources and usage of fireworks has been established. In Massachusetts, after some vigorous testing in the areas where fire works have been used, in one case only in one well out of 97, perchlorate was detected at a reporting limit of 1  $\mu$  g/L and in another case out of 31 wells, perchlorate was detected in 17 of them at a reporting limit of 0.20  $\mu$  g/L (Massachusetts Department of Environmental Protection, 2005).

During recent years, perchlorate at concentrations of less than 10 parts per billion has been detected in the Colorado River Aqueduct system waters and Colorado River waters. Through the Colorado River Aqueduct system, water was imported into the Simi Valley area from the early 1960s to early 1970s.

The Colorado River Aqueduct system with a capacity of 1.3 million acre-feet annually, is owned and operated by the Metropolitan Water District of Southern California (MWD). The Colorado River Aqueduct system construction began in 1933 and went into operation in 1941. In 1960, a local water agency in Ventura County (Calleguas Water District of Ventura County) joined the MWD (Metropolitan Water District of Southern California, 2004). Subsequently, through the Calleguas Water District, Colorado River water was imported to Simi Valley for a period of about 10 years from the early 1960s to early 1970s (Figure 12).

Although, initially, perchlorate at concentrations of 5 to 8 ppb was detected in the Colorado River Aqueduct system in 1997 and "samples taken from the Lake mead outlet tower at Hoover Dam contained 8 ppb, while samples at Lake Havasu were 6 ppb" (Metropolitan Water District of Southern California, 1998), due to a lack of historical perchlorate data, it is impossible to confirm the concentration and occurrence of perchlorate, if any, in the Colorado River waters that were imported to Simi Valley in the 1960s. The oldest water samples confirming the occurrence of perchlorate in the water resources of the Colorado River, which in turn may have impacted the Colorado River Aqueduct system by perchlorate at present detectable levels, is from frozen water samples that were collected from Las Vegas Wash and Lake Mead starting in 1993 (Hogue, 2003). Based on the results of the aforementioned frozen water samples and more recently collected water samples, it has been calculated that the amount of perchlorate that entered Lake Mead through the Las Vegas Wash increased from 440 pounds/day in 1993 to 900-1000 pounds per day by 1999. Then, as a result of remedial activities, it decreased the concentrations to 500 pounds or less per day and it has been stated that by late 2004, it would have been reduced to less than 50 pounds per day (Hogue, 2003; Pitzer, 2003). Based on this data, the amount of perchlorate that entered Lake Mead was on an increasing trend in the 1990s, however lack of its presence in the Colorado River waters and in turn the Colorado River Aqueduct system between the time span of the early 1960s to early 1970s cannot be confirmed.

The source area, from which the Colorado River system has received perchlorate, started perchlorate compound manufacturing in the early 1940s and full-scale manufacturing of perchlorate compounds began in the early 1950s "at about 2,000 tons a year" and "peaked in the mid-1980s at 15,000 tons a year" (Hogue, 2003; Metropolitan Water District of Southern California, 1998). Based on groundwater flow modeling simulation results, it has been stated that "The evaluation of the time of travel of perchlorate concentration fronts revealed that the 5 ppm and 50 ppm concentration fronts had times of travel, from the industrial area to the Las Vegas Wash, of approximately 25 and 46 years, respectively." (Batista and others, 2003). This water from the Las Vegas Wash had to travel through the Colorado River system including Lake Mead and the Colorado River Aqueduct system for a distance of several hundred miles before it entered the Simi Valley area.

While perchlorate concentrations detected in the groundwater samples of Simi Valley, collected in the late 1990s and early 2000s had ranges up to just over 19 ppb, water samples collected more recently (May 2003) in the areas closer to the Hoover Dam site, are much lower (<4-8.8ppb) (Peggy Roefer, electronic communication, 2003). In addition, it is not known if the imported Colorado River water to the Simi Valley area in the 1960s and early 1970s was blended before its importation to the Simi Valley area. Possible blending with local groundwater resources would have further diluted the chemical concentrations.

Since the early 1970s, when the importation of Colorado River waters to Simi Valley ceased, a significant amount of rainwater and imported State Water Project waters have recharged Simi's aquifer system and concurrently, a significant amount of local groundwater has been discharged and exited the area through the dewatering system, seeps, springs and underflow. As a result of this, concentrations of perchlorate in the groundwater resources of the valley may have been diluted during recent years.

A limited number of surface water samples have been collected (LARWQCB files) and analyzed for perchlorate near the areas potentially impacted by the imported Colorado River water. No traceable amounts of perchlorate have been detected in water samples obtained near and down-gradient from these areas (e.g., the tunnel where the Colorado River water was conveyed to Simi Valley) and down-gradient areas of a former industrial liquid waste lagoon and a sewage disposal area (Figure 15).

In addition to water samples, the California Department of Toxic Substances Control and other agencies have sampled and analyzed many near-surface stream/canyon-bed sediment samples for occurrence and source-determination of perchlorate. Such testing has been conducted in other areas of California in source determination, characterization and extent of perchlorate contamination. Based on the aforementioned investigations in other areas of California, it has been stated that "very near-surface sediments concentrate perchlorate in areas with continuing sources." (Montgomery Watson Harza, December 2003). Although it is likely that "continued releases" from "continuing sources" may have led to accumulation of salts including perchlorate compounds in "near-surface sediments" of those areas, through a model that was proposed in 2003 (Tabidian, 2003), it has been suggested that the past releases of perchlorate to the local canyons, such as Meier and Dayton canyons, may have been intermittent and episodical, similar to more recent episodical releases to Dayton Canyon. The intermittent and episodical contaminant releases are due to the nature of temporal and spatial perchlorate-related activities and extreme variability in local climatic and hydrologic conditions in the area. For example, more recently, in stream-bed sediments collected in May 2005, perchlorate with concentrations of up to 62,000 mg/kg was measured in sediments of Dayton Creek. However, through subsequent tests that were conducted in early 2006, after several major rainfall events, no perchlorate was detected in sediments of the same areas along the Dayton Creek/Canyon.



# Figure 15. Location of a former industrial liquid waste and a sewage disposal facility in north central Simi Valley. (Source: From an unpublished map showing surface water quality for 1960 through 1964, prepared by Dr. John Mann?)

As a result of many near-surface stream/canyon-bed sediment sampling conducted north and northwest of the SSFL, only one sediment sample from Meier Canyon, which leads to Simi Valley, revealed a perchlorate concentration of 4.6  $\mu$  g/kg (Department of Toxic Substances Control, April 2003). Based on recent observations in Dayton Canyon, the present lack of perchlorate occurrence in many stream/canyon-bed sediments obtained from shallow depths is not necessarily a confirmation that the stream/canyon-bed sediments and water that passed through these streams/canyons were not contaminated by perchlorate in the past.

With respect to occurrence of perchlorate in waters and sediment of southeast Ventura County and the adjacent areas, several spatial and temporal anomalies have been observed. Recent sampling results reveal that perchlorate has been detected in water samples obtained from the NPDES outfall areas of Dayton Canyon. However, no perchlorate has been detected in samples obtained from the downstream areas. This could have been due to dilution and/or stream-bed leachate and washout similar to what has been suggested for the Las Vegas Wash, near Las Vegas, Nevada. It has been stated that for the "perchlorate which has settled in the gravels of the Las Vegas Wash...." the results of "....modeling shows that with the current level of releases into the Wash most of those deposits will flush out within about two years...." and "Sampling thus far is consistent with the model." (Siegel, 2004). Sediment samples collected at the SSFL downstream areas from where the highest perchlorate concentrations have been found (up to 71.29 mg/kg) do not contain significant amounts of perchlorate. It has been stated that "samples of sediment collected along the Happy Valley drainage did not indicate that the sediments were appreciably impacted, as most did not contain perchlorate above the reporting limit." (Montgomery Watson Harza, February 2003). Perchlorate may have been diluted and washed out of the surface- and near the surface-sediments of the local drainage systems similar to the Las Vegas Wash or Dayton Canyon. Such "wash outs" along with contaminated sediment load, may "pool" farther downstream in low gradient areas and contaminants may be concentrated through evaporation. Contaminated sediment load may also deposit in low gradient and less energetic areas. In addition to "wash outs", "pooling-evaporation", deposition of contaminated "sediment load" and "post-deposition dilution" other factors that may have influenced concentration of perchlorate spatially are variations in clay content of sediments and in turn lack of opportunity for perchlorate compounds to be formed and sediment erosion.

It has been reported that the clay mineral kaolinite is abundant in a major portion of rock units in the southeast Simi Valley area (Hanson, 1981). The extent of the occurrence of clay minerals in general, and montmorillonite and kaolinite in particular in rocks associated with the Chatsworth Formation and stream-bed sediments and their potential impact on perchlorate fate and transport are unknown. Some clay minerals with available negative charges, high ionic exchange capacity and availability of high surface area (Langmuir, 1997), can have a dominant impact on advection, dispersion and diffusion of contaminants in general and the negatively charged contaminants such as perchlorate in particular.

#### **Conclusions and recommendations for future study**

Based on what has been experienced in the Simi Valley area as a result of historical groundwater-related developments, in real estate transactions and land-use conversions (e.g., farming to urban), a temporal trend analysis of groundwater levels, at least in some areas, can save time, money and potential litigations. In the Simi Valley area, even though a significant amount of resources are spent annually to keep high groundwater levels under control, still, high groundwater levels, especially during the higher than normal precipitation years, remain a source of concern for local homeowners.

In addition, the discovery of perchlorate in high groundwater level areas during recent years has become another issue for some local homeowners and residents.

A detailed analysis of historical stream-aquifer data shows that groundwater depletion reversed stream-groundwater hydraulics causing Arroyo Simi to become an influent stream in the 1950s and 1960s. As a result of stream losses, local groundwater quality including the portions of the aquifer system in proximity to Arroyo Simi were likely degraded by contaminants in Arroyo Simi's water. At the present, the potential for contaminants in Arroyo Simi's water to enter the dewatering project area's lower aquifer system units is low compared to 1950s and 1960s. It is due to a reversal of groundwater hydraulics during the more recent years.

In the areas where groundwater and stream-bed sediments are contaminated with perchlorate, the past and present role of local stream systems in contaminant transport, as part of stream load in general and the dissolved load in particular, and their interactions with groundwater reservoirs must be considered. Runoff contaminated with perchlorate generated from the contaminated sites, could potentially contaminate groundwater reservoirs miles away from the source. During more recent years, with all strict monitoring and environmental regulations, perchlorate, mercury and other contaminants have been released from the SSFL to Simi Valley and the San Fernando Valley via surface runoff. Considering less stringent environmental laws and monitoring augmented with much higher chemical usage and industrial and industrial waste disposal activities in the past, it is likely that significant amounts of chemicals including perchlorate were transported to surrounding areas via local creeks and canyons.

The temporal and spatial distribution of perchlorate in the area and the extent of streams, ponds, landfills, "dumps" and liquid waste lagoons losses and gains are not known. In particular, the influence of streams' and canyons' characteristics (e.g. stream gradient, stream-bed sediments characteristics as related to bed load and suspended load) on contaminant fate and transport have not been confirmed or quantified. To better quantify stream/aquifer hydraulics, detailed discharge measurements and investigation of the aquifer hydraulics and stream-bed deposits along Arroyo Simi and its tributaries and other local canyons such as Dayton Canyon/Creek are recommended.

On an unpublished map, general surface water quality of the area for the period of 1960 through 1964 has been compiled. On this map, the locations of a sewage disposal facility/activities and an industrial lagoon with TDS of 1,336 and 22,835 mg/L respectively have been shown. The lagoon was located near the head areas of a major alluvial fan associated with Arroyo del Tapo. The source of liquid waste to this industrial lagoon, its function, which was likely oil-related, and its potential impact on water resources of the area needs to be evaluated.

Based on historical groundwater quality data, the dominant ions in the groundwater in the Quaternary deposits of the Simi Valley area are calcium, sodium and sulfate (California Department of water Resources, 1959 in California Department of water resources, 2003). To investigate and deterministically identify the Colorado River waters impact on the groundwater resources of Simi Valley, water characteristics (e.g., the dominant ions and isotopic characteristics) of those areas impacted by perchlorate should be assessed and compared to those of the Colorado River waters.

Existing shallow-depth monitoring wells at local gas stations and dewatering and domestic wells, screened against the productive zones of the Pleistocene and Holocene

deposits, have been used for perchlorate investigation by several agencies. Although the existence of perchlorate in the groundwater resources of Simi Valley (the saturated zone) has been confirmed by various agencies, the extent of the unsaturated zone contamination by perchlorate and its role in perchlorate fate and transport are unknown.

Perchlorate has been detected in shallow groundwaters and the dewatering project waters within residential areas of the western end of Simi Valley but its past and present impact on the local ecology needs to be assessed. Research has shown that occurrence of perchlorate in soil and irrigation water can be absorbed by plants (e.g. lettuce, cucumber and tobacco) (Crane et al., 2005; Ellington et al., 2001; Ellington and Evans, 2000; Susarla et al., 1999) through their root systems and in turn has entered the food supplies (e.g., milk and lettuce) and biological systems such as humans.

Although the local aquifer system has been characterized and groundwater availability has been quantified, the lack of dedicated monitoring wells and sparse perchlorate data deems it impossible to quantify the amount of perchlorate that exists in the groundwater resources of Simi Valley.

Sources of water imported to the area will likely dwindle in the future and the population of the area will increase. To satisfy demand, local aquifer systems will become an important component of local water supplies, but they will remain at risk because contaminants' sources in the area will persist for decades due to the magnitude and nature of contaminants such as TCE and due to "reverse diffusion" (Sterling et al., 2005) of contaminants along the fracture zones. It is necessary, therefore, to develop a comprehensive long-term monitoring system composed of monitoring wells developed in bedrock units as well as Pleistocene deposits and in the areas inside and outside the "one-mile distance zone" to detect, characterize and protect the quality of local groundwater resources, including the areas where two active wells, operated by the Golden State Water Company, are located. Development of "wellhead protection zone" (U.S. EPA, 1993) associated with these wells are recommended as perchlorate has been discovered in groundwater samples obtained from the production and the nearby monitoring wells.

It has been reported that three of the four public supply wells that were sampled for radiological activities had concentrations above MCL (California Department of Water Resources, 2003). It is important to investigate the source (s) of the aforementioned radio-nuclides and other contaminants in the area. In particular, in the south central areas of Simi Valley environmental monitoring and the number of monitoring wells have been scant. The development of a long-term and scientific-based monitoring system is recommended.

Although, based on the analysis of a limited number of soil and water samples obtained from the valley floor areas for perchlorate; fertilizers, fire works, explosives and road flares are not likely sources of perchlorate to groundwater resources of the area, further research is warranted. Stable isotope and isotopic analyses of perchlorate extracted from various diverse water resources in the area may be found useful in source identification (natural versus anthropogenic) (Böhlke and others, 2005).

The bedrock units and fault zones may have dominant impacts on groundwater hydraulics and in turn on solute fate and transport in the valley area. However, the full spatial extent of some of these faults is unknown and in the valley area no bedrock monitoring wells exists. Some of these faults go through both SSFL and the surrounding areas. Due to a lack of historical perchlorate-related data and comprehensive research and monitoring systems, it is difficult to confirm the source(s) of perchlorate in the groundwater resources of Simi Valley and other areas surrounding the SSFL (e.g., Dayton Creek/Canyon in West Hills). However, unless through further data collection and research confirms alternative sources of perchlorate, based on available data, the primary source of perchlorate detected in soils and waters of the area has likely occurred through various activities at the SSFL.

Hydraulically, groundwater can transport contaminants including perchlorate from the SSFL to surrounding areas including Simi Valley and the western end of the San Fernando Valley. Although, areas with preferential secondary porosity (e.g., fractures) can convey contaminants in an erratic spatial pattern, available data does not support occurrence of a typical perchlorate plume in Simi Valley and the western end of the San Fernando Valley. It is possible that contaminated groundwater from the SSFL appears as seeps and springs on hill sides or lowland areas and collects in pools and low-gradient areas of streams and canyons. Through evaporation, perchlorate compounds may concentrate in streambed sediments and sediments associated with local canyons.

Based on more recent observations of the release of perchlorate, mercury and other contaminants to local creeks and canyons draining the SSFL with all recent restrictive regulations and vigorous monitoring at the time that these chemicals are hardly being used at the SSFL, it is likely that during the times when these chemicals were used and disposed of extensively, surface runoff contaminated with perchlorate and other chemicals entered local creeks and canyons as dissolved load. In the areas where streams were influent, the stream acted as a "line source" and local groundwater reservoirs were contaminated by stream water. Perchlorate contamination of Simi Valley's groundwater reservoir in the 1950s and 1960s is supported by this model.

In addition to dissolved load, runoff and streams may transport contaminants and chemical compounds (e.g. perchlorate compounds) in granular form and/or as part of their bed load and suspended load if the contaminants are absorbed and assimilated within the body of the sediments, rocks, and concrete particulates near the areas where perchlorate compounds have been used, stored or disposed of. Assimilation of contaminants could happen through diffusion near the contaminant-source areas. Sediments and/or concrete or even chemical compounds in solid and granular form may have been quickly transported down stream/canyon on steep and rocky slopes with little infiltration and deposited in the areas where the stream gradient is low and/or near the confluence of tributaries where stream water may become less energetic. With subsequent rainstorms, depending on their characteristics and impact on the contaminant source area, more perchlorate/perchlorate compounds could be washed away or leached out through reverse diffusion and be diluted and transported further downstream and/or perchlorate may migrate downward towards the saturated zone.

The extent of historical releases of perchlorate and perchlorate compounds to Dayton Creek as dissolved, suspended, and bed load is not known. Although alternative sources of perchlorate and mechanism of its movement (e.g., advection through fractures and fault zones, old "dumps") to Dayton Creek should be investigated, however, as a result of NPDES requirements, it has been confirmed that perchlorate as "dissolved load" has been released from the SSFL to Dayton Creek since 1998. Recent discovery of extremely high concentrations (up to 62,000 mg/kg) of perchlorate at sporadic locations in sediments associated with gentler portions of Dayton Creek may have formed through deposition of contaminated suspended and bed load and through "pooling" and evaporation of water can lead to concentration and ultimately deposition of various chemical compounds. Such high concentrations of perchlorate in stream sediments may directly impact local groundwater resources if the contaminants persist in stream-bed sediments for a sufficient time. Installation of monitoring wells and long term characterization and monitoring of groundwater resources near the contaminated areas and in the areas down gradient from the contaminated areas are recommended.

Several factors can influence the concentration of contaminants in stream- and canyon- bed sediments. Along the streams, local flow characteristics can directly be influenced by stream and stream-bed deposit characteristics. Another factor that may influence the deposition of chemical compounds and their anomalies in concentration along the local canyons is the smaller tributaries. During a storm, depending on the water quality of these adjoining tributaries, concentration of contaminants in sediments along the main trunk of the streams itself may increase or decrease. If the stream's water velocity decreases, the contaminated suspended load and the bed load may accumulate in low velocity areas.

To improve this paper and for a better understanding of the area's hydrology and in order to minimize or eliminate further impact of contaminants to the environment and in turn to the biological systems, development of a long term scientific-based monitoring system and data collection and appropriate remedial actions as deemed necessary through a sincere cooperation of various agencies are recommended.

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