NAS7.10422
NASA-JPL
SSIC No. 9661

National Aeronautics and
Space Administration
Office of Program and Institutional Integration

NASA Management Office

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Reply to Attn of:

January 31, 2007

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Mr. Ripperda, Mr. Iskarous, and Mr. Zaidi,

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION (NASA), JET PROPULSION LABORATORY (JPL) – EPA ID# CA9800013030. TECHNICAL MEMORANDUM: ADDITIONAL INVESTIGATION RESULTS

The enclosed technical memorandum documents the results of the additional investigation performed as part of NASA's Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) program at JPL. Since completing the Remedial Investigation (RI) in 1999, NASA has implemented several cleanup activities at JPL, including treatment systems for soil and groundwater, as well as supplemental studies and data collection efforts. The additional investigation is a supplemental study that was conducted to achieve the following objectives:

1. Evaluate the downgradient (southern) extent of chemicals originating from the JPL facility and
2. Determine if the occurrence of perchlorate in the Sunset Reservoir area was associated with migration from the JPL facility.

Over the years, a significant amount of data collection and analysis has been performed associated with groundwater geochemistry, groundwater chemical concentrations, and groundwater modeling in the Raymond Basin. The additional investigation evaluated each of these tools again and also included performing an isotope study. In addition, two new multi-port monitoring wells, MW-25 and MW-26, were installed as part of the additional investigation and both wells have been added to the quarterly groundwater monitoring program at JPL. Well construction reports were prepared to document the installation and initial sampling of these wells.

This technical memorandum and the well construction reports have been added to the administrative record and are available via the information repositories and NASA JPL Groundwater Cleanup website (http://JPLwater.nasa.gov).

If you have any questions or comments regarding the attached document, please contact me at (818) 393-6683.

Sincerely,

Steven Slaten
NASA Remedial Project Manager
JPL CERCLA Program

cc: Mr. Gary Takara (Pasadena Water and Power)
Mr. Alan Sorsher (California Department of Health Services)

Technical Memorandum

Additional Investigation Results
National Aeronautics and Space Administration,
Jet Propulsion Laboratory, Pasadena, California

Final January 31, 2007

This technical memorandum documents the results of the additional investigation associated with the Remedial Investigation (RI) Addendum Work Plan[1] and performed as part of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) program at the National Aeronautics and Space Administration (NASA) Jet Propulsion Laboratory (JPL). The objectives of the additional investigation were to (1) evaluate the downgradient (southern) extent of chemicals originating from the JPL facility and (2) determine if the occurrence of perchlorate in the Sunset Reservoir area was associated with migration from the JPL facility.

As part of the additional investigation, two new multi-port monitoring wells, MW-25 and MW-26, were installed between the former southernmost JPL monitoring well, MW-20, and the Sunset Reservoir area (see Figure 1). Well construction reports were prepared to document the installation and initial sampling of these wells.[2,3] In addition, both wells have been added to the quarterly groundwater monitoring program and the analytical results are documented in quarterly technical memoranda.[4]

Over the years, a significant amount of data collection and analysis has been performed by NASA and local water companies associated with groundwater geochemistry, groundwater chemical concentrations, and groundwater modeling[5,6] in the Raymond Basin. The additional investigation evaluated each of these tools again and also included performing an isotope study. Samples for the isotope study were collected from select JPL monitoring wells and production wells (Lincoln Avenue Water Company #3 [LAWC#3], Las Flores Water Company #2 [LFWC#2], Sunset Well, Bangham Well, and Garfield Well) to improve the understanding of groundwater origin and flow, and to attempt to distinguish between perchlorate sources (see Attachment 1 for laboratory data). Isotopic analyses were performed by independent laboratories and included:

- Perchlorate: chlorine ($\delta^{37}Cl$) and oxygen ($\delta^{18}O$ and $\Delta^{17}O$), conducted by the University of Illinois at Chicago (UIC);
- Groundwater: oxygen ($\delta^{18}O$), hydrogen ($\delta^{2}H$), and inorganic chloride ($\delta^{37}Cl$), conducted by UIC;
- Strontium: $^{87}Sr/^{86}Sr$, conducted by the Massachusetts Institute of Technology (MIT); and
- Tritium/helium: $^{3}H/^{3}He$, conducted by the University of Miami.

Figure 1 shows the Raymond Basin, the Monk Hill Subarea, and the locations of JPL monitoring wells and certain Raymond Basin production wells, including the Sunset Reservoir Wells.

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[1] NASA. 2004. *Operable Unit 3 Remedial Investigation (RI) Addendum Work Plan (Pasadena Sampling Plan [PSP]-2004-1).* Prepared by Battelle for the National Aeronautics and Space Administration. November.
[2] NASA. 2005. *Operable Unit 3 Remedial Investigation Addendum Monitoring Well 25 Construction Report.* Prepared by Battelle for the National Aeronautics and Space Administration. July.
[3] NASA. 2005. *Operable Unit 3 Remedial Investigation Addendum Monitoring Well 26 Construction Report.* Prepared by Battelle for the National Aeronautics and Space Administration. July.
[4] NASA. 2006. *Technical Memorandum for Third Quarter 2006, Groundwater Monitoring Results.* Prepared by Battelle for the National Aeronautics and Space Administration. November.
[5] Geoscience. 2004. *Technical Memorandum Raymond Basin Ground Water Flow Model Predictive Simulations.* December.
[6] NASA. 2003. *JPL Groundwater Modeling Report.* December.

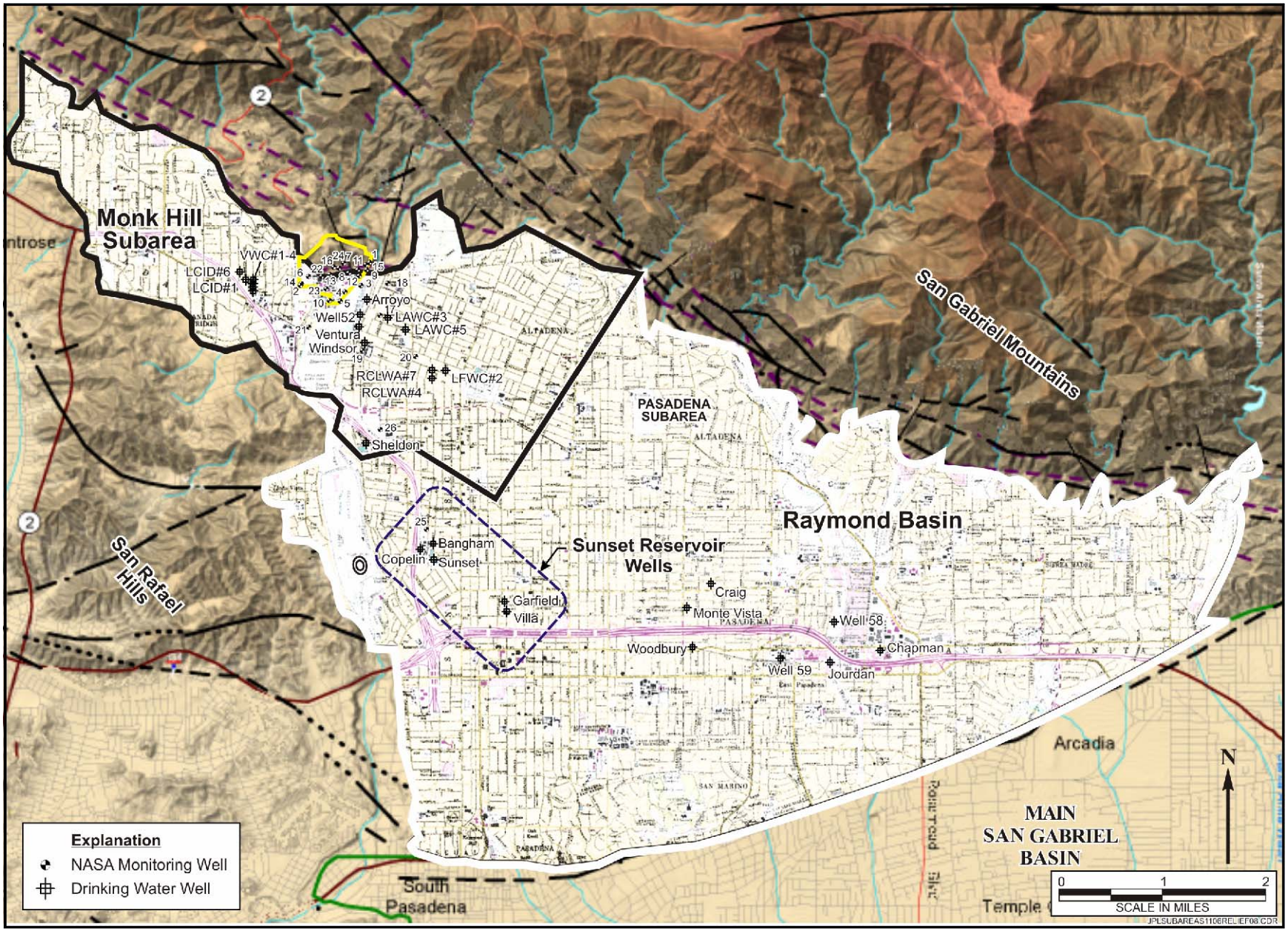

Figure 1. The Sunset Reservoir Wells are located outside the Monk Hill Subarea of the Raymond Basin, approximately three miles south of the JPL Facility

EXECUTIVE SUMMARY

Historic waste disposal practices associated with research conducted in the 1940s and 1950s at the JPL facility are a known source of perchlorate in the Monk Hill Subarea of the Raymond Basin. While the highest concentrations of perchlorate in the Raymond Basin have been detected in groundwater beneath the JPL facility, sources of perchlorate in the environment other than those associated with solid rocket propellant are widespread and well documented,[7,8] including road flares, fireworks, blasting operations, and naturally-occurring mineral deposits used in fertilizer production. Since analysis for perchlorate began in 1997, perchlorate detection in the Raymond Basin has been widespread.[9] In the Raymond Basin, perchlorate has been detected beneath and adjacent to JPL, at locations hydraulically cross-gradient/upgradient of JPL (thus not associated with JPL), at the Sunset Reservoir Wells located approximately three miles hydraulically downgradient from JPL, and at wells even further from JPL (i.e., to the south and east of the Sunset Reservoir Wells).

Over the past decade, NASA has monitored groundwater to determine the extent of perchlorate associated with historic operations and originating from the JPL facility. A review of the groundwater chemical and geochemical data prompted NASA to conduct an additional investigation to evaluate the downgradient (southern) extent of chemicals originating from the JPL facility, and to determine if the occurrence of perchlorate in the Sunset Reservoir area was associated with migration from the JPL facility. The additional investigation field activities included installation of two new multi-port monitoring wells, MW-25 and MW-26, and a comprehensive stable isotope study.[1] Four different tools were used to evaluate the downgradient extent of chemicals and the origin of perchlorate in the Sunset Reservoir area: (1) groundwater modeling, (2) groundwater geochemistry, (3) groundwater chemical concentration data collected from production wells and from JPL monitoring wells as part of quarterly groundwater sampling, and (4) perchlorate isotope analysis.

Groundwater Modeling: Groundwater modeling conducted by NASA[6] and the Raymond Basin Management Board (RBMB)[5] indicates that dissolved perchlorate originating from JPL would be contained by the production wells located in the Monk Hill Subarea and not migrate to the Sunset Reservoir Wells. Several production wells located hydraulically downgradient of JPL and within the Monk Hill Subarea (including Arroyo Well, Ventura Well, LAWC#3, Rubio Cañon Land and Water Association Well No. 4 [RCLWA#4], and LFWC#2) began pumping groundwater in the 1920s and 1930s. Perchlorate was not used as a component of solid rocket propellant until 1941. In addition, historical pumping records indicate that there were no times since the early 1940s of sustained shutdown of all of these Monk Hill Subarea wells, which would have allowed chemicals to migrate out of the Subarea. Therefore, groundwater modeling indicates an origin of perchlorate in the Sunset Reservoir area which is not associated with JPL.

Groundwater Geochemistry: Groundwater cation and anion concentration data within the Raymond Basin are available dating back to the early 1900s. These data were evaluated as part of this additional investigation to determine temporal and spatial differences in groundwater geochemistry. Three

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[7] Strategic Environmental Research and Developmental Program (SERDP). 2005. *Alternate Causes of Wide-Spread, Low Concentration Perchlorate Impacts to Groundwater*. May.
[8] Massachusetts Department of Environmental Protection (MassDEP). 2005. *Draft Report: The Occurrence and Sources of Perchlorate in Massachusetts*. August.
[9] California Department of Health Services. 2005. Data obtained from http://www.dhs.ca.gov/ps/ddwem/chemicals/perchl/monitoringupdate.htm.

separate water types were determined to be present in the Monk Hill Subarea during the Remedial Investigation (RI)[10] and were confirmed during this investigation.

An important aspect of the evaluation of groundwater geochemistry is related to the fact that large amounts of water from the Colorado River (approximately 1.0M acre-ft) have been imported by water suppliers to the Raymond Basin since the 1940s to supplement local drinking water supplies.[11,12] Large quantities of this imported water have mixed with native water in the aquifer as a result of infiltration from irrigation, direct injection as part of aquifer storage and recovery programs, unsewered areas, and leaking distribution pipelines. Mixing of imported water and native groundwater is observed in the historical groundwater geochemistry data and is supported by the groundwater, strontium, and tritium isotope analysis collected as part of the additional investigation.

Colorado River water is known to contain perchlorate originating from two former perchlorate production facilities in Henderson, Nevada. Concentrations of perchlorate in the Colorado River water were not analyzed prior to 1997; however, the facilities began manufacturing and disposing of perchlorate in the 1940s.[13] Perchlorate remediation efforts near the Henderson, Nevada facilities began in 1999 and perchlorate concentrations in the imported Colorado River water have since declined. Nonetheless, perchlorate has been imported from the Colorado River to the Raymond Basin aquifer. Groundwater geochemistry from the Sunset Reservoir Wells indicates an influence by Colorado River water and, thus, the Colorado River water is a potential source of perchlorate in groundwater near the Sunset Reservoir Wells.

Groundwater Chemical Concentration Data: As part of the CERCLA program at JPL, NASA collects samples from 25 monitoring wells on a quarterly basis. These samples are routinely analyzed for volatile organic compounds (VOCs) and perchlorate, and hundreds of other chemicals have been evaluated during previous investigations.[10] In addition, the Department of Health Services (DHS) requires drinking water purveyors to routinely collect and analyze samples from their production wells. These data were evaluated as part of the additional investigation.

The VOC carbon tetrachloride is a reliable tracer for chemicals originating from JPL because significant quantities were disposed of at JPL during historical operations and because no other source of carbon tetrachloride is known to exist in the Monk Hill Subarea. Other VOCs, including trichloroethylene (TCE) and tetrachloroethylene (PCE), have been detected at relatively low levels in soil and groundwater beneath JPL. However, other sources of these VOCs exist in the Monk Hill Subarea, such as former dry cleaning sites and unsewered areas in La Cañada Flintridge[10] so they cannot be used as tracers for chemicals originating from JPL. Analytical results of groundwater samples collected from JPL monitoring wells and production wells indicate that the carbon tetrachloride plume originating from JPL is fully delineated and contained within the Monk Hill Subarea.

In addition, carbon tetrachloride was used at JPL during the same timeframe as perchlorate[14] and, based on the hydrogeology, carbon tetrachloride and perchlorate would follow similar flow paths. Therefore, co-location of carbon tetrachloride and perchlorate in samples adjacent to and hydraulically connected to

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[10] Foster Wheeler Environmental Corporation (FWEC). 1999. *Final Remedial Investigation Report for Operable Units 1 and 3: On Site and Off-Site Groundwater*. August.
[11] Raymond Basin Management Board (RBMB). 1985-2002. Watermaster Reports for the Raymond Basin.
[12] Blomquist, William. 1992. *Dividing the Waters*: *Governing Groundwater in Southern California*.
[13] Schumacher, Joseph C. 1999. *History of Establishing a Source of Potassium and Ammonium Perchlorates for Use in Solid Propellant Rockets*. 35th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, 20-24 June 1999, Los Angeles, California.
[14] Ebasco. 1998. *Preliminary Assessment/Site Inspection Report, Jet Propulsion Laboratory*. April.

JPL indicates a source of perchlorate originating from JPL. For example, samples from all the source area wells (MW-16, MW-24 [Screen 1], and MW-7) have contained both perchlorate and carbon tetrachloride. In addition, off-facility wells such as MW-17 (Screen 3), Arroyo Well, Well 52, LAWC#3, and LAWC#5 have historically contained both perchlorate and carbon tetrachloride.

Groundwater monitoring data delineates the extent of carbon tetrachloride originating from the JPL facility as approximately one mile southeast of the JPL facility. Carbon tetrachloride has not been detected in the Sunset Reservoir Wells. Groundwater monitoring data on the extent of carbon tetrachloride correlates well with the aforementioned Raymond Basin Management Board (RBMB) and NASA groundwater modeling predictions. Based on differences in chemical properties, it is recognized that, in the absence of groundwater pumping, perchlorate could move more rapidly in groundwater than carbon tetrachloride. Even so, the absence of carbon tetrachloride outside the Monk Hill Subarea strengthens the reliability of the groundwater modeling predictions and supports an origin of perchlorate in Sunset Reservoir Wells not associated with JPL.

Perchlorate Isotope Data: As part of the additional investigation, perchlorate isotope analysis was performed by UIC. Isotope analysis can fingerprint perchlorate sources based on the ratios of different isotopes (e.g., $^{18}O/^{16}O$ and $^{37}Cl/^{35}Cl$).[15,16,17,18,19] The perchlorate isotope data indicate that the JPL perchlorate isotopic fingerprint, or signature, is distinct within the Raymond Basin and that the perchlorate isotopic signature in the water from wells near Sunset Reservoir is different than the JPL perchlorate isotope signature. The Sunset Reservoir Wells appear to be influenced by at least two separate (non-JPL) sources, including a naturally-occurring/fertilizer source (e.g., imported nitrate fertilizer from Chile) and at least one synthetic (i.e., man made) source.

CONCLUSION

The investigation employed use of four different analytic tools. *Taken together, the results of the analysis lead to the conclusion that (1) the chemicals from the JPL facility are contained within the Monk Hill Subarea, and, (2) the perchlorate detected at the Sunset area wells is of a different origin than that used at, and originating from, JPL.* This conclusion is supported by (1) groundwater modeling; (2) groundwater geochemical data and supporting groundwater, strontium, and tritium/helium isotope data; (3) groundwater carbon tetrachloride and perchlorate data collected as part of the JPL Groundwater Monitoring program and production well sampling; and (4) perchlorate isotope data. Each of these supporting components is discussed in more detail in the following sections.

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[15] Duncan, B.P., R.D. Morrsion and E. Vavricka. 2005. "Forensic Investigation of Anthropogenic and Naturally Occurring Perchlorate." *Environmental Forensics*. 6:205-215.

[16] Bao, H. and B. Gu. 2004. "Natural Perchlorate has a Unique Isotopic Signature." *Environmental Science and Technology*. 38:5073-5077.

[17] Böhlke, J.K., N.C. Sturchio, B. Gu, J. Horita, G.M. Brown, W.A. Jackson, J. Batista, and P.B. Hatzinger. 2005. "Perchlorate Isotope Forensics." *Analytical Chemistry*. 77:7838-7842.

[18] Sturchio, N.C., J.K. Böhlke, B. Gu, J. Horita, G.M. Brown, A. Beloso, Jr., L.J. Patterson, P.B. Hatzinger, W.A. Jackson, and J.R. Batista. 2006. "Stable Isotopic Composition of Chlorine and Oxygen in Synthetic and Natural Perchlorate." B. Gu, and J.D. Coates, eds., *Perchlorate- Environmental Occurrence, Interactions and Treatment*: Springer, New York, p. 93-109.

[19] Sturchio, N.C., J.K. Bohlke, and P.B. Hatzinger. Archived perchlorate samples from former perchlorate manufacturing facilities in Nevada are based on unpublished data from ongoing ESTCP project, personal communication.

GROUNDWATER MODELING

Background

- The Raymond Basin, where the JPL facility is located, is bordered on the north by the San Gabriel Mountains, on the west by the San Rafael Hills, and on the south and east by the Raymond Fault. The Raymond Basin is further divided into three subareas based on differences in groundwater elevations and flow directions: the Pasadena Subarea, the Santa Anita Subarea, and the Monk Hill Subarea. JPL is located in the Monk Hill Subarea and the Sunset Reservoir wells are located in the Pasadena Subarea.
- The aquifer in the Monk Hill Subarea and the Pasadena Subarea is generally considered to be an unconfined, or water table, aquifer. However, vertical hydraulic head differences with depth are observed between screens in deep JPL multi-port monitoring wells located near active production wells. This indicates that the aquifer does not exhibit truly unconfined conditions, due to the presence of relatively thin, silt-rich layers located throughout the alluvial aquifer that inhibit vertical flow of groundwater. The Monk Hill Subarea aquifer can be divided into four groundwater aquifer zones above the crystalline basement complex, based to a large extent on how these silt-rich intervals influence the hydraulic heads in the aquifer during pumping periods at the nearby municipal wells.
- In the Raymond Basin, groundwater generally flows southerly from areas of recharge at the base of the San Gabriel Mountains to areas of discharge along the Raymond Fault. A confluence of groundwater flow regimes occurs within the Monk Hill Subarea where JPL is located. At the western end of the Monk Hill Subarea (west of JPL) the groundwater flow is predominantly to the southeast; at the eastern end of the Monk Hill Subarea (east of JPL) the groundwater flow is predominantly to the south.
- The groundwater flow direction and magnitude (hydraulic gradient) beneath the study area are dynamic. In general, natural groundwater flow is across the facility to the southeast. However, the aquifer is affected by various natural and human influences that include: (1) pumping from nearby municipal production wells, (2) groundwater recharge from Arroyo Seco spreading basins, (3) seasonal and regional groundwater recharge from precipitation, and (4) regional groundwater flow. The extraction of water from municipal production wells has the most significant effect on the natural groundwater flow.
- The groundwater surface has been measured in the JPL monitoring wells at depths ranging from approximately 22 ft (groundwater mound near the mouth of the Arroyo Seco) to 270 ft below ground surface (bgs). This wide range of depths to groundwater can primarily be contributed to the relatively steep topography present at the JPL facility and local groundwater mounding. It also can be accounted for by seasonal groundwater recharge from nearby spreading grounds and the extraction of groundwater from nearby municipal production wells. Based on monitoring data collected since 1996, groundwater elevations have fluctuated up to 75 ft each year beneath JPL, primarily as a result of these influences.
- A calibrated groundwater flow model was developed independently from JPL for the RBMB[5] and used as a tool to make predictive analyses of potential changes in groundwater levels and movement of groundwater under various conjunctive use scenarios. The RBMB model is a two-layer model constructed for the entire Raymond Basin, including a portion of the Main San Gabriel Basin. Observed hydrologic conditions for a 22-year period between 1981 and 2002 were used to calibrate the RBMB model. This model is a transient model, meaning that input parameters such as extraction rates and recharge rates were varied over the 22-year period to match actual conditions.
- A calibrated, steady-state groundwater flow model was developed by NASA as part of the JPL CERCLA Program to evaluate treatment alternatives and groundwater flow in the Monk Hill Subarea.[6] The JPL Groundwater Model consists of four layers, corresponding to four hydrostratigraphic units as defined in the RI report.[11] Boundary conditions for the JPL Groundwater Model include the San Gabriel Mountains to the north and the San Rafael Hills to the west and

southwest. The base of the alluvium (the interpreted elevation of bedrock) represents the bottom of the flow system and was represented by a no-flow boundary. The eastern model boundary was selected to represent an approximate groundwater flow line and is represented in the model as a no-flow boundary. The southern boundary corresponds with the relatively consistent location of a groundwater elevation contour line and is represented in the model by a constant-head boundary. As part of the steady-state model development, a transient model was constructed using data from 1996-2000. Results from the transient model calibration indicated the calibrated flow field in the steady-state groundwater flow model was similar to that generated under transient conditions. As such, the steady-state model was determined to be appropriate for use in predictive simulations. Table 1 provides the dates of installation of the Monk Hill Subarea production wells.

Table 1. Several production wells located hydraulically downgradient of JPL and within the Monk Hill Subarea (including Arroyo Well, Ventura Well, LAWC#3, RCLWA#4, and LFWC#2) began pumping groundwater in the 1920s and 1930s. Perchlorate was not proposed as a component of solid rocket propellant until 1941.

Production Well	Installation Date	Total Depth
Arroyo Well	August 1930	660 ft
Well 52	August 1977	640 ft
Ventura Well	April 1924	473 ft
Windsor Well	July 1969	600 ft
LAWC#3	January 1924	601 ft
LAWC#5	January 1971[(a)]	588 ft
RCLWA#4	March 1924	636 ft
RCLWA#7	January 1998[(b)]	NA
LFWC#2	January 1926	540 ft

(a) LAWC#5 replaced LAWC#2, which was installed in January 1915.
(b) RCLWA#7 replaced RCLWA#5, which was installed in May 1926.

Results of Groundwater Modeling

- Although the JPL Groundwater Model and the RBMB basin-scale model were created to satisfy different groundwater modeling objectives, the flow fields predicted by both models in the Monk Hill Subarea are very similar. Particle tracking simulations performed using both the RBMB model and the JPL Groundwater Model indicate that particles released in the vicinity of JPL would not migrate downgradient to the Sunset Reservoir wells. Rather, they would be captured by extraction wells in the Monk Hill Subarea.
- Figures 2 (entire Raymond Basin) and 3 (Monk Hill Subarea) show the results of particle tracking simulations performed by the RBMB.[5] The RBMB model indicates that wells in the Monk Hill Subarea would capture groundwater originating from the JPL Facility. The RBMB model also indicates that groundwater originating to the west of JPL in La Cañada Flintridge flows south of the JPL Facility and then towards the Sunset Reservoir Wells.
- Figure 4 shows the results of particle tracking simulations performed using the JPL Groundwater Model[6] using the average extraction rates observed between 1960 and 2000. Similar to the RBMB model, the JPL model indicates that groundwater originating from the JPL facility would be contained by wells in the Monk Hill Subarea. In fact, the vast majority of the groundwater originating from the JPL facility would be captured by Arroyo Well, Well 52, and LAWC#3.

Groundwater modeling performed independently by NASA and the RBMB indicate that dissolved chemicals originating from the JPL facility would be contained by production wells in the Monk Hill Subarea and not migrate to the Sunset Reservoir Wells.

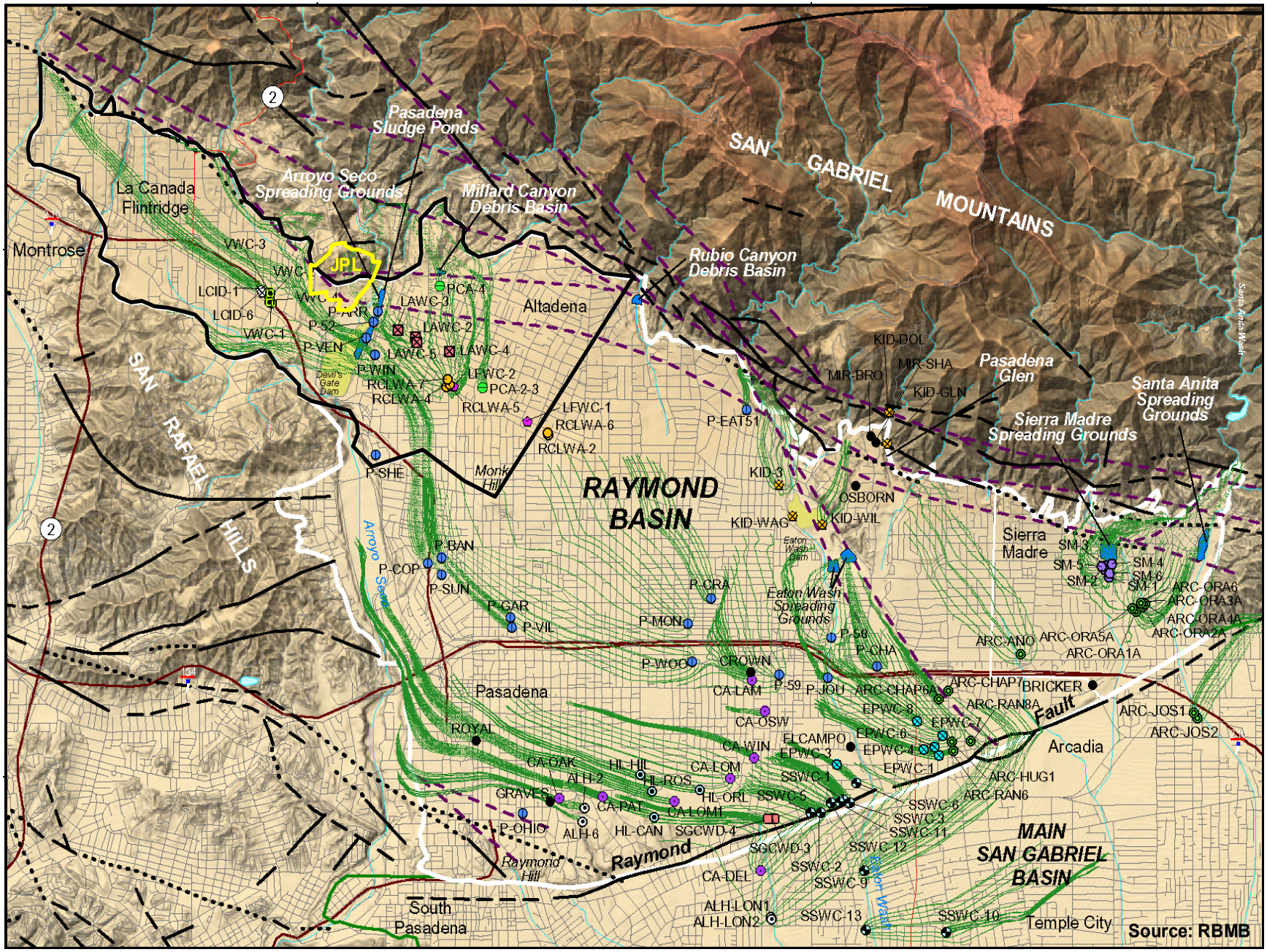

Figure 2. Particle tracking simulations using the independently-developed RBMB Model indicate that capture zones of the Sunset Reservoir Wells are south of the JPL Facility.

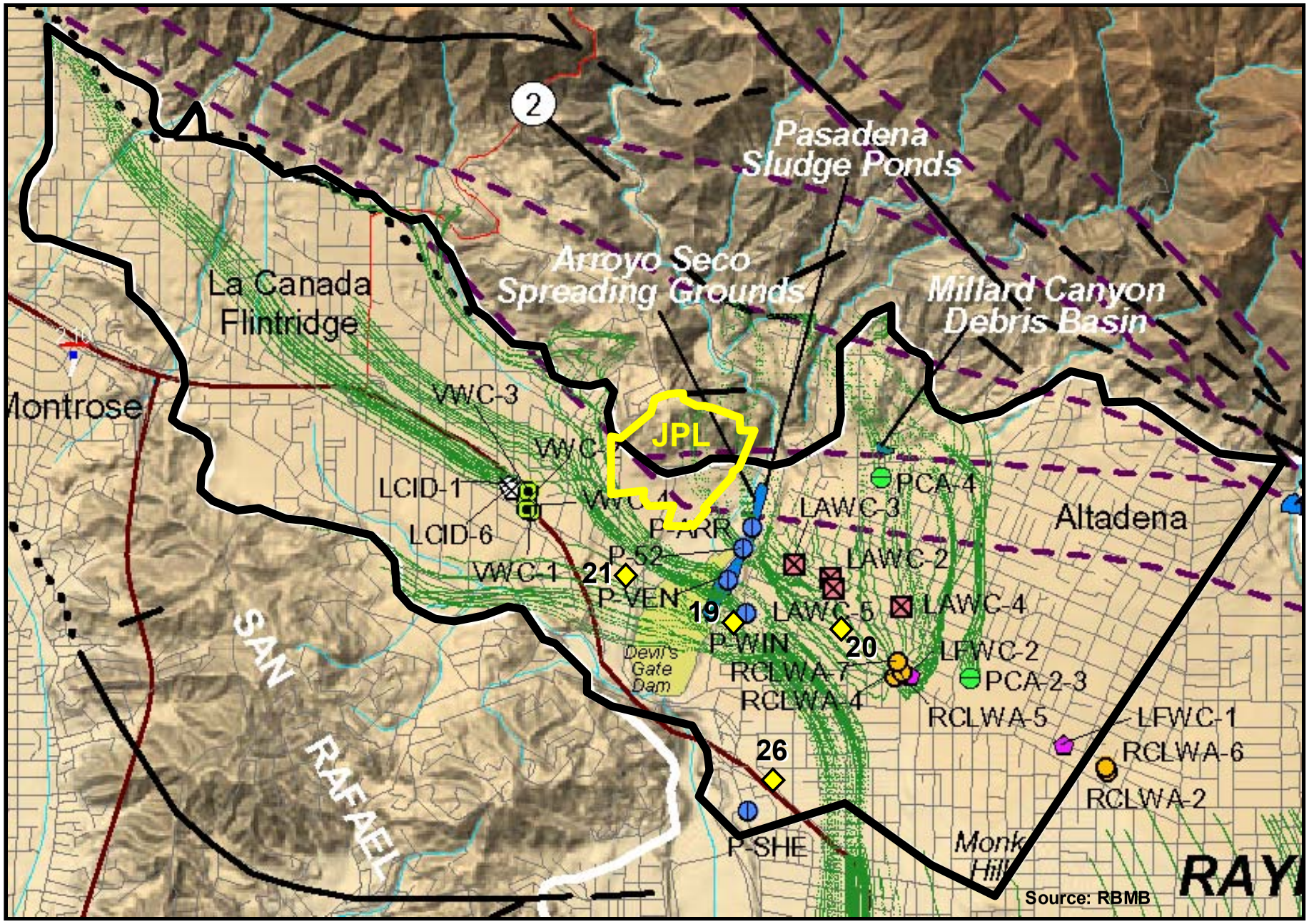

Figure 3. Particle tracking simulations using the independently-developed RBMB Model indicate that chemicals originating from the JPL Facility would be captured by the Monk Hill production wells and not migrate to the Sunset Reservoir wells.

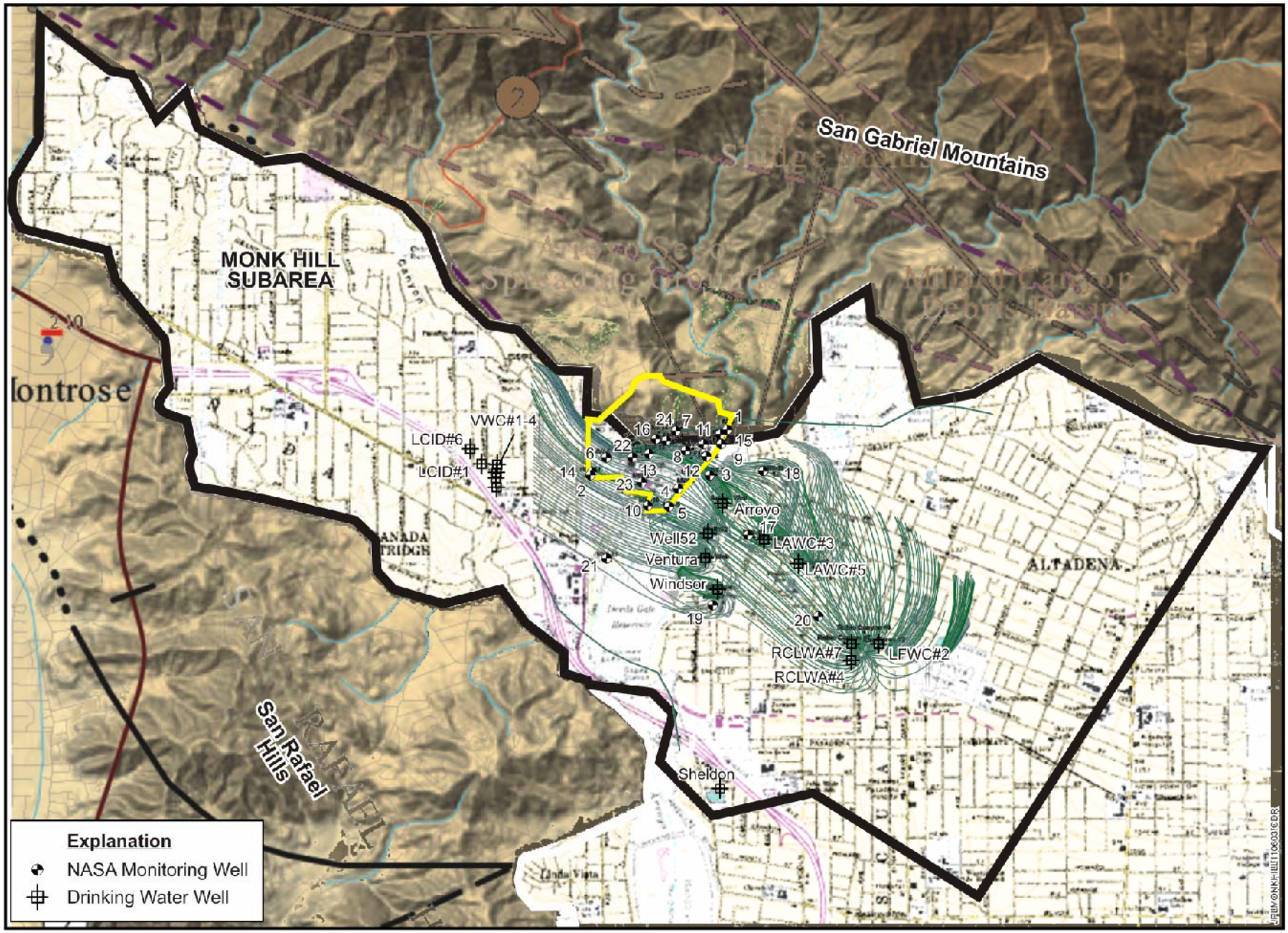

Figure 4. Similar to the RBMB Model, particle tracking simulations using JPL Groundwater Model indicate that chemicals originating from the JPL Facility would be captured by the Monk Hill production wells and not migrate to the Sunset Reservoir wells.

- Since 1960, the longest time period when Arroyo Well, Well 52, LAWC#3, and LAWC#5 were not operating was five years (1985-1990).[5] Groundwater modeling indicates that particles in groundwater could travel 1,500 to 2,000 feet in five years.[6] Much of the chemicals would have been drawn back upon reinitiating operation of these wells based on their location and capture zones. The remaining chemicals would likely have been captured by other production wells in the Monk Hill Subarea. The other wells in the Monk Hill Subarea (Ventura Well, Windsor Well, RCLWA#4, and RCLWA#7) were operational from 1985 to 1990. Therefore, based on the historical record, it does not appear that there was a significant period of time when the Monk Hill Subarea production wells were not operating and groundwater originating from JPL would escape containment in the Monk Hill Subarea.

GROUNDWATER GEOCHEMISTRY

Conventional Geochemistry:

- Groundwater geochemistry is the science concerned with chemical composition of groundwater, which is the combined result of water entering the aquifer (primarily via infiltration of rainwater) and the reactions of naturally-occurring minerals in the subsurface that may modify the water composition.
- The most common factors that may change the water composition include weathering and dissolution of naturally-occurring minerals, precipitation of dissolved minerals in the water, ion exchange reactions, mixing of different water sources, and human activities.
- Chemical impurities commonly found in water in significant quantities include calcium, magnesium, sodium, potassium, bicarbonate, chloride, sulfate, and nitrate. These chemicals are often referred to as cations and anions, depending on their ionic charge. Lesser amounts of other ions such as lead, copper, arsenic, manganese, and organic compounds are also common. Some of these are naturally occurring and some are from human activities.
- The primary purpose of groundwater geochemistry is to evaluate drinking water quality. Because the groundwater in the Raymond Basin has been used as a source of drinking water for over 100 years, chemical data are available from production wells dating back to the early 1900s.
- Connection of the Metropolitan Water District (MWD) aqueduct tunnel at Sunset Reservoir was completed in 1941 and delivery of Colorado River water began on June 17, 1941. Based on available records from 1952 to 2002,[11,12, 20] over 1,300,000 acre-feet of MWD water was imported to the Raymond Basin to supplement local drinking water supplies. The State Water Project (surface water from northern California) was completed in 1972 and since that time MWD water has been a blend of northern California water and Colorado River water. Table 2 shows the quantities of water imported to the Raymond Basin by year, including the percentage of imported water from the Colorado River. Over 30% (approximately 1.0M acre-feet) of the water used in the Raymond Basin between 1952 and 2002 was from the Colorado River.
- The total estimated storage in the Raymond Basin is approximately 820,000 acre-ft and the total volume of water extracted from the Basin on an annual basis is approximately 35,000 acre-ft. [5]
- It is estimated that 25%[21] of the water used in the Basin ends up as artificial recharge of the aquifer due to leaking distribution pipelines, return flow from applied waters (e.g., watering lawns), unsewered areas, and injection of water as part of aquifer storage and recovery programs.

[20] Metropolitan Water District of Southern California (MWD). 2005. *Regional Urban Water Management Plan*. November.
[21] CH2M Hill. 1990. *Devil's Gate Multi-Use Project*. January.

Table 2. Over 1.3M acre-feet of water has been imported by MWD to the Raymond Basin since the 1940s and approximately 1M acre-feet of the imported water was from the Colorado River. Over 30% of the water used in the Raymond Basin between 1952 and 2002 was from the Colorado River.

Year	Decreed Rights (acre-ft)	Water Imported (acre-ft)	Total Water Use in Basin (acre-ft)	Amount of Imported Water from the Colorado River[20] (acre-ft)
1945	21,451	NA	NA	NA
1946	21,451	NA	NA	NA
1947	21,451	NA	NA	NA
1948	21,451	NA	NA	NA
1949	21,451	NA	NA	NA
1950	21,451	NA	NA	NA
1951	21,451	NA	NA	NA
1952	21,451	12,952	NA	12,952
1953	21,451	20,163	NA	20,163
1954	21,451	22,546	NA	22,546
1955	30,622	21,187	NA	21,187
1956	30,622	22,237	NA	22,237
1957	30,622	20,655	NA	20,655
1958	30,622	17,416	47,019	17,416
1959	30,622	23,885	54,241	23,885
1960	30,622	27,448	51,833	27,448
1961	30,622	29,941	52,306	29,941
1962	30,622	25,887	49,213	25,887
1963	30,622	26,362	50,654	26,362
1964	30,622	26,391	48,354	26,391
1965	30,622	26,341	49,031	26,341
1966	30,622	20,353	47,597	20,353
1967	30,622	18,103	47,626	18,103
1968	30,622	21,472	49,934	21,472
1969	30,622	20,461	46,565	20,461
1970	30,622	21,888	52,401	21,888
1971	30,622	26,843	51,701	26,843
1972	30,622	30,913	54,420	NA
1973	30,622	23,027	49,655	NA
1974	30,622	22,801	51,622	NA
1975	30,622	24,130	48,931	NA
1976	30,622	26,615	54,914	14,762
1977	30,622	22,282	51,145	19,406
1978	30,622	23,603	45,089	13,067
1979	30,622	23,042	51,851	13,750
1980	30,622	15,391	51,104	9,032
1981	30,622	25,558	52,419	12,757
1982	30,622	22,489	52,089	10,027
1983	30,622	20,062	48,840	14,027
1984	30,622	22,426	55,319	15,956
1985	30,622	30,271	53,567	19,140
1986	30,622	31,708	60,004	20,066
1987	30,622	30,261	59,285	18,911
1988	30,622	32,385	54,606	18,038
1989	30,622	31,582	56,476	15,718
1990	30,622	35,901	64,281	16,345
1991	30,622	33,642	63,637	22,464
1992	30,622	29,261	55,249	17,779
1993	30,622	32,493	58,457	20,573

Table 2. Over 1.3M acre-ft of water has been imported by MWD to the Raymond Basin since the 1940s and approximately 1M acre-ft of the imported water was from the Colorado River. Over 30% of the water used in the Raymond Basin between 1952 and 2002 was from the Colorado River (Continued).

Year	Decreed Rights (acre-ft)	Water Imported (acre-ft)	Total Water Use in Basin (acre-ft)	Amount of Imported Water from the Colorado River[20] (acre-ft)
1994	30,622	40,542	62,682	24,313
1995	30,622	25,578	58,873	17,258
1996	30,622	25,424	64,355	16,004
1997	30,622	29,345	67,666	17,870
1998	30,622	24,863	60,014	16,017
1999	30,622	30,684	NA	18,018
2000	30,622	34,376	74,167	15,826
2001	30,622	36,004	65,887	19,015
2002	30,622	37,090	70,143	14,993
Total Imported Water (acre-ft)		1,326,281	2,415,221	969,230

NA = Not Available

- Applied water (e.g., watering lawns) may account for more than 50% of the water used in the Basin on an annual basis.[22] Due to evapotranspiration, much of the applied water would not infiltrate to the aquifer during the warmer and dryer summer months. However, the chemicals (e.g., sulfate and perchlorate) in the applied water would accumulate in the shallow soil until heavier periods of rain occurred, which would dissolve these chemicals as the water infiltrates to the aquifer. Therefore, it is likely that the water recharged to the Basin from applied water would have higher concentrations of chemicals than the purveyed water due to the chemicals being concentrated as a result of evapotranspiration.
- Based on available records, between 1992 and 2003, 8,570 acre-ft of MWD water were injected into the aquifer as part of aquifer storage and recovery programs.[5] Almost 5,000 acre-ft of MWD water injection occurred in the Valley Water Company (VWC) wells between 1994 and 2003. These wells are located cross-gradient/upgradient of JPL, with groundwater originating from these wells flowing south of the JPL facility and then toward the Sunset Reservoir wells. In addition, over 2,000 acre-ft of MWD water was injected into two Sunset Reservoir wells (Bangham and Garfield) between 1992 and 1996.
- During the RI,[10] groundwater samples collected from JPL monitoring wells and from municipal production wells were analyzed for major cations (including calcium, magnesium, sodium, potassium, and iron), major anions (including chloride, sulfate, nitrate, and alkalinity), and total dissolved solids (TDS). Three separate water types were determined to be present in the Monk Hill Subarea during the RI and were confirmed during this current investigation:
    - Type 1: Calcium-bicarbonate groundwater − Groundwater with calcium as the dominant cation and bicarbonate as the dominant anion. Type 1 water appears to originate as runoff from the San Gabriel Mountains and enters the study area through the Arroyo Seco and the spreading grounds.
    - Type 2: Sodium-bicarbonate groundwater − Groundwater with sodium as the dominant cation and bicarbonate as the dominant anion. Type 2 water is typically found in deeper portions of the aquifer.
    - Type 3: Calcium-bicarbonate/chloride/sulfate groundwater − Groundwater with calcium as the dominant cation and bicarbonate the dominant anion, but with relatively elevated chloride and sulfate concentrations. This water type consistently has higher levels of TDS than the other two types.

[22] Heaney, J.P., W. DeOreo, P. Mayer, P. Lander, J. Harpring, L. Stadjuhar, B. Courtney, and L. Buhlig. 2006. "Nature of Residential Water Use and Effectiveness of Conservation Programs." http://bcn.boulder.co.us/basin/index.html.

- Figure 5 is a Piper diagram showing the distribution of water types. Piper diagrams are used to depict cation and anion data in triangular plots as milliequivalent percentages. That is, the cation and anion concentration data are converted to milliequivalents per liter and then the individual ions are depicted as a percentage of the total on the triangular plots. The relative percentage of a cation/anion increases as it nears a vertex on the triangular plot, each of which is associated with a particular chemical. Data points from the two triangles are then projected onto a third diamond shape plot, providing a tool to visualize geochemical variations in data sets.

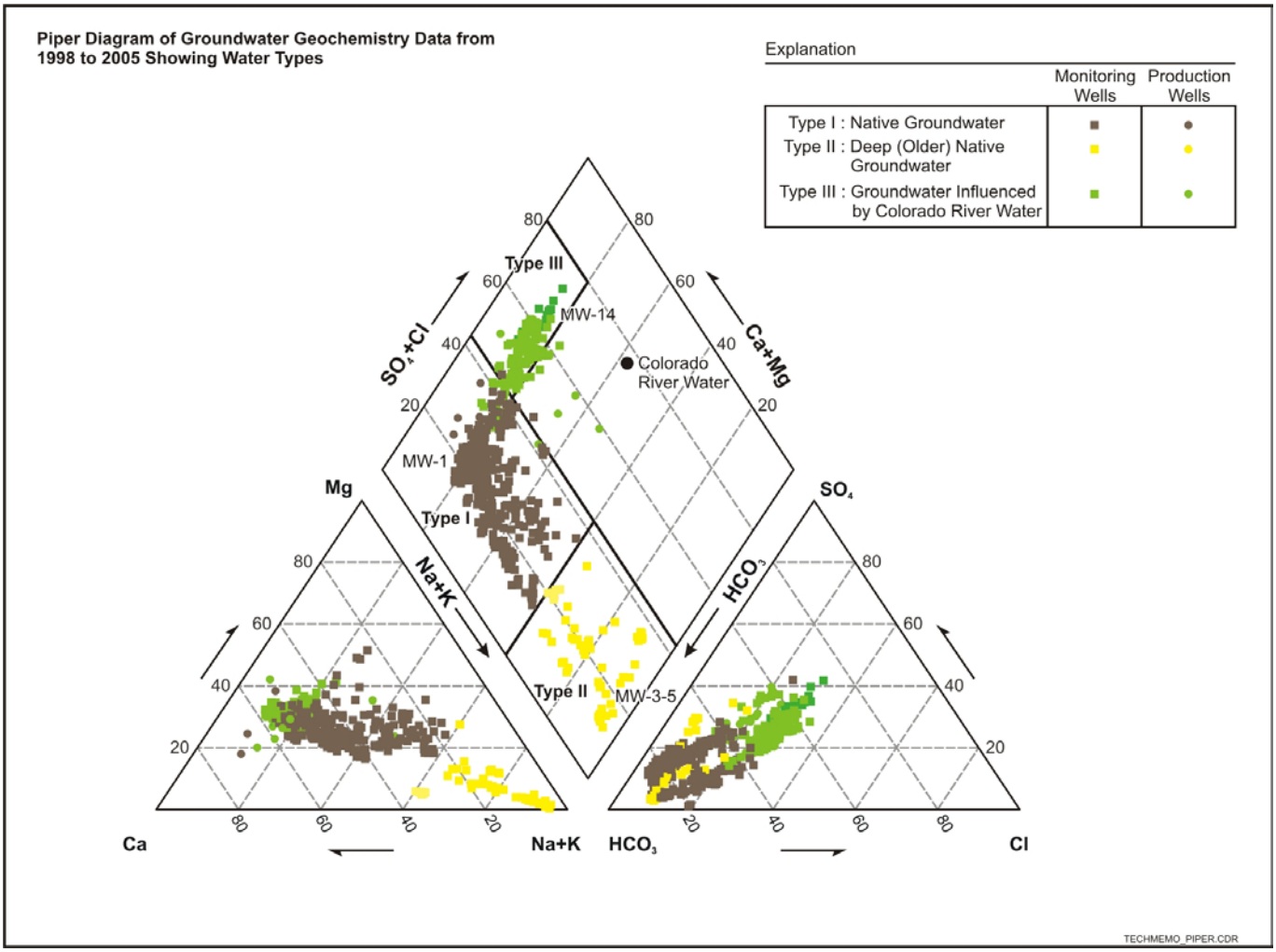

Figure 5. Groundwater in the Monk Hill Subarea and near the Sunset Reservoir wells has been categorized into three water types as shown on the Piper diagram. Type 3 water is a mixture of native water and imported water.

- Type 3 water is most prevalent in wells located cross-gradient/upgradient of JPL, to the south of the JPL facility, and near Sunset Reservoir. Geochemical analysis indicates that Type 3 water is created by ion exchange of imported Colorado River water as it passes through the subsurface soil (see Figure 3). This results in water becoming enriched in calcium (primarily) and magnesium (i.e., calcium and magnesium are released from the soil), and depleted in sodium (primarily) and potassium (i.e., sodium and potassium are preferentially sorbed onto soil). Because only cations are affected by this process, sulfate and chloride, which are elevated in the river water, migrate to the aquifer where they contribute to the overall increase in TDS. The bicarbonate concentration may actually decrease somewhat, due to precipitation of calcium carbonate (calcite).

- A simple mixture of two source waters will plot on a straight line connecting the two source waters. Once the ion-exchanged river water mixes with native groundwater, it causes a range of concentrations between the Type 1 and Type 3 end members, as illustrated in the Piper diagram. This Piper diagram also shows that mixing occurs between Type 1 and Type 2 groundwater. Mixing between Type 1 and Type 3 groundwater and between Type 1 and Type 2 groundwater is represented by the red mixing lines on Figure 6.
- Depending on the amount of time Colorado River water is in the subsurface, ion exchange reactions may not be complete before mixing occurs with native water. This process is represented by the black mixing line on Figure 6.

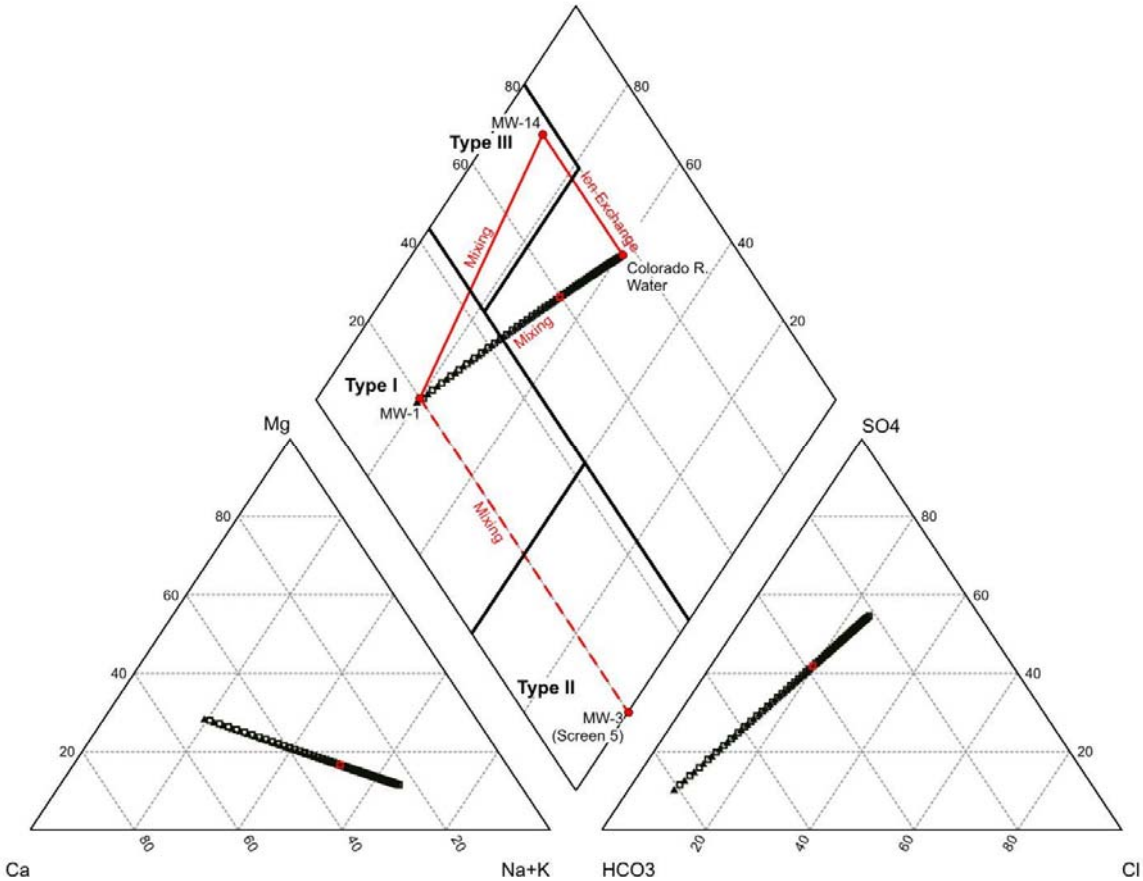

Figure 6. Ion exchange and mixing are understood to be responsible for the different water types observed in the study area.

- The Bangham and Garfield wells have been used as injection wells for imported water and have somewhat similar geochemical characteristics, in that they fall outside the water typing boundaries. Data from both wells indicate a direct influence of imported water via mixing of Type 1 groundwater and Colorado River water.
- A Piper diagram for groundwater data collected from the Sunset Well (Figure 7) demonstrates the influence of the imported water on the groundwater in the Sunset Reservoir area (see Attachment 2 for Piper diagrams of other production wells in the Raymond Basin). The groundwater samples collected in 1940[5] exhibit typical Type 1 characteristics, indicative of the native water. However, with the introduction of the MWD water in the area since the 1940s, there is a gradual change in the geochemical parameters of the aquifer resulting in the movement of the Sunset Well data from Type 1 water to Type 3 water. This change indicates that Sunset Reservoir area groundwater is highly

impacted by infiltration of imported MWD water, which typically contains more than 50% Colorado River water, and at certain times consists of 100% Colorado River water (see Table 2).

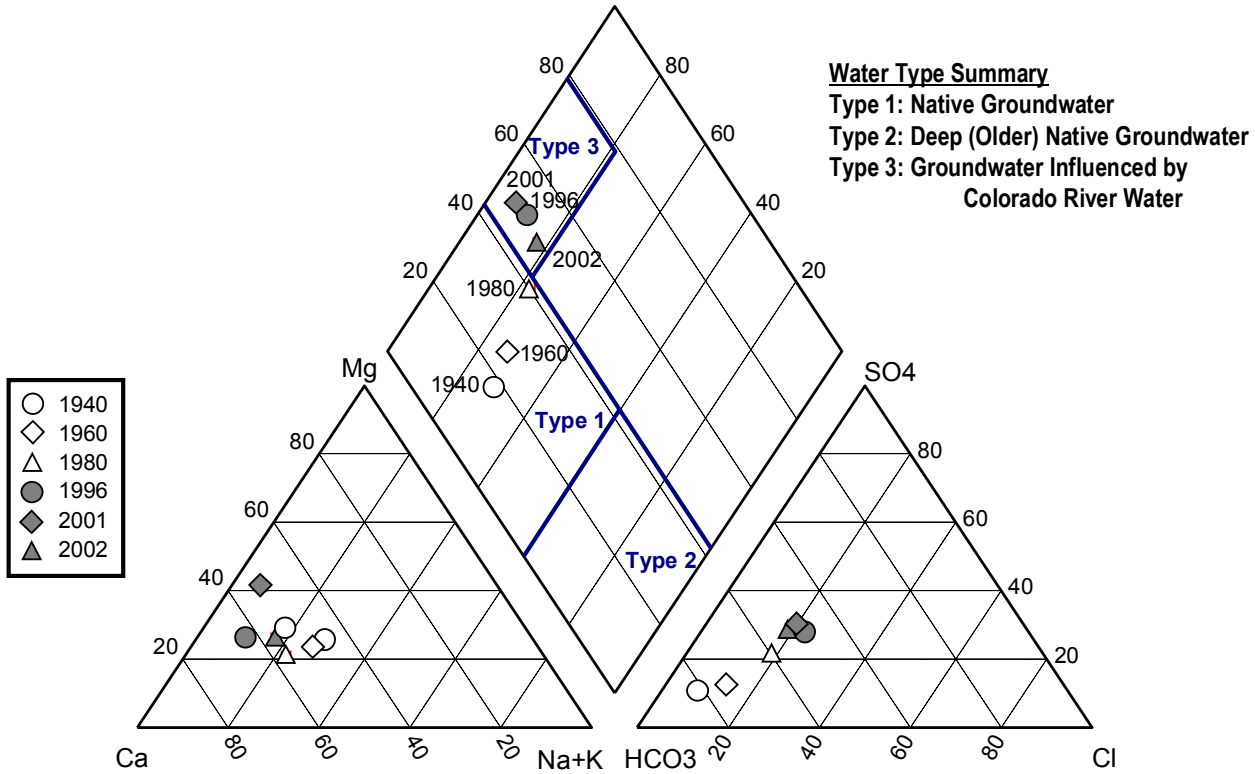

Figure 7. The Sunset well water quality has shifted from Type 1 water to Type 3 water since the 1940s. This demonstrates the influence on Colorado River water in the Sunset Reservoir area.

- Sulfate concentrations in the Raymond Basin groundwater have increased significantly over the past 50 years. Sulfate can be considered a reliable tracer chemical associated with the introduction of imported water into the Basin. This is because sulfate levels in the Colorado River are an order of magnitude higher than native water in the Raymond Basin (> 300 mg/L versus < 30 mg/L) and there is no other reasonable explanation for the increase in groundwater sulfate concentrations. Therefore, elevated levels of sulfate in the Raymond Basin groundwater are an indicator of the influence of imported Colorado River water. In addition, the aerobic conditions present in the Raymond Basin aquifer prevent sulfate from being removed from the groundwater through biodegradation.
- Figures 8 and 9 show sulfate iso-concentration contours in groundwater samples collected in 1950 and 1999, demonstrating the influence of Colorado River water on the aquifer (see Attachment 3 for graphs of sulfate concentrations over time in production wells in the Raymond Basin). Note that the concentrations are greatest along the western edges of the Pasadena Subarea, suggesting that the aquifer recharge is greatest along this corridor. Recharge along this corridor is likely a result of injection, irrigation of the golf course near the Rose Bowl (Pasadena Water and Power's largest water user), and the significant amount of drinking water infrastructure (connections to the MWD feeder line, reservoirs, and pipelines). These plots reinforce the conclusion that the imported water from the Colorado River has impacted the groundwater geochemistry in the Raymond Basin leading to the formation of Type 3 water.

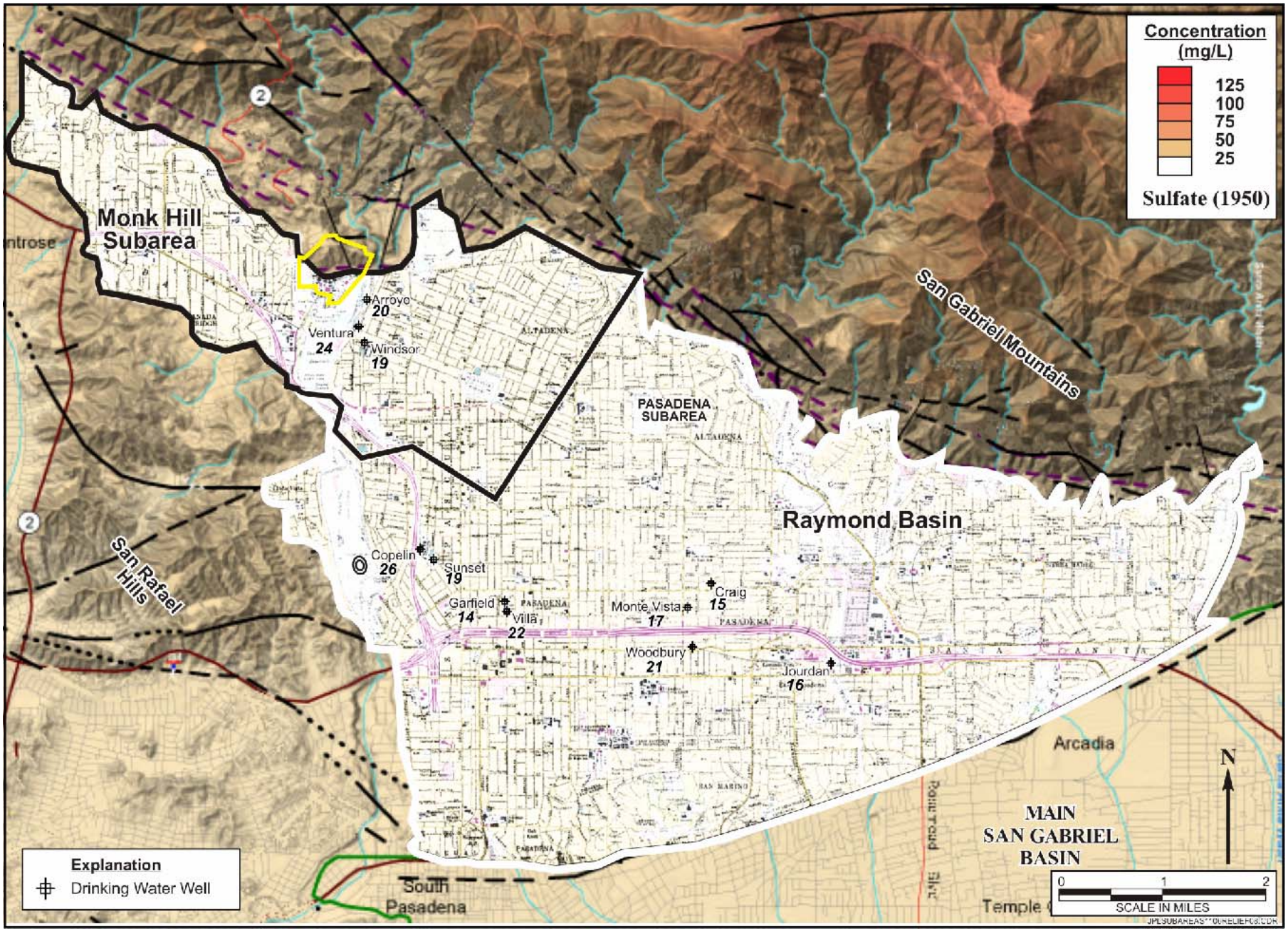

Figure 8. Sulfate concentrations in Raymond Basin were relatively low in 1950 (less than ten years after the connection to the Colorado River was established in the Raymond Basin). These relatively low sulfate levels are associated with native Type 1 water.

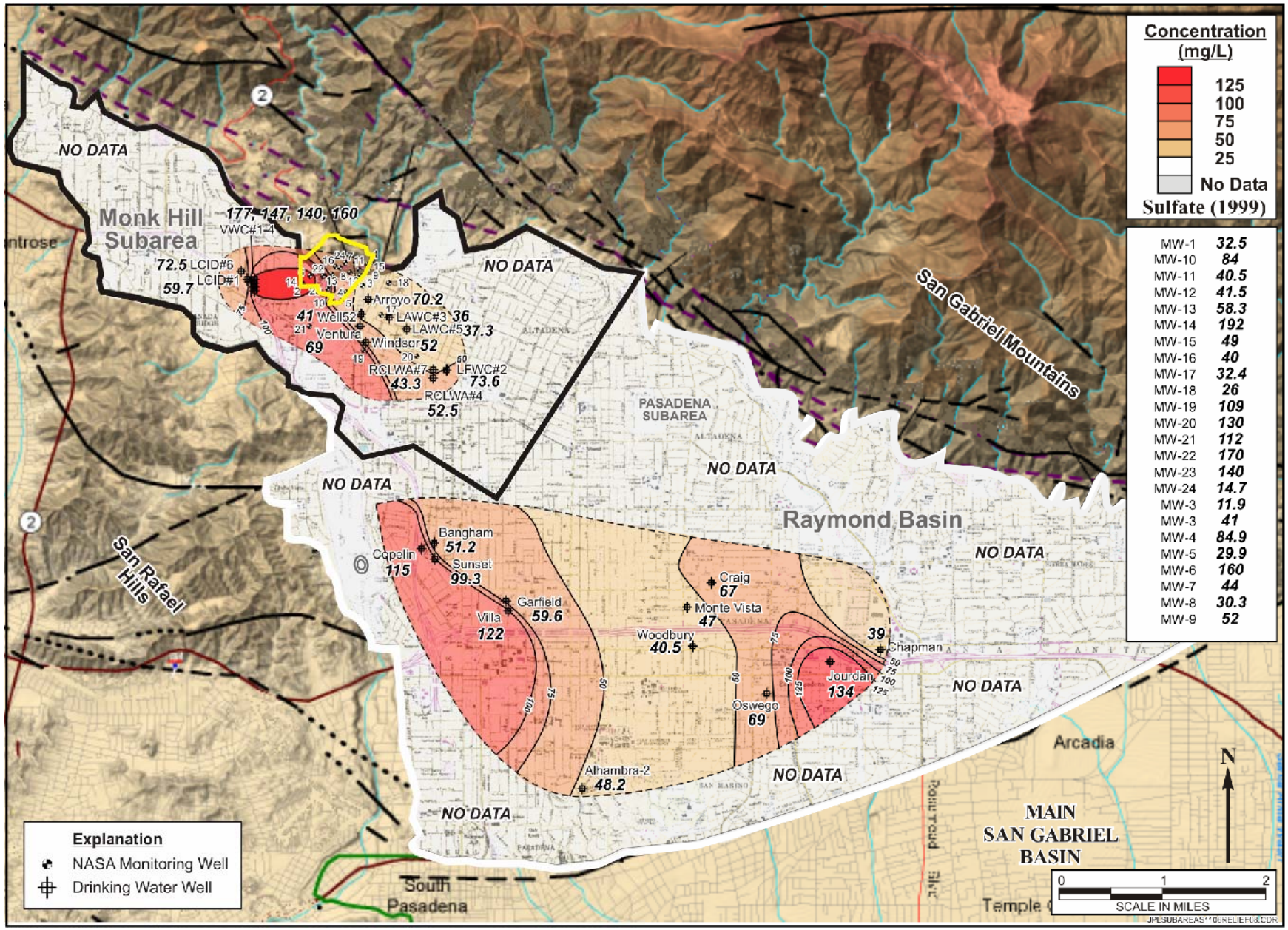

Figure 9. Sulfate concentrations in the Raymond Basin had increased dramatically by 1999 (over 50 years after the connection to imported water was established), demonstrating the influence of imported Colorado River water.

- Colorado River water is known to contain perchlorate. Perchlorate in the Colorado River originates from the Basic Management and Industrial (BMI) complex in Henderson, Nevada. Since the late 1940s, the BMI complex area includes two former perchlorate manufacturing facilities that were among the largest perchlorate manufacturing plants in the United States.[23] The disposal practices at this area led to perchlorate contamination in the Las Vegas Wash Area which discharged perchlorate into Lake Mead, ultimately reaching the Colorado River.[24,25] Cleanup action in this area began in 1999.
- The highest documented perchlorate concentrations in the Las Vegas Wash were 570 to 850 µg/L. Perchlorate concentrations in the range of 5 to 9 µg/L have been reported in Lake Mead since analysis began in 1997. Perchlorate concentrations as high as 9 µg/L have been reported in MWD Colorado River water since 1997.[26] Perchlorate concentrations in MWD water prior to 1997 are not known because perchlorate analyses were not performed, however, the facilities began manufacturing, and disposing of, perchlorate in the 1940s.[13]
- Assuming perchlorate was present in the river water prior to its discovery in 1997, a large mass of perchlorate could have been introduced to the Raymond Basin aquifer via leaks in the distribution system, injection, unsewered areas, and irrigation. To illustrate, even if one assumes only 25% of the imported perchlorate mass makes it to the aquifer (due to leaks in the distribution system, injection, irrigation, etc.) and an average perchlorate concentration of 5 µg/L between 1952 and 2002 (the amount of Colorado River water imported to the Raymond Basin between 1952 and 2002 is approximately 969,000 acre-ft), over 3,000 lbs of perchlorate could have been introduced to the Raymond Basin aquifer.

Colorado River water is known to contain perchlorate originating from perchlorate production facilities in Henderson, Nevada. Concentrations of perchlorate in the Colorado River water are not known prior to 1997; however, the facilities began manufacturing, and disposing of, perchlorate in the 1940s.

Additional Investigation Isotope Results Associated with Groundwater Geochemistry:

- Groundwater, strontium, and tritium isotope data were collected as part of the additional investigation to improve our understanding of groundwater geochemistry.
- Figure 10 depicts the water isotopes ($\delta^{18}O$ and hydrogen [$\delta^{2}H$]) that were collected as part of the additional investigation. There is considerable variability and overlap in the isotopic compositions of the three water types identified above. In general, water Types 1 and 2 are isotopically similar on average and lie along the Global Meteoric Water Line, but Type 3 water is isotopically lighter on average relative to Types 1 and 2 and lies below the Global Meteoric Water Line. This reflects the presence of a significant amount of imported MWD water in Type 3 water because MWD water is depleted in $\delta^{2}H$ and enriched in $\delta^{18}O$ relative to Types 1 and 2 water, resulting in the distinctive geochemistry of Type 3 water. Previous work on groundwater hydrology in the Los Angeles metropolitan area has demonstrated the widespread occurrence of mixing between local meteoric water and imported MWD water.[27,28,29]

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[23] Batista, J.R., L. Papelis, K. Kesterson, and P. Amy. 2005. *Potential for Bioremediation of the Perchlorate-Contaminated Sediments in the Las Vegas Wash Area, Henderson, Nevada*. Published Online in Wiley Interscience.

[24] EPA. 2003. *Final Report :The Fate and Transport of Perchlorate in a Contaminated Site in the Las Vegas Valley. Part A: Investigation of the Influence of Biological Degradation and Sorption on the Fate of Perchlorate. Part B: Modeling of the Transport of Perchlorate in the Las Vegas Wash.*

[25] Roshan, Manjula. 2001. Master Thesis. *Transport of Perchlorate in the Las Vegas Wash and Lake Mead*.

[26] Urban Water Research Center (UWRC). 2004. *Perchlorate in Drinking Water: A Science and Policy Review.* University of California, Irvine. June.

[27] Williams, A.E. 1997. "Stable Isotope Tracers: Natural and Anthropogenic Recharge, Orange County, California." *Journal of Hydrology*. 201:230-248.

[28] Williams, A.E. and D.P. Rodoni. 1997. "Regional Isotope Effects and Application to Hydrologic Investigations in Southwestern California." *Water Resources Research.* 33:1721-1729.

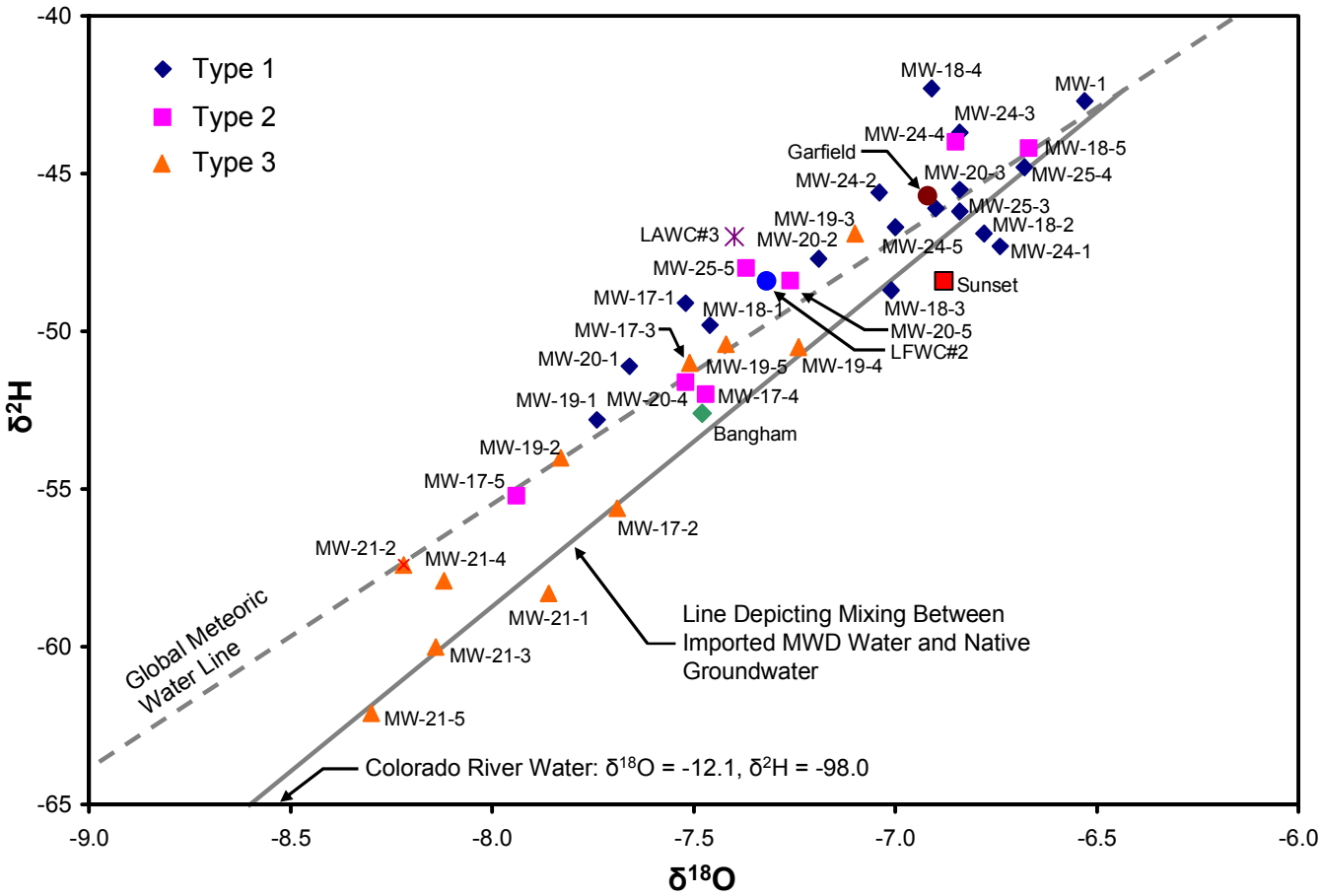

Figure 10. The groundwater isotope data do not provide a clear separation in water types, although there does appear to be some correlation with Type 3 water and mixing with imported MWD water.

Groundwater, strontium, and tritium/helium isotope results confirm the determination of water typing using groundwater concentrations of cations and anions.

- Figure 11 is a graph of the strontium stable isotope ratio ($^{87}Sr/^{86}Sr$) versus the inverse strontium concentration (1/[Sr]). The graph depicts a mixing between the native Type 1 water and imported Colorado River water.[30] Native water in the area is generally heavier in its strontium isotope ratio than the Colorado River water. Groundwater collected from MW-24, located in the northern portion of the facility, has historically been categorized as Type 1, associated with run-off from the San Gabriel Mountains. This explains why MW-24 is heavier in its strontium isotope ratio. MWD water on the other hand, is lighter in its strontium isotope composition. Most of the other wells contain groundwater with an isotopic signature between these two end-points indicating mixing of the two waters. With ion-exchange and precipitation reactions occurring as the water passes through the subsurface, the strontium concentration is depleted and deeper screens, with Type-2 water, contain water with lower strontium concentrations but almost identical strontium isotope ratios. Thus, Figure 11 reinforces the water typing as the different water types arrange in distinct clusters in the plot.

[29] United States Geological Survey (USGS). 2001. *Low-Level Volatile Organic Compounds in Active Public Supply Wells as Ground-Water Tracers in the Los Angeles Physiographic Basin, California, 2000*. Water-Resources Investigations Report 01-4188.
[30] Faure, Gunter. 1997. *Principles of Isotope Geology*. Smith-Wylie Intermediate Geology Series, 1st Edition.

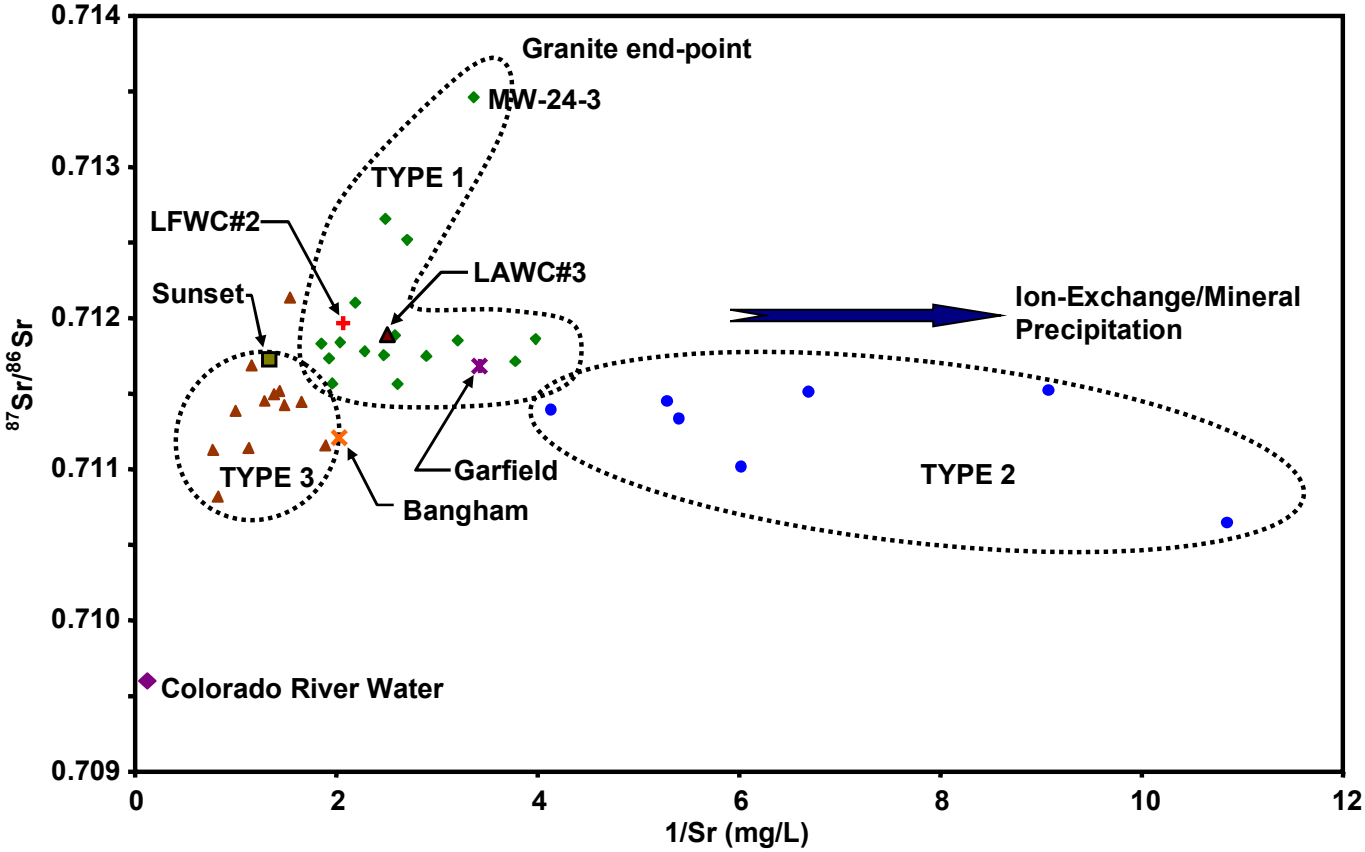

Figure 11. The strontium isotope data correlate with the water typing, grouping in distinct clusters on the above plot that can be explained by mixing and ion-exchange/mineral precipitation.

- Tritium concentration (activity) is a useful parameter for assessing the age of water for periods of up to 60 years, due to its relatively short half-life of 12.4 years.[31] Tritium atoms in the atmosphere react with oxygen to form water, which then enters the aquifer via precipitation (or injection of imported water). Tritium levels are measured in tritium units (TU), where 1 TU equals 1 atom of tritium in 10^{18} atoms of hydrogen. Tritium levels vary based upon the time since the water was in contact with the atmosphere, with higher values generally correlating with more recent atmospheric contact. The complexity of mixing that takes place in the aquifer and the uncertainty regarding when infiltration occurred make quantitative calculation of age impossible. However, investigators[32] have attempted to generalize the age of water based on relative levels of tritium, where <0.8 TU represents water recharged prior to 1952, and where tritium levels between 2 and 8 TU represent modern recharge.
- Figure 12 qualitatively depicts different recharge times according to the tritium levels measured during the additional investigation. Only groundwater collected from MW-19 and MW-21, located south of JPL and immediately downgradient to the VWC wells (where the water is currently being injected) have TU values greater than 8. These higher TU values correlate with Type 3 water and our understanding of the influence of water injected into the VWC wells. Groundwater samples collected from deeper screens had tritium levels below 0.8 TU, indicating an age prior to 1952 and correlating with Type 2 water. Most of the groundwater samples had tritium levels between 2 and 8 TU, indicating modern groundwater.

[31] Motzer, W.E., T.K. Mohr, S. McCraven, and P. Stanin. 2006. "Stable and Other Isotope Techniques for Perchlorate Source Identification." *Environmental Forensics*. 7:89-100.
[32] Clark, I. and P. Fritz. 1997. *Environmental Isotopes in Hydrogeology*. Lewis Publishers.

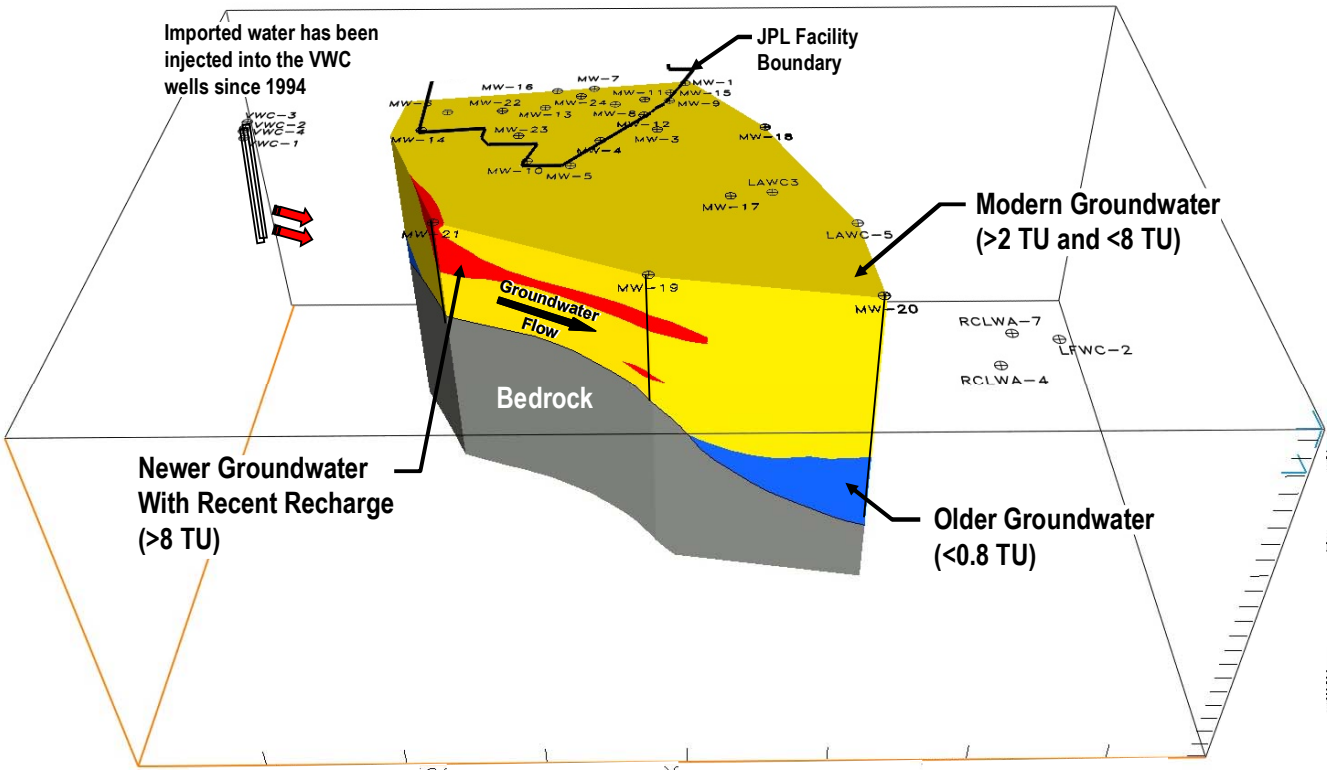

Figure 12. Tritium isotope data support the understanding of the transport of imported MWD water injected into the VWC wells and tritium levels less than 0.8 TU correlate with deep, Type 2 water.

GROUNDWATER CHEMICAL CONCENTRATIONS

Carbon Tetrachloride

- As part of the JPL groundwater monitoring program, groundwater samples are collected from 25 JPL monitoring wells (MWs), both on- and off-facility. The groundwater monitoring program is conducted according to the *Work Plan for Performing a Remedial Investigation/Feasibility Study*.[33]
- The VOC carbon tetrachloride is a reliable tracer for chemicals originating from JPL because significant quantities were disposed of at JPL during historical operations[10] and because no other source of carbon tetrachloride are known to exist in the Monk Hill Subarea.[4, 34] Other VOCs, including TCE and PCE, have been detected at relatively low levels in soil and groundwater beneath JPL. However, other sources of these VOCs exist in the Monk Hill Subarea, such as former dry cleaning sites and unsewered areas in La Cañada Flintridge[10] so they cannot be used as tracers for chemicals originating from JPL.

Results from the samples collected from JPL groundwater monitoring wells and from production wells indicate that carbon tetrachloride is unique to the JPL within the Monk Hill Subarea. The extent of carbon tetrachloride is known, does not extend outside the Monk Hill Subarea, and correlates closely with groundwater modeling predictions.

[33] Ebasco. 1993. *Work Plan for Performing a Remedial Investigation/Feasibility Study*. National Aeronautics and Space Administration Jet Propulsion Laboratory, Pasadena, California. December.
[34] NASA. 2003b. *Annual Report on the JPL Long-Term Groundwater Monitoring Program, January, 2002 to November, 2002*. Prepared by SOTA Environmental Technology, Inc. for National Aeronautics and Space Administration. May

- Analytical results of groundwater samples collected from JPL monitoring wells and production wells indicate that the carbon tetrachloride plume originating from JPL is fully delineated and contained within the Monk Hill Subarea.
- In addition, carbon tetrachloride was used at the facility during the same timeframe as perchlorate[14] and, based on the hydrogeology, carbon tetrachloride and perchlorate would follow similar flow paths. Therefore, co-location of carbon tetrachloride and perchlorate in samples adjacent to and hydraulically connected to JPL indicates a source of perchlorate originating from JPL. For example, samples from all the source area wells (MW-16, MW-24 [Screen 1], and MW-7) have contained both perchlorate and carbon tetrachloride. In addition, off-facility wells such as MW-17 (Screen 3), Arroyo Well, Well 52, LAWC#3, and LAWC#5 have historically contained both perchlorate and carbon tetrachloride (see Attachment 4 for perchlorate and carbon tetrachloride graphs for production wells in the Raymond Basin and JPL monitoring wells).
- Groundwater monitoring data delineate the extent of carbon tetrachloride originating from the JPL facility as approximately one mile southeast of the JPL facility. Carbon tetrachloride has not been detected in Sunset Reservoir wells, nor has it been detected in NASA's furthest downgradient monitoring wells, MW-19, MW-20, MW-21, and MW-26, with the exception of an isolated detection in August/September 1996 (0.5 µg/L in MW-19 [Screen 4]).
- The extent of carbon tetrachloride is shown in Figure 13 and correlates well with groundwater modeling predictions (see above) in that it does not extend outside the capture zones of Arroyo Well, Well 52, LAWC#3, and LAWC#5.
- Based on differences in chemical properties, it is recognized that perchlorate could move more rapidly in groundwater than carbon tetrachloride. Even so, the absence of carbon tetrachloride outside the Monk Hill Subarea strengthens the reliability of the groundwater modeling predictions and supports an origin of perchlorate in Sunset Reservoir Wells not associated with JPL.
- Biodegradation of carbon tetrachloride in groundwater under aerobic conditions found in the Monk Hill Subarea would not be expected to reduce concentrations significantly.[35]

Perchlorate

- Since 1997, perchlorate has consistently been detected in the Sunset Reservoir wells, with maximum concentrations of 31.6, 17.7, 25.3, 27.7, and 9.75 µg/L in the Sunset, Bangham, Copelin, Garfield, and Villa wells, respectively.[9] Figure 14 provides the perchlorate concentrations over time in the Sunset Reservoir Wells.
- Sporadic detections of perchlorate have been observed in samples collected from MW-20 (Screen 4) since 1998 associated with deeper portions of the aquifer and Type 1 or 2 water quality (consistent with a source originating from JPL). Specifically, samples collected from MW-20 (Screen 4) contained perchlorate concentrations of 20 µg/L, 30 µg/L, 58.5 µg/L, and 124 µg/L in October/November 1998, April/May 2002, October/November 2002, and April/May 2003.[4,34] All other samples from Screen 4 have shown non-detect concentrations of perchlorate. Groundwater modeling indicates that MW-20 is located within the capture zone of the RCLWA wells (see Figures 11 and 12).[5,6] Therefore, the groundwater represented by samples collected from MW-20 would be captured by the RCLWA wells and not migrate to the Sunset Reservoir wells.
- Samples collected in Screen 1 of MW-20 (located approximately 2 miles north of the Sunset Reservoir wells) contained low levels of perchlorate from 1997 to 2001; however, these samples were collected from locations in the uppermost hydrostratigraphic layer and were associated with Type 3 water, indicating a source other than JPL.

[35] Agency for Toxics Substances Disease Registry (ATSDR). 2005. *Toxicological Profile for Carbon Tetrachloride*. August.

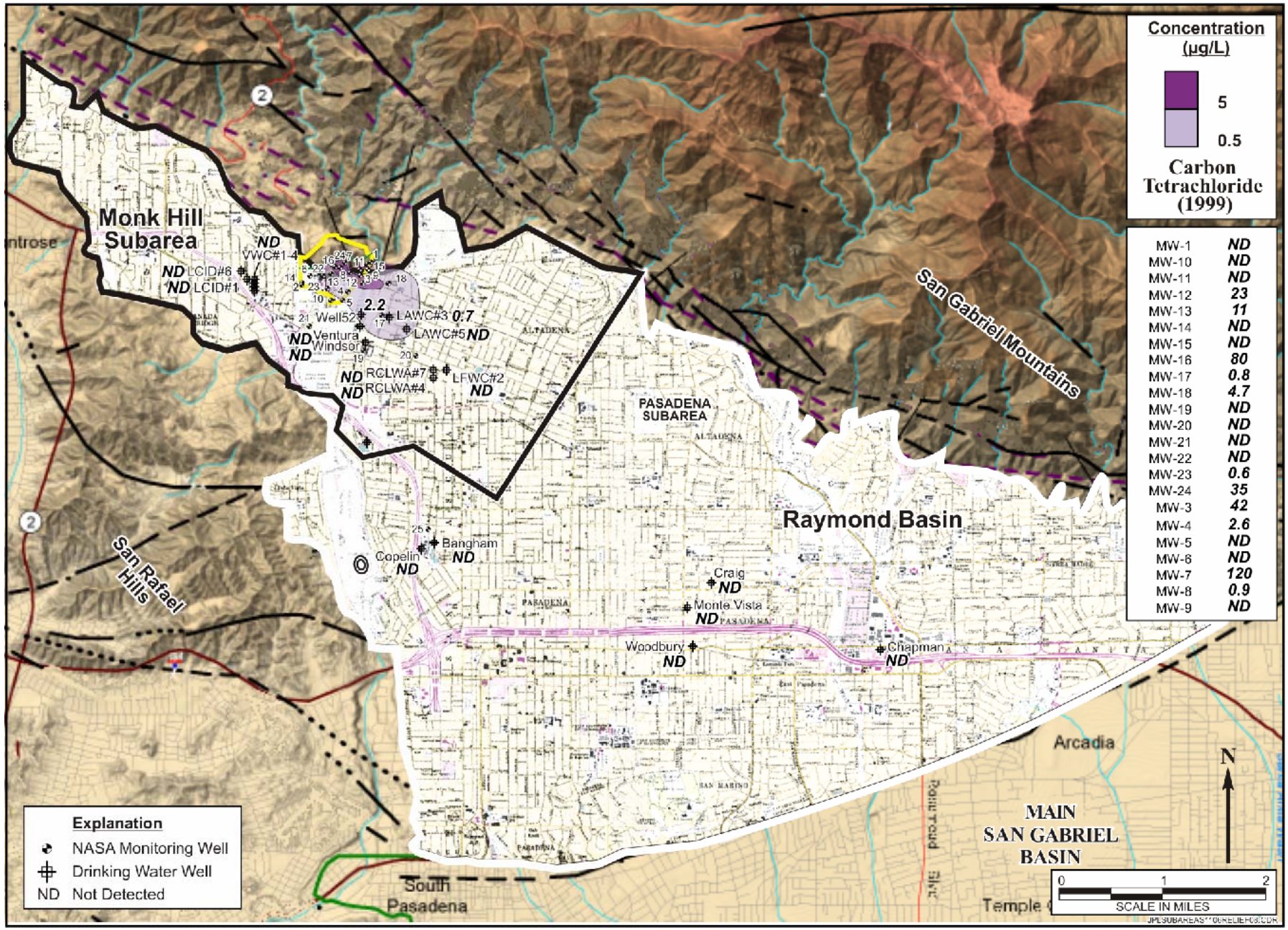

Figure 13. Carbon tetrachloride is unique to JPL within the Monk Hill Subarea and is considered a tracer for chemicals originating from the JPL Facility. Carbon tetrachloride has not been detected in the Sunset Reservoir Wells, MW-20, MW-26, or MW-25. The southernmost detection of carbon tetrachloride has been at LAWC#5. The extent of carbon tetrachloride supports the understanding of capture zones of production wells in the Monk Hill Subarea.

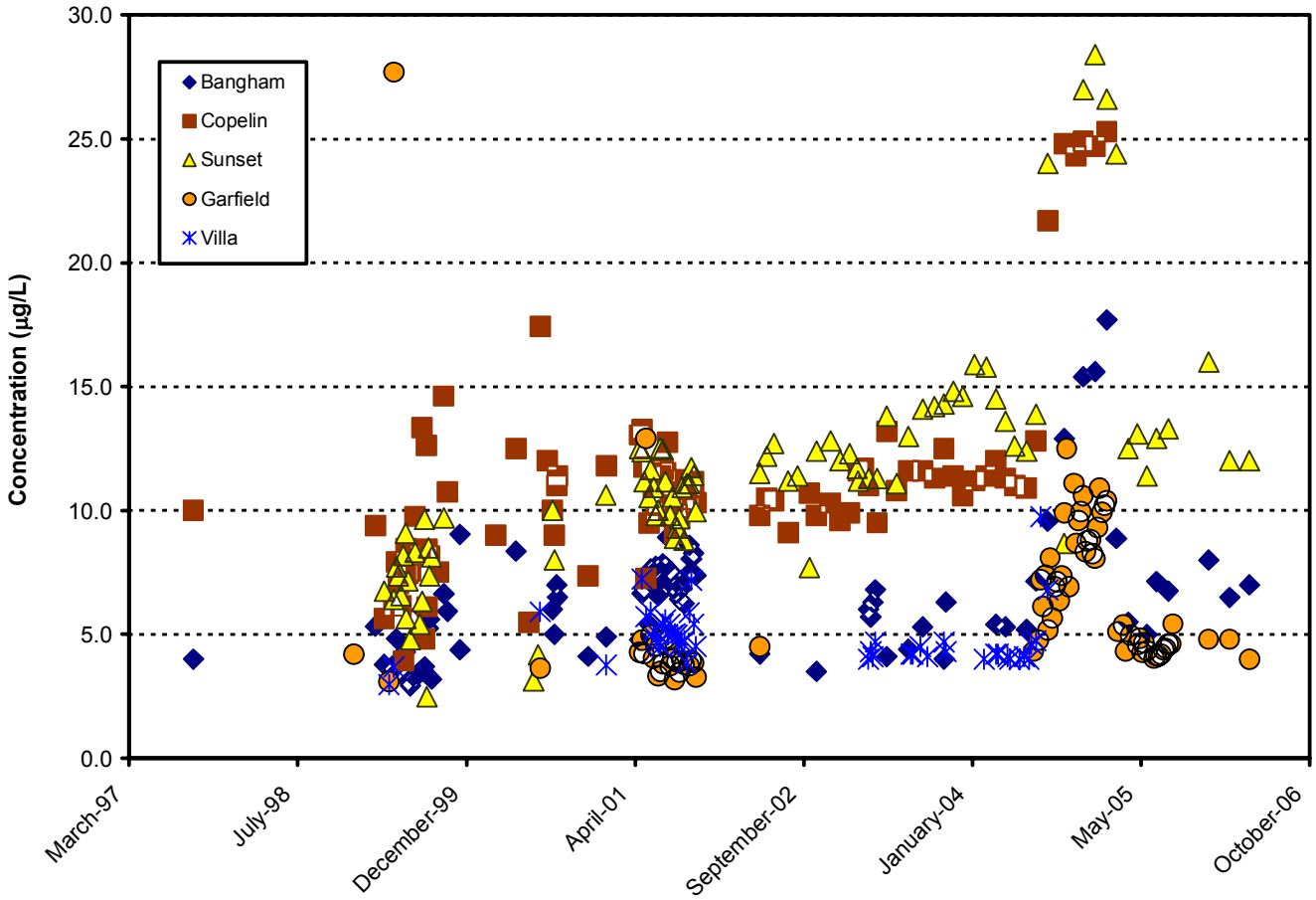

Figure 14. Perchlorate was first detected in the Sunset Reservoir area in 1997 and the majority of detections have been in the 5 to 15 µg/L range.

- Low levels (less than 10 µg/L) of perchlorate have been detected in MW-19 (Screens 2, 3, and 5). MW-19 is not within the flow path of groundwater originating from JPL and is within the flow path of groundwater originating from the VWC wells (see Figures 11 and 12). In addition, samples collected from MW-19 show a strong influence of imported water (see discussion above) and have perchlorate concentrations that are comparable to the levels detected in the upgradient VWC wells. Therefore, the perchlorate detections in MW-19 are not believed to be associated with JPL.
- During quarterly groundwater monitoring, perchlorate concentrations have not been detected in the new MW-26, located approximately mid-way between JPL and the Sunset Reservoir wells, using EPA Method 314.0. During the second quarter 2005 monitoring event, samples collected from MW-26 were also analyzed using a lower detection limit method, EPA Method 8321a (liquid chromatography/double mass spectrometry), and concentrations of 1.5 µg/L and 1.0 µg/L were detected in Screens 1 and 2, respectively. MW-26 is outside the capture zones of the Monk Hill Subarea production wells and thus, not within the flow path of groundwater originating from JPL. MW-26 is within the flow path of groundwater originating upgradient/cross-gradient to JPL.
- Perchlorate concentrations in the new MW-25, located just north of the Sunset Reservoir wells, are in the same range as the Sunset Reservoir wells (i.e., 5 to 15 µg/L).
- In MW-21, perchlorate has been detected in the first screen with a maximum concentration of 19 µg/L in 1997 (see Figure 15). Since 2001, the concentrations have dropped considerably with only sporadic occurrences of perchlorate concentrations near 4 µg/L. Perchlorate concentrations in the other screens (2, 3, 4, and 5) have been low, with the highest recorded level of 6.2 µg/L (2004). MW-21 is cross-gradient to JPL, in the flow path from and heavily influenced by injection of imported

water into the VWC wells as demonstrated by the geochemical data and tritium isotope data, and representative of groundwater cross-gradient/upgradient of JPL. In addition, MW-21 is outside the capture zones of the Monk Hill Production wells and within the capture zone of the Sunset Reservoir wells according to the RBMB groundwater model (see Figures 10 and 11).[5] The elevated levels of perchlorate in MW-21, which were detected from when perchlorate sampling began in 1997 to 2000, provide evidence of a more significant source of perchlorate that did not originate from JPL. The reductions in perchlorate concentrations in MW-21 beginning around 2001 may be a result of reductions in perchlorate levels in MWD imported water following its discovery in 1997. Reductions in perchlorate levels in imported MWD water are likely associated with blending with other MWD water sources prior to injection into VWC wells.

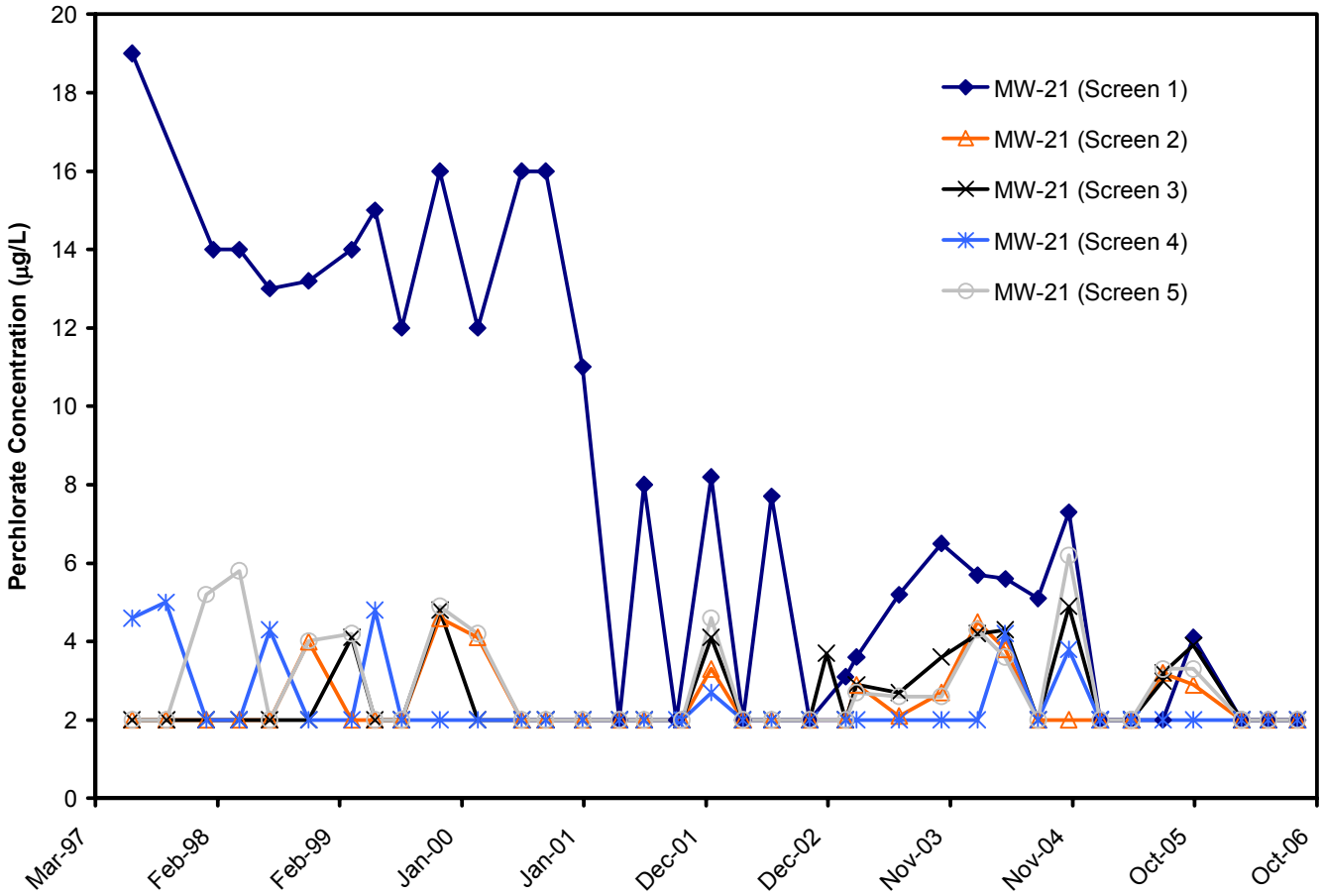

Figure 15. Elevated perchlorate levels in MW-21 between 1997 and 2000 provide evidence of a significant source of perchlorate that did not originate from JPL. MW-21 is located within the capture zone of the Sunset Reservoir wells according to the RBMB Groundwater Model.

PERCHLORATE ISOTOPE ANALYSIS

Background

- Sources of perchlorate (other that those associated with solid rocket propellant) are well documented,[7,8] including road flares, fireworks, blasting operations, and naturally-occurring mineral deposits used for fertilizer production.
- The most well documented natural occurrence of perchlorate is in nitrate salt deposits of the Atacama Desert in Chile. These deposits have been exported extensively since about 1870 for use as agricultural fertilizer. According to the California Department of Agriculture, more than 477,000 metric tons of Chilean nitrate were used in the State as fertilizer between 1923 and 1998.[36] Although synthetic nitrogen sources are now used in most fertilizer applications, more than 55,000 metric tons of the Chilean nitrate material was shipped to California between 1995 and 2000, primarily for fertilizer application. The concentration of perchlorate in processed Chilean nitrate fertilizer reportedly ranges from approximately 1,750 to 7,700 mg/kg.[37] Thus, one metric ton of this material can contain as much as 7.7 kg of perchlorate, enough to contaminate more than 340 million gallons of groundwater to above the current California Action level of 6 µg/L. Since 1999, the primary exporter of this material (SQM Corp.) has changed its production process to reduce the perchlorate concentration to below 100 mg/kg. In addition to the perchlorate found in Chilean nitrate and other natural salt deposits, natural background levels of perchlorate up to 2 µg/L have been reported in samples of rain, snow and groundwater.[38,39] It is believed that natural perchlorate may originate in the stratosphere from reactions between ozone and volatile species of chlorine.
- Colorado River water delivered by MWD was known to contain perchlorate and has had a significant impact on the water quality in the Raymond Basin (see above).
- Naturally-occurring/fertilizer perchlorate and different synthetic sources of perchlorate have unique isotopic fingerprints.[15,16,17,18,31]

Summary of Perchlorate Isotope Results

- Perchlorate associated with JPL has a distinct isotopic fingerprint as seen by the results from MW-16 and source area treatment plant influent (see Figures 16 and 17), which are located on JPL within the source area for chemicals. The $\delta^{18}O$ values in the samples collected from MW-16, MW-17-3, LAWC#3, and the source area treatment plant influent were lower than any other samples measured in this study. The available records indicate that the perchlorate used at the JPL facility was manufactured in the Los Angeles area.[13] Differences in the isotopic composition of source materials account for the differences in the perchlorate isotopic composition.

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[36] California Department of Food and Agriculture. 1999. *Fertilizing Materials Tonnage Report*. July-December.

[37] U.S. Environmental Protection Agency. 2001. *Survey of Fertilizers and Related Materials for Perchlorate Final Report*. May.

[38] Dasgupta, P.K., P.K. Martinelango, W.A. Jackson, T.A. Anderson, K. Tian, R.W. Tock, and S. Rajagopalan. 2005. "The Origin of Naturally Occurring Perchlorate: The Role of Atmospheric Processes." *Environmental Science and Technology*. 39:1569-1575.

[39] Plummer, L.N., J.K. Böhlke, and M.W. Doughten. 2006. "Perchlorate in Pleistocene and Holocene Groundwater in North-central New Mexico." *Environmental Science and Technology*. 40: 1757-1753.

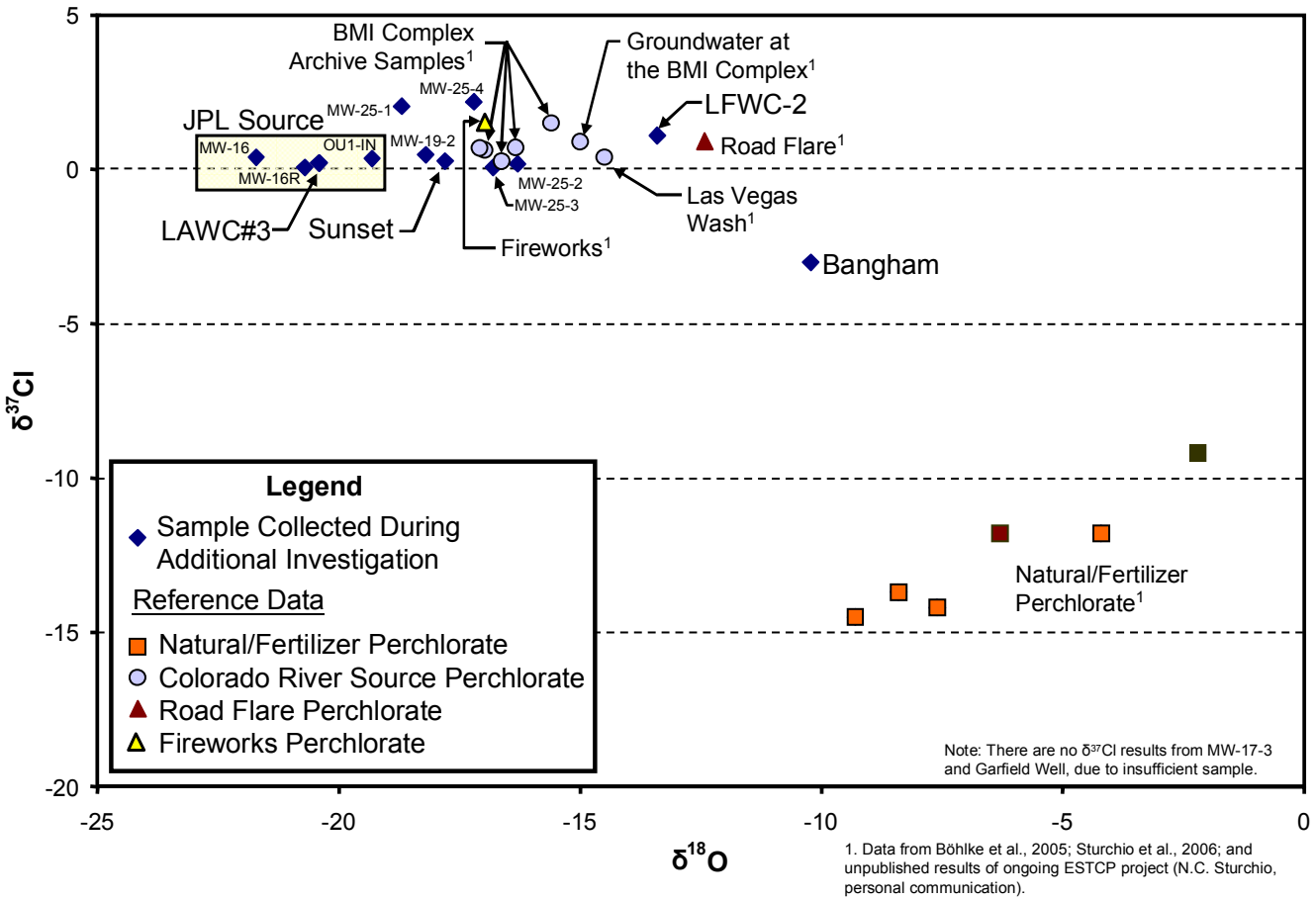

Figure 16. Perchlorate originating from JPL has a distinct isotopic signature, with a $\delta^{18}O$ values ranging between approximately -19‰ and -21‰.

- The isotopic signature of JPL perchlorate is maintained during transport. This is demonstrated by the similarity in signatures between MW-16, located in the source area, and MW-17-3 and LAWC#3, located approximately 3,000 feet downgradient (see Figure 17).
- The only processes that might cause a significant change in isotopic composition of perchlorate during subsurface transport are (1) biodegradation[40] and (2) mixing with perchlorate having a different isotopic composition.
- Biodegradation is most likely not occurring since the dissolved oxygen (DO) levels are near saturation and nitrate is relatively high (generally greater than 1 mg/L as NO_3), indicating that the anaerobic conditions necessary for reductive degradation of the perchlorate are not present. DO and nitrate are competing electron acceptors and would be biodegraded preferentially before perchlorate degradation occurs.

[40] Sturchio, N.C., J. K. Böhlke, A. D. Beloso, S. H. Streger, L. J. Heraty and P. B. Hatzinger. 2007. "Oxygen and Chlorine Isotopic Fractionation During Perchlorate Biodegradation: Laboratory Results and Implications for Forensics and Natural Attenuation Studies." *Environmental Science and Technology*. 41 (In Press).

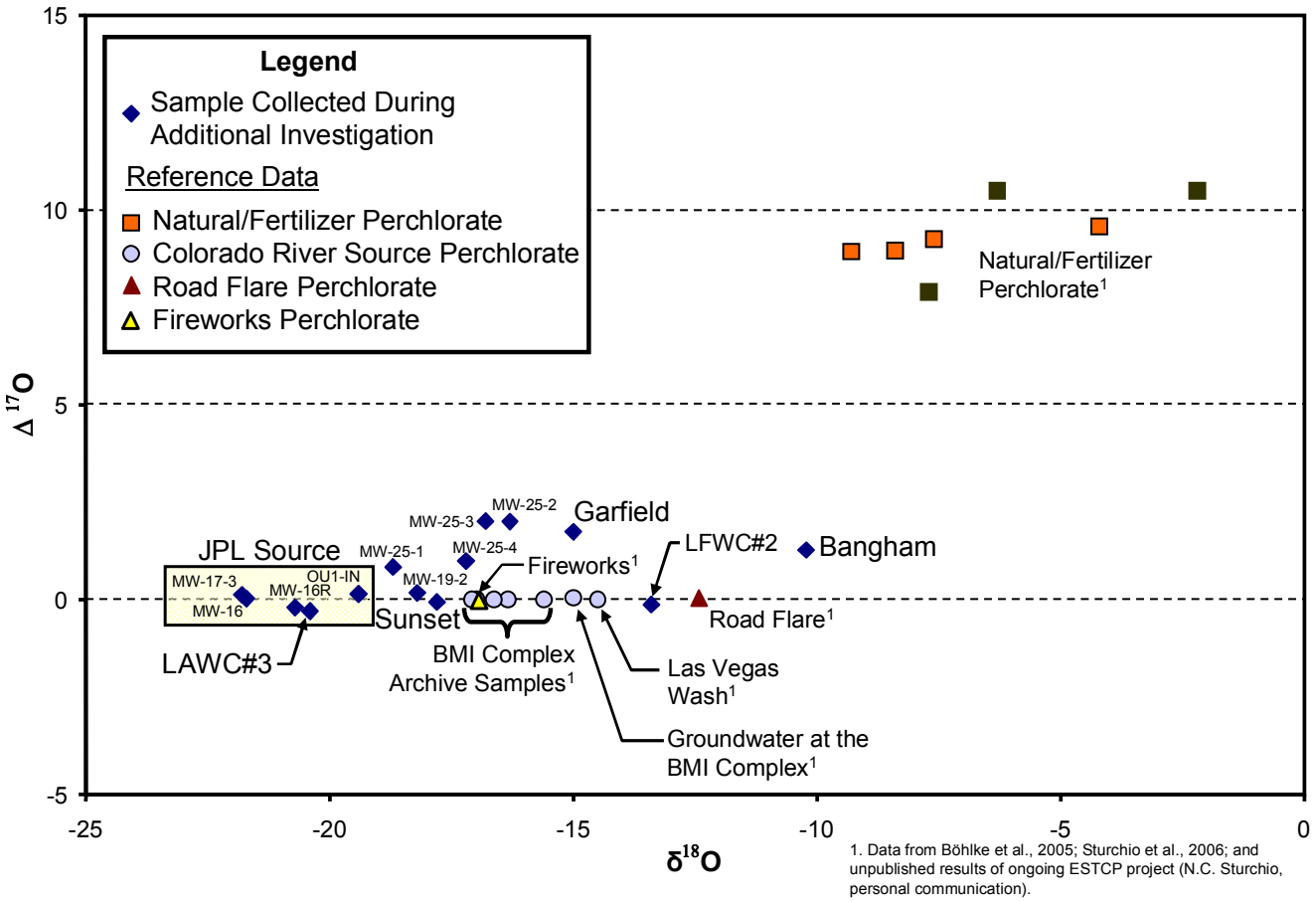

Figure 17. The isotopic signature of JPL perchlorate is maintained during transport, as demonstrated by the isotopic signature of MW-17-3. MW-17-3 is located approximately 3,000 feet downgradient, in between Arroyo Well and LAWC#3.

- The absence of perchlorate biodegradation in the aquifer is supported by the functional genomics testing performed as part of the additional investigation. These tests show that the *cld* gene (the gene which produces the chlorite dismutase (*cld*) enzyme, a highly conserved enzyme unique to organisms capable of perchorate reduction)[41] was present in six of the nine samples analyzed. However, the activity of the perchlorate-reducing bacteria (indicating that these bacteria are metabolizing perchlorate) was assessed by identifying the presence of *cld* mRNA, which indicates activity of the *cld* gene. The test for *cld* mRNA was reported as positive in only two of the nine samples, including background well MW-1 and also MW-24-1 (located in the source area).
- The functional genomics testing supports more conventional geochemical analyses, including pH, DO, oxidation-reduction potential (ORP), nitrite/nitrate, dissolved nitrogen, total Kjeldahl nitrogen, ammonia, ferrous/ferric iron, sulfite/sulfate, dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and total organic carbon (TOC). These analyses were performed at 41 sampling locations to evaluate if appropriate conditions are present within the aquifer to support biodegradation of the perchlorate. Appropriate geochemical conditions include a pH between 6.5 and 7.5, depleted oxygen, and low nitrate levels.[42] Overall, the following evaluation of these data suggest that perchlorate degradation is likely not occurring at the site:
    - DO levels are near saturation and nitrate levels are relatively high (generally greater than 1 mg/L as NO_3).

[41] Bender, K.S., M.R. Rice, W.H. Fugate, J.D. Coates and L.A. Achenbach. 2004. "Metabolic Primers for the Detection of (Per)chlorate-reducing Bacteria in the Environment. *Appl. Environ. Microbiol.* 70:5651-5658.
[42] ITRC. 2002. *A Systematic Approach to In Situ Bioremediation in Groundwater*. August.

- ORP levels ranged from -39 to 276 mV, and most measurements were greater than 100 mV.
- At many sample locations, the absence of ferrous iron indicates that iron reduction is not occurring.
- TOC levels are low, indicating that the amount of electron donors present is inadequate to support biodegradation.

- The lack of biodegradation implies that the differences in isotopic composition between JPL perchlorate and the perchlorate in the Sunset, Bangham, and Garfield wells is not caused by biodegradation but is likely to reflect the presence of multiple, isotopically distinct sources of perchlorate in the Raymond Basin.
- Mixing of JPL perchlorate and another source does not appear to be a viable explanation for the perchlorate signatures observed in the Sunset, Bangham, or Garfield wells.
- The isotopic compositions of perchlorate in the MW-19, MW-25, Sunset, Bangham and Garfield wells are all significantly different (higher $\delta^{18}O$ values) from those of the JPL source area and MW-17-3 (downgradient near JPL). The isotopic compositions of perchlorate in wells MW-19, MW-25, Sunset, Garfield, and LFWC#2 are similar to those of fireworks, road flares, perchlorate manufactured at the BMI complex in southern Nevada, and a surface water sample taken from the Las Vegas Wash as well as a groundwater sample taken near the BMI complex.

JPL perchlorate isotopic signature is distinct in the Monk Hill Subarea. The perchlorate in the wells near Sunset Reservoir appear to be influenced by at least two separate (non-JPL) sources, including a naturally occurring/fertilizer source and one or more synthetic source(s).

- The $\Delta^{17}O$ values of perchlorate in wells MW-25, Garfield, and Bangham show evidence of mixing with up to about 25% natural perchlorate (which is enriched in ^{17}O relative to synthetic perchlorate). This natural perchlorate component could have been introduced by infiltration of agricultural fertilizers.
- The perchlorate in the Sunset well is isotopically indistinguishable from that of MW-19 (Screen 2) but different from that sampled on-site at JPL. Carbon tetrachloride has never been detected in MW-19 (Screen 2). In addition, MW-19 is cross-gradient from JPL (i.e., not within the flow path of a particle originating from JPL), and groundwater flows from MW-19 toward Sunset. Therefore, these two wells may contain perchlorate from the same source but not from JPL.
- Mixing does not explain the perchlorate in Sunset Well, since the perchlorate signature is consistent with MW-19 and MW-19 is not associated with JPL. In addition, perchlorate isotope data collected from fireworks and from perchlorate manufacturing facilities in Nevada,[19] the source of the Colorado River water perchlorate, is in the same range as the isotopic signature of the Sunset Well.
- The perchlorate isotope fingerprint at LFWC#2 is distinct from that of the JPL area. LFWC#2 appears to be synthetic perchlorate ($\Delta^{17}O \approx 0‰$) with heavier $\delta^{18}O$ compared to the JPL facility. As seen in Figures 15 and 16, $\delta^{18}O$ and $\delta^{37}Cl$ values of perchlorate present in LFWC#2 are significantly different than those at JPL indicating a different source than JPL for the perchlorate present in the LFWC#2 well. The isotopic composition of perchlorate in LFWC#2 approaches that which is characteristic of perchlorate used in road flares.

CONCLUSION

The objectives of the additional investigation were to (1) evaluate the downgradient (southern) extent of chemicals that originate from the JPL facility and (2) determine if the occurrence of perchlorate in the Sunset Reservoir area were associated with migration from the JPL facility. The investigation employed the use of four different analytic tools to achieve the objectives. *Taken together, the results of the groundwater modeling, groundwater geochemistry, groundwater chemical concentration data, and isotopic analysis, lead to the conclusion that (1) NASA has determined that the chemicals from the JPL facility are contained within the Monk Hill Subarea, and (2) the perchlorate detected at the Sunset area wells is of a different origin than that used at, and originating from, JPL.*