The Late Quaternary History and Groundwater Quality of a Coastal Aquifer, San Diego, California

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ABSTRACT

Prior to World War II, the City of San Diego, California, extracted millions of gallons of high-quality groundwater daily from alluvial gravels in the lower San Diego River Valley that have since become contaminated with brackish water and hydrocarbons. The origin of this brackish groundwater and of the Quaternary sedimentary geology of the valley is interpreted through archived reports, journal articles, U.S. Geological Survey data, and samples from new city wells in the alluvial gravels. Eocene sediments were inundated by seawater during the last interglacial period (ca. 120 ka), when sea levels were ~19 ft (6 m) higher than present levels. The brackish groundwater present in these Eocene sediments appears to be relict seawater from this inundation. We hypothesize that the city's pre–World War II well field—referred to herein as the Mission Valley Aquifer—was a buried channel gravel created following the Last Glacial Maximum of the Pleistocene Epoch (~20 ka). As such, it would have been similar to other long (~11 km, 7 mi) buried channel gravels along the southern Californian coast described in previous reports. We present evidence of groundwater freshening of the Eocene sedimentary rock that has led to increasing total dissolved solids in the Mission Valley Aquifer, which acts as a high-permeability drain for the valley. Freshening occurs as a Ca-HCO_3 groundwater replaces a Na-Cl water, which we propose was derived from the marine inundation of 120 ka.

INTRODUCTION

The City of San Diego is dependent for ~80 percent of its water supply from distant sources that could be interrupted by seismic events, severing the aqueducts from the Colorado River (San Diego Project) and northern California (State Water Project). In addition, surface-water sources such as the California State Water Project and the Colorado River are threatened by drought and thus are no longer as reliable as in the past.

Prior to World War II (WWII), the City of San Diego utilized groundwater from a high-permeability alluvial aquifer in the lower San Diego River Valley ("the valley"). This aquifer, which is the subject of this article, was developed in 1914 but abandoned before WWII. It is the city's goal to re-develop this groundwater resource once remediation of the Mission Valley Terminal (MVT) fuel release has been completed and thus provide further diversification of the city's water supply. It is the intent of this remediation to restore background groundwater quality conditions (San Diego RWQCB, 2005). Our motivation in preparing this article is to identify the background groundwater quality (GWQ) in the valley to bring closure to the MVT remediation that began in 1992; a discussion of background GWQ concludes this article.

The study area (Figure 1) consists of the lower San Diego River Valley, from its outlet near Mission Bay eastward and upstream along the San Diego River to the vicinity of Qualcomm Stadium, a distance of approximately 8 km (5 mi). The main axis of the valley contains the San Diego River and its related floodplain. Murphy Canyon Creek is now confined to a concrete channel that directs flow into the river and thence to the Pacific Ocean. The lower San Diego

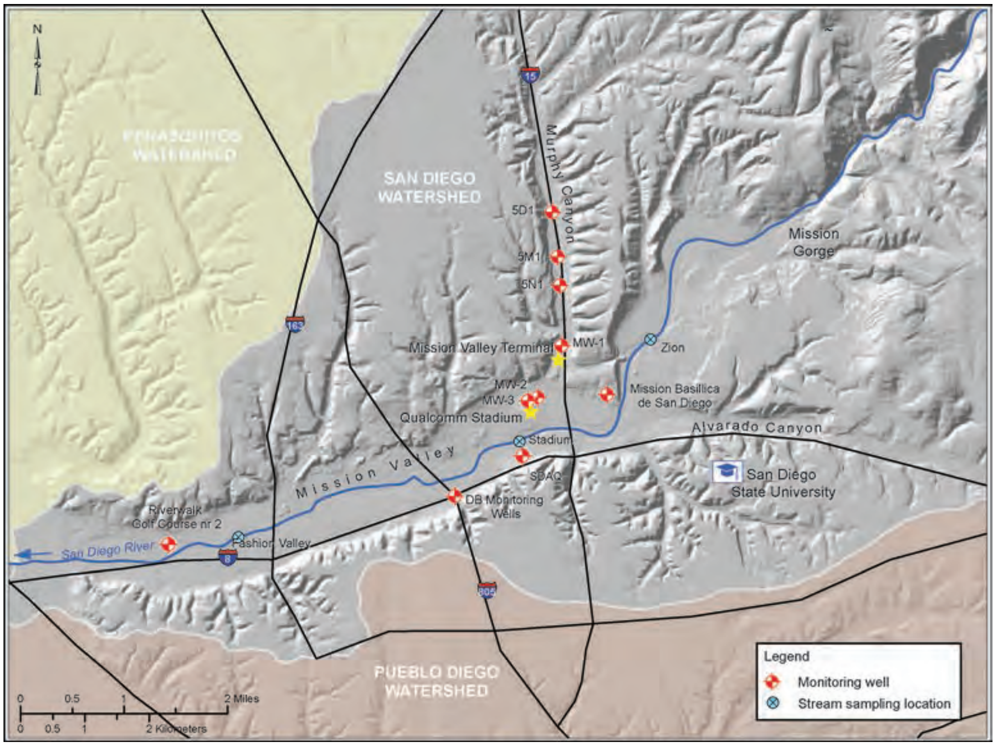


Figure 1. The lower San Diego River Valley showing the locations of the monitoring wells, stream sampling locations, the Mission Valley Terminal, and the Qualcomm Stadium, all of which are mentioned in the text.

River Valley is frequently identified as "Mission Valley"; however, we use this term only to refer to the high-permeability alluvial aquifer, i.e., the Mission Valley Aquifer (MVA), which was pumped as the pre-WWII groundwater supply.

Our primary objective is to present a hypothesis describing the Quaternary history of the valley based upon similar histories elsewhere along the southern Californian coastline (e.g., Edwards et al., 2009) and evidence from borehole logs and cores collected in the valley. We then use that hypothesized history to explain the occurrence of brackish GWQ in the Quaternary-age alluvial deposits and the deeper, Eocene-age sedimentary rocks beneath the Valley.

GEOLOGIC HISTORY OF THE LOWER SAN DIEGO RIVER VALLEY

Sources of Information

The valley contains Cretaceous through Holocene rocks and sediments deposited over the past 145 m.y. under a multitude of paleoenvironmental conditions. Understanding the geologic history and stratigraphic relationships of the rock layers is important to characterize the aquifer now intended for sustainable development. Accordingly, we summarize the stratigraphy and geologic history of the valley based mainly on the investigations of Geofirma and INTERA from 2010 through 2014, on reconstructions of the broad geologic history of the San Diego area (Abbott, 1999; Kennedy and Peterson, 2001), and on interpretation of new, site-specific subsurface lithologic and GWQ data.

Most of our detailed stratigraphic interpretations of the Quaternary alluvial deposits are based on geologic logs of groundwater monitoring wells prepared for Kinder Morgan Energy Partners (KMEP). KMEP is the owner and operator of the Mission Valley Terminal (MVT) bulk fuel storage facility located at the mouth of Murphy Canyon. In addition, the City of San Diego has installed since 2011 several monitoring wells in the buried channel aquifer at the intersection of Interstates 8 and 805, as well as one north of the MVT within Murphy Canyon and two more on the northern edge of the Qualcomm Stadium parking lot (see Figure 1). These new wells now provide site-specific information about the alluvium and Friars Formation bedrock through lithologic and geophysical logs, petrographic analysis, and laboratory grain-size analysis. In 2004, the U.S. Geological Survey (USGS, 2014) installed a monitoring well cluster known as the Aquaculture Well (SDAQ, San Diego), a multi-depth monitoring well consisting of five nested piezometers, which also provides geologic context. This well is located on the south side of the river across from Qualcomm Stadium (see

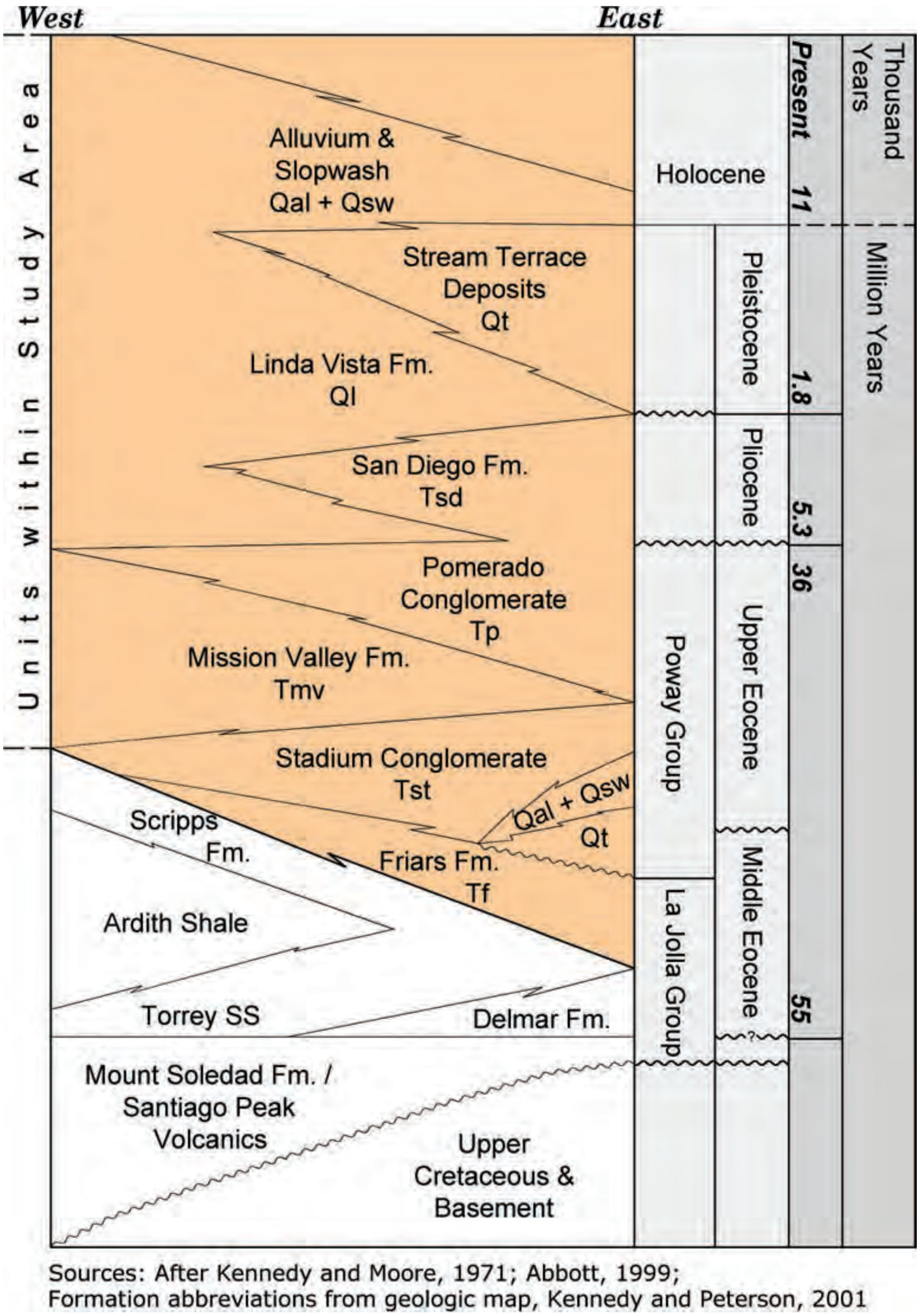


Figure 2. The stratigraphic column for the San Diego River Valley (Kennedy and Peterson, 2001) showing units present within the study area.

Figure 1); it provides a vertical stratigraphic column to a depth of approximately 940 ft (286 m) below ground surface (bgs). The lithologic and geophysical logs of this well and periodic water sampling and analysis provide a deep vertical profile of Quaternary sediments, Eocene bedrock, and GWQ within the valley.

Stratigraphic History

Figure 2 is a stratigraphic column illustrating the geologic units in the study area. The oldest deposits exposed in the area are of Late Jurassic age and of volcanic and marine origin, regionally known as Santiago Peak Volcanics (Jsp) (Kennedy and

Peterson, 2001), and outcrops of these rocks occur in the San Diego River Valley about 3 miles (4.8 km) east of Qualcomm Stadium. Kennedy and Peterson (2001, cross section B-B′, *La Mesa Quadrangle Geologic Map*) show these rocks underlying the entire cross section. The Santiago Peak formation consists of volcanic, volcaniclastic, and sedimentary rocks, but it also includes small plutons. These rocks are in non-conformable contact (sedimentary/volcanic rocks in contact with igneous rocks) with the Cretaceous-age southern California batholith (Tanaka et al., 1984).

The depositional environment during the Eocene was that of an advancing and retreating shallow sea, which resulted in transgressive-regressive sedimentary sequences. Alluvial fans were built seaward, pushing the shoreline to the west (Abbott, 1999). Sediments deposited during this time consisted of both the La Jolla Group, west of the study area, and the Poway Group, which constitutes the rocks in the San Diego River Valley in the vicinity of Qualcomm Stadium. The La Jolla Group is only represented by the Friars Formation in the study area. The Poway Group includes the Stadium, Mission, and Pomerado Formations and consists of sediments laid down by the Eocene Ballena River, an ancestral west-flowing channel originating east of San Diego but now displaced by lateral and vertical movements of the San Andreas and related fault systems (Abbott and Smith, 1989).

The late middle Eocene–age Friars Formation (Tf) of the La Jolla Group overlies the Santiago Peak Volcanics throughout the San Diego River Valley area. The Friars Formation crops out extensively on the walls of Murphy Canyon and San Diego River canyon and is named for exposures along the north side of the valley near Friars Road on the La Jolla and La Mesa geologic quadrangles (Kennedy and Peterson, 2001). The Friars Formation consists of sand- and clay-stone and contains both non-marine and lagoonal facies, up to 492 ft (150 m) thick in the study area. Table 1 presents the mineralogical composition of the Friars Formation.

The Stadium Formation (Stadium conglomerate) lies directly over the Friars Formation in the study area and contains clasts rounded from fluvial transport and composed predominantly of rhyolite, dacite, and quartzite, according to Abbott and Smith (1989). The Stadium conglomerate is about 160 ft (50 m) thick and crops out on the sides of Murphy Canyon and the sides of Serra Mesa, bordering Qualcomm Stadium. Abbott and Smith (1989) postulated that the Stadium formation originated from volcanic sources near Sonora, Mexico, an area that has since been separated from San Diego by lateral slip along the intervening San Andreas and related plate-boundary faults.

The Stadium conglomerate is overlain by the Mission Valley Formation (Tmv) and the Pomerado Conglomerate (Tp), completing the Poway Group of Eocene sand and gravel deposits. The Mission Valley Formation is about 200 ft (60 m) thick, while the Pomerado is about 180 ft (55 m) thick. These units inter-tongue from east to west.

The Pliocene units directly overlie the Eocene strata. The Pliocene rocks consist of the San Diego Formation (Tsd) marine sandstone. During Pliocene time (5.3–1.8 m.y. ago), continental glaciers grew in the Northern Hemisphere, resulting in a sea-level fall of about 625 ft (190 m), according to Abbott (1999). Invertebrate, marine mammal, fish, and bird fossils are abundant in the 100-ft-thick (30-m-thick) San Diego Formation, readily seen in road cuts on the south side of the valley near the mesa top.

Quaternary Geology and Hydrogeology

The Pleistocene rocks and sediments in the study area consist of the Linda Vista Formation (Ql) and terrace alluvium (Qt). The Linda Vista Formation, which consists of redeposited sand and conglomerate derived from nearby older sediments, is mapped on the top of the mesa bordering the valley. The Pleistocene stream-terrace deposits within the valley, as mapped by Kennedy and Peterson (2001), are located at the foot of the mesas on the north side of the valley and extend from the mesa slopes to the banks of the river, a distance of up to ~3000 ft (1 km). Holocene deposits are San Diego River alluvium (Qal) and slopewash (Qsw) (Kennedy and Peterson, 2001). These sediments have been largely covered by urban development, including the paved parking lot of Qualcomm Stadium, and are described as "poorly consolidated, conglomeratic sand deposits" (Kennedy and Peterson, 2001, p. 50).

Petrographic analysis of the terrace alluvium in MW-03 at 59 ft (18 m) bgs reveals these sands are composed of almost entirely polycrystalline porphyritic dacite volcanic and pyroclastic lithic grains, equigranular granite to granodiorite intrusives, and subordinate metamorphic lithic grains and monocrystalline quartz. Table 1 presents the mineralogical composition by DePangher (2014); locations of wells are shown in Figure 1.

The geomorphic feature extending from the mouth of Murphy Canyon to the modern San Diego River has been interpreted as the Murphy Canyon alluvial fan (Geofirma Engineering Ltd. and INTERA, 2011), which is fed by a drainage basin of 13 mi^2 (33.6 km^2). The fan dimensions and morphology are presented in

Table 1. *Mineralogical composition of the basal gravel unit of the MVA and of the Friars Formation at MW-3.*

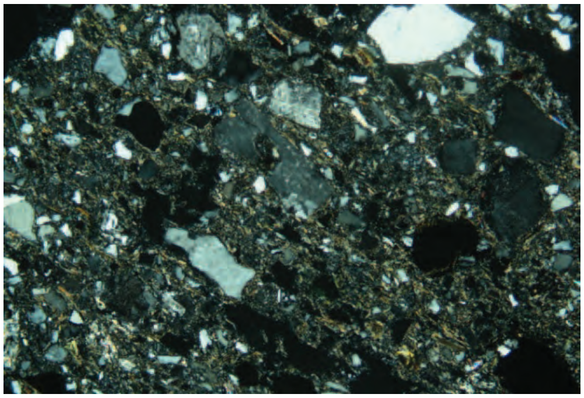
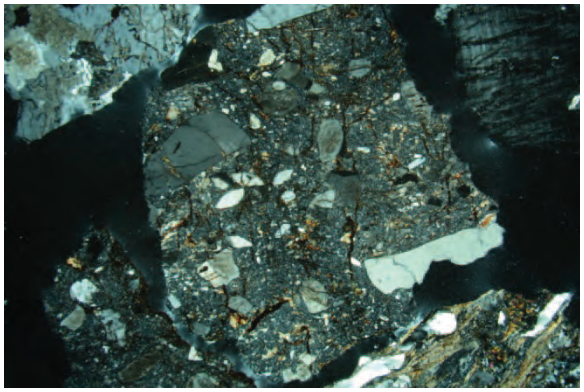
Mineral	Percent	Photomicrograph	Lithologic Description
Quartz Plagioclase K-feldspar Clay Organic matter Carbonate Biotite Illite Chlorite	26 20 20 20 5 3 2 2 1		Friars sandstone Scale: ~27 mm across The sample is an unconsolidated sand derived almost entirely from a carbonaceous clayey arkose sandstone protolith From borehole at MW-3, sampled at 67 ft (20 m) bgs (DePangher, 2014).
Plagioclase Quartz K-feldspar Hornblende Actinolite Ferric oxide Sericite Biotite and chlorite	74 10 8 2 2 2 1 <1		Basal gravel unit of the MVA Scale: ~27 mm across The sample is an unconsolidated lithic sand composed almost of entirely polycrystalline lithic grains: polycrystalline porphyritic dacite volcanic and pyroclastic lithic grains, equigranular granite to granodiorite intrusives, and subordinate metamorphic lithic grains and monocrystalline quartz From borehole at MW-3, sampled at 59 ft (18 m) bgs (DePangher, 2014).

Table 2. These dimensions suggest that the Murphy Canyon alluvial fan fits the type II fans identified by Blair and McPherson (1994) with sediment transport dominated by sheetflow.

We believe the Murphy Canyon fan was derived primarily from the Poway Group and the Friars sandstone. The evidence for this interpretation stems mainly from lithofacies in the boring logs of monitoring wells throughout the area. In particular, the rounded volcanic cobbles described in the KMEP boring logs and observed in core from the city's recent (INTERA, 2014) monitoring well borings—often described as up to 4 in. (100 mm) in diameter—are evidence of the correlation between the cobbles in the Stadium and Pomerado conglomerates and the cobbles in the basal and surficial gravel deposits in the Murphy Canyon alluvial fan.

Table 2. *Dimensions of the Murphy Canyon alluvial fan.*

Parameter	Value
Width of toe of fan, m (mi)	1,584 (1)
Length from mouth to toe, m (mi)	800 (0.5)
Slope from mouth to toe, m (ft)	6 (20)
Angle of slope, deg	0.43

Textural analysis of the basal gravel within the alluvium (MW-3, 59 ft or 18 m bgs) describes the material as poorly graded gravel with sand: median grain size d_{50} = 12 mm and uniformity coefficient $C_u = d_{60}/d_{10} = 69$. By comparison, the Friars Formation (MW-3, 67 ft or 20 m bgs) is finer grained: d_{50} = 0.17 mm and C_u = 171 (Daniel B. Stephens and Associates, Inc., 2014). Figure 3 presents grain-size distribution curves for these samples.

Lithologic logs from monitoring wells installed in these sediments for the MVT remediation project have been used to map the subsurface lithofacies of the Qt stream-terrace deposits (Geofirma Engineering Ltd. and INTERA, 2011). Schematic geologic cross section A-A′ (Figure 4) illustrates the vertical and lateral distribution of various sediment types within the Qt deposits. The cross section identifies three principal layers within the Qt beneath the MVT and off-terminal remediation area: the basal gravel

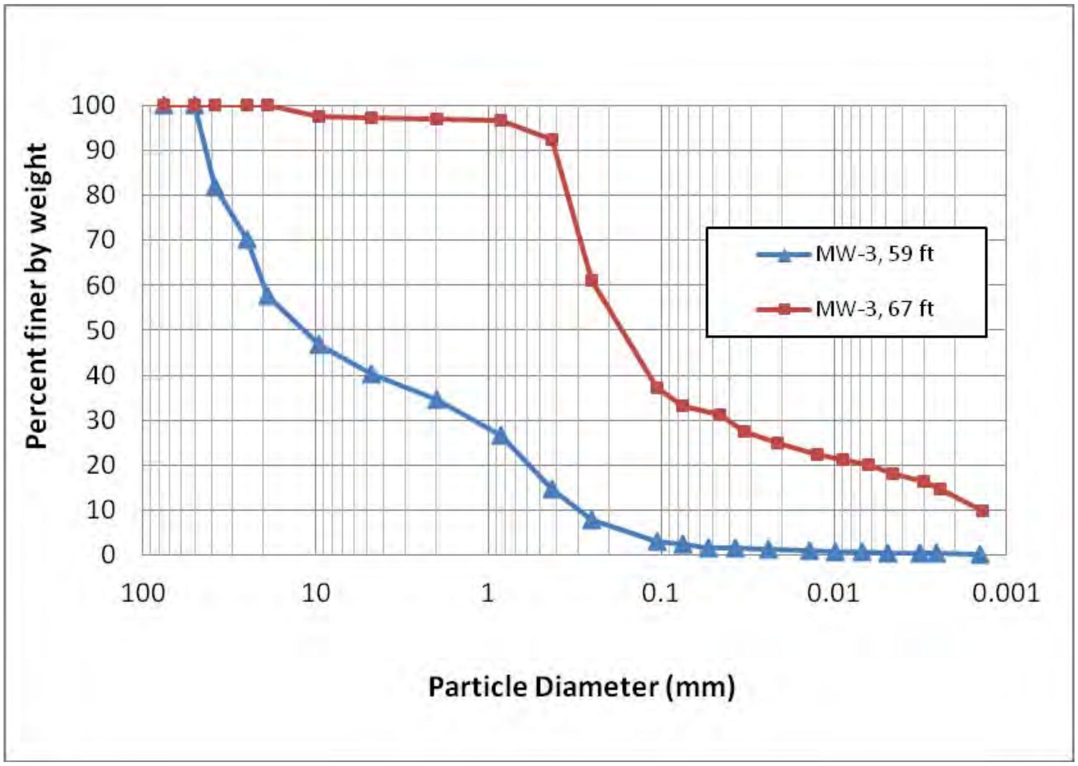


Figure 3. Grain-size distribution in samples of the basal gravel (59 ft bgs, 18 m) and the Friars Formation (67 ft bgs, 20 m), MW-3 borehole, front entrance to the Qualcomm Stadium, Friars Road, San Diego.

(eroded into the Friars Formation); the middle sand layer (including zones of silt and clay within the sand); and the upper gravel layer.

These three units are generally identifiable in the wells across the MVT site (although the upper gravel is absent in some of the lithologic logs). The basal gravel contains a channel structure ("paleochannel") that trends northeast to southwest beneath the Qualcomm Stadium parking lot. This basal gravel deposit, including the paleochannel, together with the overlying middle sand unit comprise the MVA in the context of both the MVT remediation program and its future use as a city water-supply aquifer (Geofirma Engineering Ltd. and INTERA, 2011, 2013). This paleochannel, now obscured beneath the stadium parking lot, was the location of several of the City of San Diego water-supply wells completed and operated prior to WWII (Fay, 1914; Ellis and Lee, 1919). Additional city wells were located along the axis of the river downstream from the alluvial fan. This combination of unconsolidated gravel, sand, silt, and clay beneath Qualcomm Stadium represents a Pleistocene fluvial depositional environment with its major source in Murphy Canyon. A schematic block diagram (Figure 5) illustrates the various layers and their spatial relationships.

We describe three Qt lithofacies—the basal gravel, middle sand, and upper gravel—using Miall's (1985) classification. We interpret the basal gravel deposit, with its principal lithofacies of massive, matrix-supported gravel (Gms) with massive or crudely bedded gravel (Gm) and coarse to very coarse sand (St), to be a channel (CH) element. The coarse sand matrix would result in high hydraulic conductivity for this basal gravel layer, which is consistent with the grain-size analysis and hydraulic conductivity estimates from sediment samples of the basal gravel in the Murphy Canyon and stadium parking lot wells installed by the City of San Diego (INTERA, 2014). In addition, the concave-up erosional base (as defined by the elongate and trough-like contact between the basal gravel and the Friars Formation) fits with the third-order contact within the hierarchy of bedding contacts as described by Allen (1983). Our classification is consistent with the CH architectural element interpretation of Miall (1985, 1992).

Because Quaternary terrace deposits do not crop out in the immediate study area, we illustrate the depositional model from well-known examples near Socorro, New Mexico (Figure 6). The photograph shows a typical matrix-supported gravel overlying a sand unit similar to the Qt channel contact with the underlying Friars sandstone. Our lithofacies classification is provided in Table 3, and the stratigraphic architectural elements are given in Table 4 (Miall, 1985).

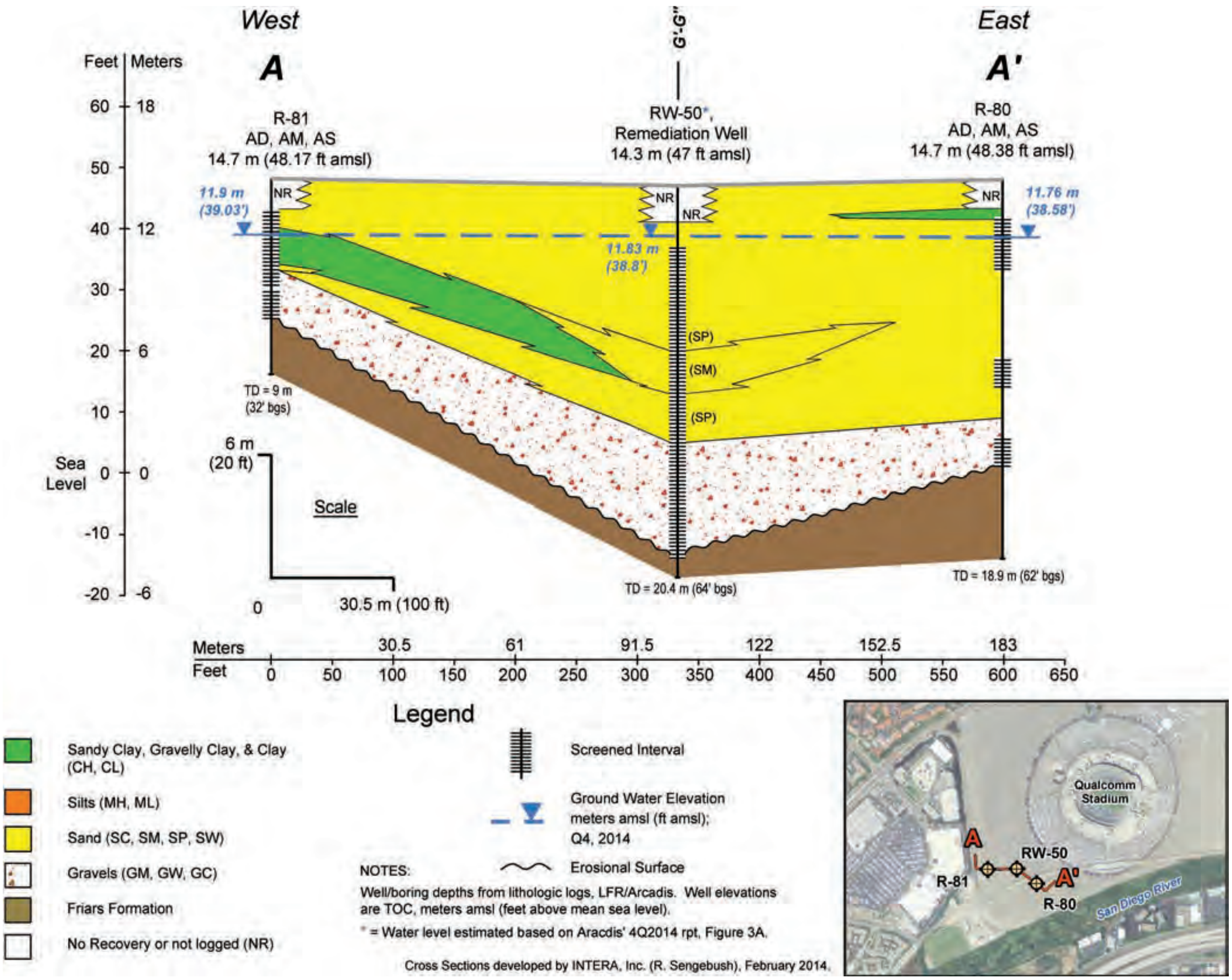


Figure 4. Cross section A-A′ through the Qt stream-terrace and alluvial-fan deposits indicating the basal gravel paleochannel aquifer (MVA), Qualcomm Stadium area, San Diego.

Pleistocene Paleochannels

The Murphy Canyon alluvial fan contains a Pleistocene gravel channel beneath the Qualcomm Stadium parking lot (the "paleochannel"), which extends from the mouth of Murphy Canyon southwest beneath the Qualcomm Stadium parking lot to the river. This paleochannel (within the area mapped as Quaternary terrace deposits, Qt; Kennedy and Peterson, 2001) incises the Friars Formation and is mapped by lines of equal gravel thickness (Figure 7) based on the gravel lithofacies thickness in monitoring well logs (Geofirma Engineering Ltd. and INTERA, 2011). Additionally, the elevation of the contact surface at the base of the gravel and the top of the Friars Formation was mapped (Figure 8). This shows a thalweg that spatially coincides with the axis of the gravel thickness isopach map. This subsurface structure ranges from about 300 ft (91 m) to 600 ft (183 m) wide and is 3,600 ft (1,097 m) long from the mouth of Murphy Canyon to the toe of the alluvial fan. The slope of the channel parallel to the channel axis is as much as 29 ft (8.75 m) over the length of 3,637 ft (1109 m), or 0.46 degrees. The channel bank slope (perpendicular to the channel axis) near the southwest corner of the stadium parking lot is 3.8 degrees.

Bull (1991, p. 172) observed that "unusually warm sea-surface temperatures at about 125 ka should have favored stronger and more frequent tropical storms in the San Gabriel Mountains" in Los Angeles County; this is no doubt true for San Diego County at the same time. Such storms would have accelerated the erosion of Cenozoic sediments in the coastal areas of southern California, potentially leading to the erosion of the San Diego River Valley and its tributaries. The paleochannel down cut through existing Eocene sediments in the valley, in particular, the Friars Formation, and was filled with an upward-fining sequence of gravels, sands,

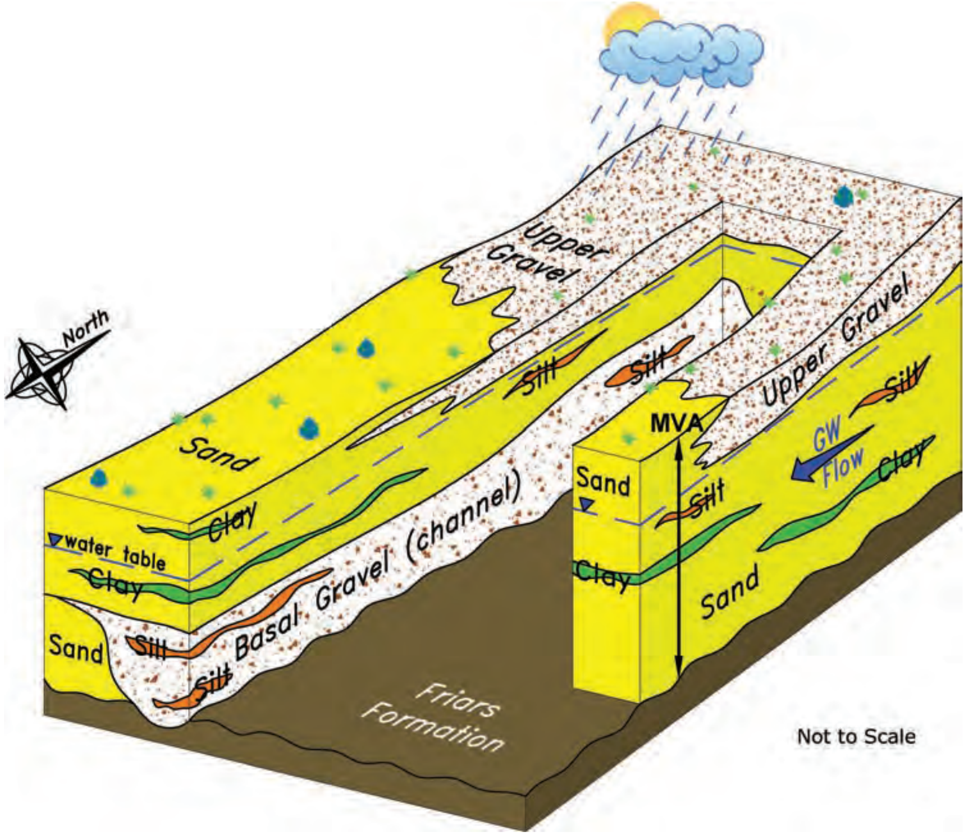


Figure 5. Conceptual block diagram of sedimentary lithofacies, Qualcomm Stadium area, San Diego.

and silts similar to modern gravel channels found throughout the Basin and Range Province. This buried-channel aquifer beneath the Qualcomm Stadium parking lot (within the Murphy Canyon alluvial fan) and the buried channel beneath the San Diego River itself—collectively defined as the MVA—was used by the City of San Diego prior to World War II as its primary water supply, yielding from 2–5 million

Figure 6. Alluvial deposit outcrop showing channel gravel unit in erosional contact with sand unit, Socorro, NM, analogous to basal gravel contact with the Friars Formation. Vertical scale approximately 10 ft (3m).

Table 3. *Lithofacies classification for Qt deposits (from Miall, 1985).*

Facies Code	Lithofacies	Sedimentary Structures	Interpretation
Gms	Massive, matrix-supported gravel	Grading	Debris-flow deposits
Gm	Massive or crudely bedded gravel	Horizontal bedding, imbrication	Longitudinal bars, lag deposits, sieve deposits
Gt	Gravel, stratified	Trough cross-beds	Minor channel fills
Gp	Gravel, stratified	Planar cross-beds	Linguoid bars or deltaic growths from older bar remnants
St	Sand, medium to v. coarse, may be pebbly	Solitary (theta) or grouped (pi) trough cross-beds	Dunes (lower flow regime)
Sp	Sand, medium to v. coarse, may be pebbly	Solitary (alpha) or grouped (omikron) planar cross-beds	Linguoid, transverse bars, sand waves (lower flow regime)

gallons per day of high-quality groundwater (~400 mg total dissolved solids [TDS]/L; Ellis and Lee, 1919).

The buried paleochannel within the Murphy Canyon alluvial fan is interpreted as analogous to the late Pleistocene buried channel of the lower Santa Margarita River, as described by Shlemon (1979), and to other buried Pleistocene channels along the southern California coast that grade to marine isotope stage 2, indicating the eustatically lowered sea levels of the Last Glacial Maximum (LGM) (Shlemon, 1979; Edwards et al., 2009; and Lee and Normark, 2009). The Santa Margarita River and its estuary are located in northern San Diego County, 40 mi (64 km) north of San Diego River Valley. The buried channel lies beneath the modern Santa Margarita River and is identified by buried gravels 75 ft (23 m) thick, extending to a depth of 150 ft (45 m) below sea level and 7 mi (11 km) long. The late Pleistocene shoreline was over 1.8 mi (3 km) west of the present coast, and the gradient in the channel was steep compared to that of the modern Santa Margarita River. Subsequent sea-level rise covered the channel with finer-grained sediments, resulting in a fining-upward sedimentary sequence.

We believe that the paleochannel mapped beneath the Qualcomm Stadium parking lot intersects and is tributary to a larger and deeper paleochannel beneath the San Diego River (Figure 9), similar to the Santa Margarita River buried paleochannel. This paleochannel beneath the river was the location of several of the city's pre-WWII MVA water-supply wells (Figure 10).

Last Interglacial Sea-Level Highstand

In the San Diego area, and in the lower San Diego River Valley in particular, the Pleistocene was a time of repeated sea-level rise and fall as worldwide glaciers advanced and retreated (Abbott, 1999). Erosional features related to these sea-level changes may be seen today as terraces in and around La Jolla, San Diego, and on the mesas above San Diego River Valley. The number and spacing of terraces were determined by the rate of tectonic uplift and nature of coastal processes. The oldest terrace is generally correlated with the early Pleistocene (1.18 Ma to 120 ka) according to Muhs et al. (2002).

Kern and Rockwell (1992) documented 16 separate marine terraces, ranging in age from 1.29 Ma to 80 ka. These erosional wave-cut platforms mark the highest sea-level elevations maintained during glacial/interglacial time. Muhs et al. (2002) also described marine terraces with a focus on those near Point Loma, the lower Bird Rock terrace at about 26 ft (8–9 m) above present sea level, and the higher, Nestor terrace, about 75 ft (23–24 m) above present sea level. The Nestor terrace dates to 120 ka, while the Bird Rock terrace is more recent, dated at 80 ka. The Bird Rock terrace formed at about −6 ft (−2 m) relative to present sea level, while the higher Nestor terrace formed about 20 ft (6 m) above present sea level (Table 3; Kern and Rockwell, 1992). Based on the estimated tectonic land-surface uplift that has taken place over the past

Table 4. *Architectural elements for the observed lithofacies in the Qt fluvial deposits (from Miall, 1985).*

Element	Symbol	Principal Lithofacies Assemblage	Geometry and Relationships
Channels	CH	Any combination	Finger, lens or sheet; concave-up erosional base; scale and shape highly variable; internal concave-up secondary erosion surfaces common
Gravel bars and bed forms	GB	Gm, Gp, Gt	Lens, blanket; usually tabular bodies; commonly interbedded with SB
Sandy bed forms	SB	St, Sp, Sh, Sl, Sr, Se, Ss	Lens, sheet, blanket, wedge; occurs as channel fills, crevasse splays, minor bars

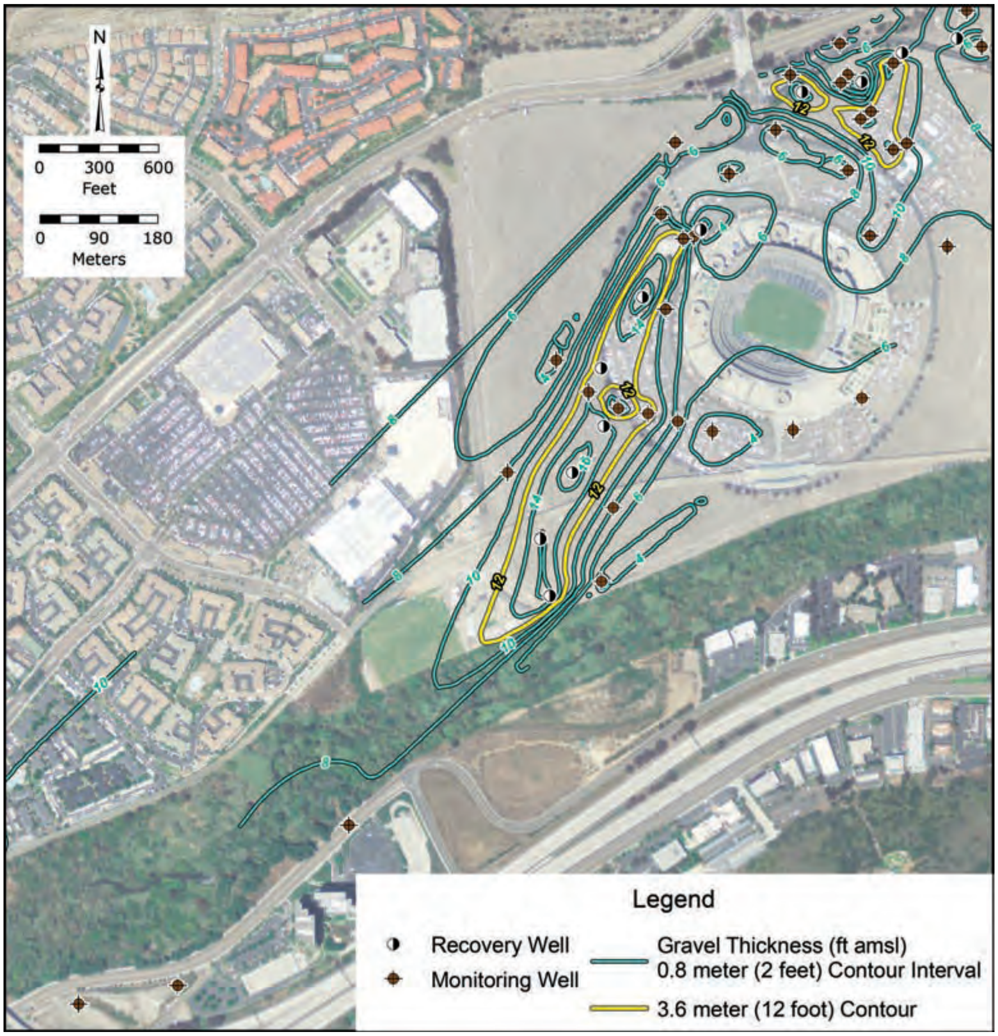


Figure 7. Paleochannel gravel isopach map showing channel gravel thickness.

120,000 years, the inland extent of the 120 ka (Nestor) sea-level invasion may be estimated.

Uplift resulting from offset on the Rose Canyon fault dominates the tectonic history of the San Diego coast. Uplift has occurred at a rate of 0.13–0.14 m/k.y., with both higher and lower rates near the Rose Canyon fault zone (Kern and Rockwell, 1992). Consequently, the uplift is interpreted to be 55 ft (17 m) since the last interglacial ca. 120 ka. Additionally, the sea level represented by the Nestor terrace was 19 ft (6 m) above the present sea level prior to uplift. Therefore, the elevation of the marine inundation of the valley would have been 74 ft (23 m) above the present sea level, which is shown in Figure 11. This illustration shows the marine inundation of the valley to a maximum position in the vicinity of the San Diego Mission, with some inundation of Murphy Canyon. Abbott (1999, pages 202–203) has calculated and shown a similar marine highstand during this interglacial.

GROUNDWATER QUALITY IN THE LOWER SAN DIEGO RIVER VALLEY

The late-middle Eocene–age sediments, such as the Friars Formation, were deposited ca. ~50 to ca. 34 Ma and were inundated repeatedly by rising sea levels during the Pleistocene. These Eocene sedimentary rocks contain brackish groundwater with TDS ~2,000 mg/L, which is either (1) connate water trapped during sedimentary deposition or (2) seawater that inundated the valley during Pleistocene time. In both cases, the residual salinity would have become diluted by freshwater recharge flowing through the valley flow system. In this section, we evaluate the role of two Pleistocene events: (1) the marine inundations during the last interglacial (marine oxygen isotope substage 5e; Shackleton, 1969) and earlier Pleistocene interglacials and (2) the subsequent MVA deposition during the LGM. Then, we attempt to determine how they might have influenced the GWQ in the valley since 1915, when measurements began.

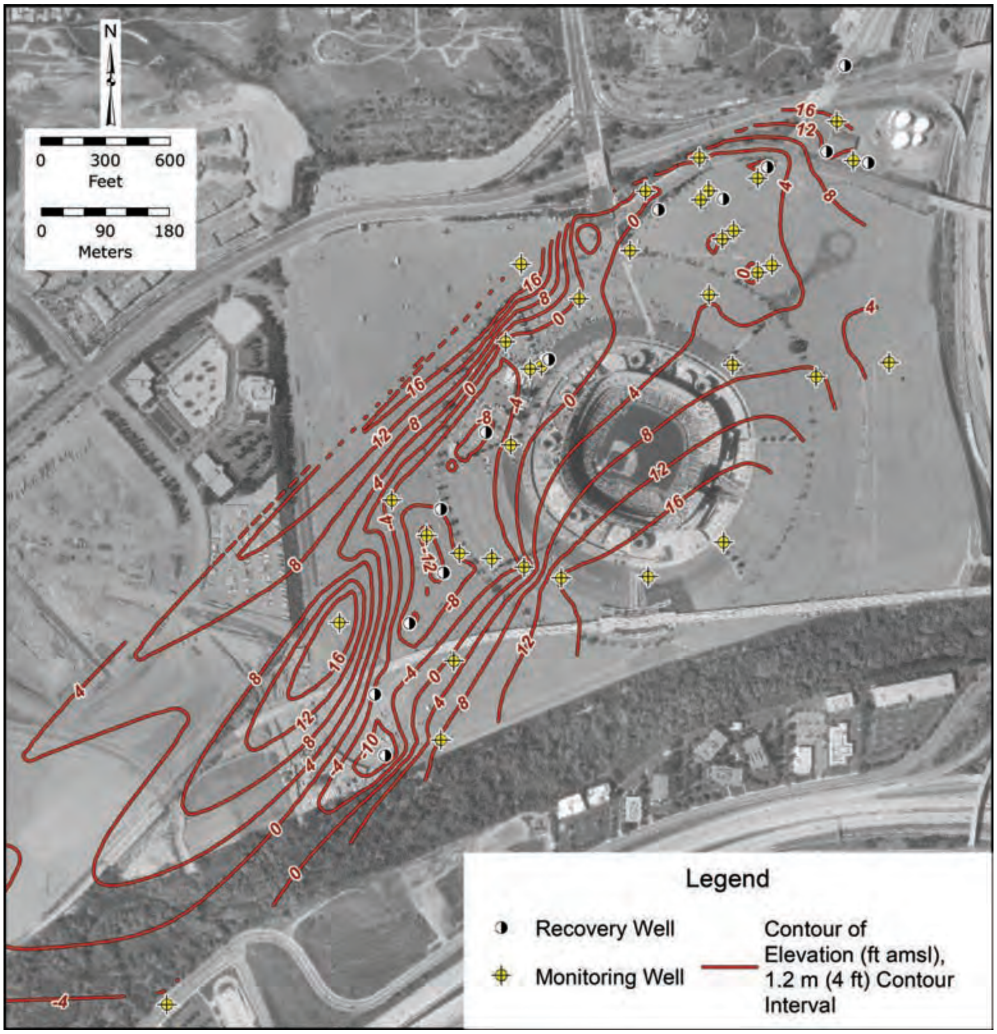


Figure 8. Paleochannel morphology map showing erosional surface at contact between Qt basal gravel and Tf sandstone.

We initially present USGS data for the San Diego Aquaculture monitoring-well cluster that provide a reference set of GWQ data for the sedimentary sequence beneath the valley. Other USGS, DWR, and city GWQ data are then presented, followed by stable isotope values of oxygen and deuterium to show the differences evident in groundwaters from monitoring wells throughout the valley. The GWQ data are subsequently interpreted to demonstrate "freshening" of the Eocene groundwaters reported in the 1965 California Department of Water Resources (DWR) GWQ data; this freshening is accompanied by increased salinity in the MVA itself. We then identify background GWQ conditions prior to the urban development of the valley during the 1960s based on the evidence of geological history and hydrogeochemical analysis.

Sources of Information

The GWQ in the valley prior to the development of both the MVT and the Qualcomm Stadium in the 1960s can be defined by reference to studies by Ellis and Lee (1919) and DWR. The DWR conducted a series of studies of the groundwater hydrology of the San Diego region during the 1950s and 1960s (DWR, 1959, 1965, 1967), prior to the urbanization of the valley. This information is supplemented with more recent data collected by the City of San Diego and by the USGS San Diego Hydrogeology Project.

Ellis and Lee (1919) conducted an early survey of the GWQ in the city's new well field. The sample collected was a composite sample from the 13 drilled wells of the city's Mission Valley well field, which had depths ranging from 15 to 30 m (45 to 90 ft) bgs. Figure 10 shows the approximate position of the first 12 of the 13 wells based on records of the San Diego Water Department. Presumably, because just one sample from June 1915 was analyzed (see Table 5), the sample was collected from a manifold at the pumping station that mixed the groundwater from the 13 wells drilled the year before by the city (Fay, 1914).

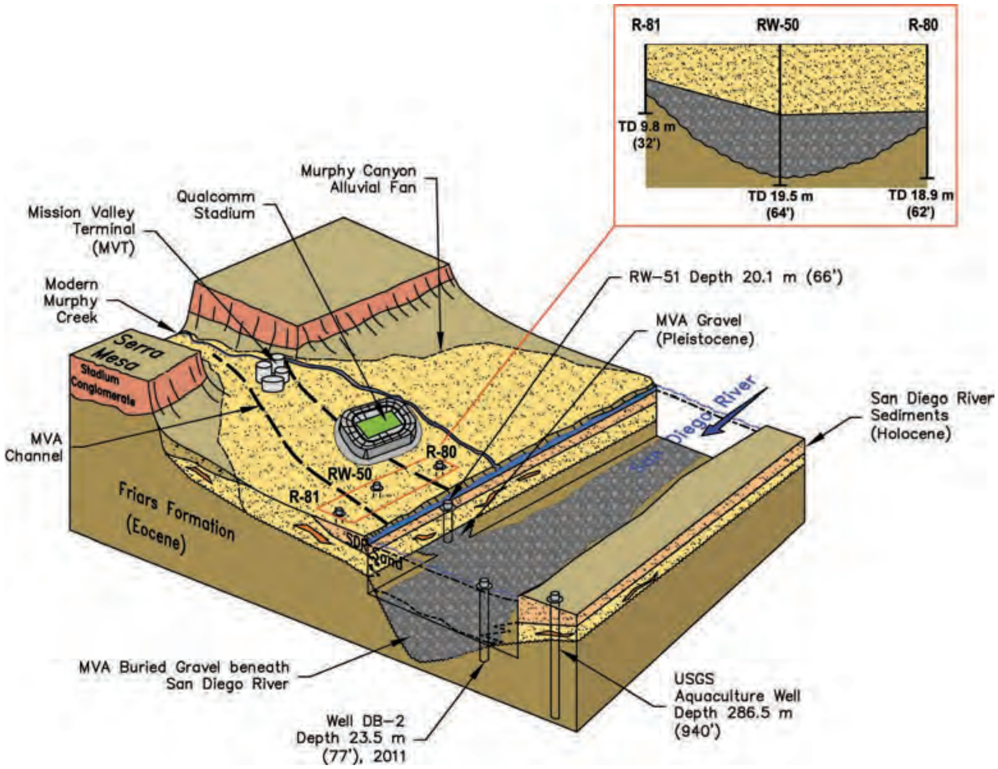


Figure 9. Block diagram of Pleistocene river channel with city wells and MVA.

Ellis and Lee's table 46 referred to this sample as K 47 and identified its origin as 13 drilled wells belonging to the City of San Diego located in the "Pueblo lands and Ex Mission of San Diego." These data are reproduced as Table 5.

DWR evaluated the GWQ in the valley prior to the construction of the MVT tank farm and the Qualcomm Stadium in the 1960s but following the abandonment of the city's well field in the late 1930s. An initial report (DWR, 1959) presented the hydrogeology of the region, including the valley. A subsequent report (DWR, 1965) contained an account of the GWQ in that part of the valley shown in Figure 1, including data (see Table 6) from a number of residential and farm wells that are located on Figure 10. Well construction and screen depths for these wells were not reported. A final report (DWR, 1967) identified the variability in GWQ in both inland and coastal regions. These DWR studies were conducted over the same area "in support of the activities of the San Diego Regional Water Quality Control Board" (DWR, 1967, p. xiii), which exists to this day as the regional regulator.

The seven wells for which the data are presented in Table 6 (DWR, 1965) are those along or adjacent to the axis of the Murphy Canyon paleochannel (i.e., its thalweg) and thus constitute a set of data that is useful in reconstructing the ambient or baseline GWQ of the MVA prior to the establishment of the MVT in 1963. Three of the wells, 5D1, 5M1, and 5N1, are in Murphy Canyon itself (see Figure 1), while two others are at the mouth of Murphy Canyon (17D1 and 17D2; see Figure 10). The sixth well, 18Q3, was likely the city's former well no. 6 in the pre-WWII well field (see Figure 10). A seventh well, 18N1, was outside the MVA and located in an area now built over near Friars Road and is shown in Figure 10.

The USGS San Diego Hydrogeology Project began an extensive study of the San Diego region in 2001 (http://ca.water.usgs.gov/sandiego/) that has yielded much useful information on background GWQ in the region (Wright et al., 2005; Wright and Belitz, 2011; and Anders et al., in review). In particular, Anders et al. (2014) has studied GWQ in the Pliocene-age San Diego Formation. The data presented in Table 7 are

Table 5. *Groundwater quality analyses by the U.S. Geological Survey for a sample from the City of San Diego Mission Valley Aquifer well field (from Ellis and Lee, 1919). (All measurements are given in mg/L.)*

SiO_2	Fe	Ca	Mg	Na + K	CO_3	HCO_3	SO_4	Cl	NO_3	TDS
24	Trace	57	17	54	0.0	151	81	85	1.0	394

Table 6. *Groundwater quality data for the era prior to urban development of the Lower San Diego River Valley (DWR, 1965). Wells 5D1, 5M1, and 5N1 are located on Figure 1, while the others are shown on Figure 10.*

	Well						
Parameter (Unit)	5D1	5M1	5N1	17D1	17D2	18N1	18Q3
Sample date	Feb 1959	May 1960	April 1959	May 1960	Feb 1963	April 1959	April 1955
Temperature (°C)	n.m.	28	n.m.	26	n.m.	n.m.	22
pH (pH units)	7.3	7.5	7.6	7.2	7.1	7.8	7.2
SEC (μS/cm)	1,400	1,406	1,432	3,160	n.m.	2,931	1,786
TDS† (mg/L)	1,039	975	994	2,155	1,776	1,944	1,105
Sodium (mg/L)	132	214	230	363	n.m.	340	215
Potassium (mg/L)	2	8	4	5	n.m.	5	4
Calcium (mg/L)	149	54	51	226	189	122	103
Magnesium (mg/L)	35	28	20	68	93	115	46
Chloride (mg/L)	216	206	241	615	593	703	368
Sulfate (mg/L)	288	111	118	383	360	154	146
Bicarbonate (mg/L)	250	346	315	432	n.m.	416	303
Nitrate-NO_3 (mg/L)	7.6	0	0	9	2.0	4	2.5
Boron (mg/L)	0.13	0.4	0.08	0.6	n.m.	0.44	0.14

n.m. = not measured. SEC = specific electrical conductance.
†Total dissolved solids (TDS) by evaporation to 180°C.

from the data compilation of Anders et al. (in review). These analyses are considered "complete" in the hydrogeochemical sense in that a full suite of major inorganic ions and some stable and radiogenic isotopes were analyzed. Table 7 presents the results of three samples from the valley.

The USGS Aquaculture (SDAQ) well cluster was installed in 2004 on the south side of the river opposite the Qualcomm Stadium (see Figure 1). This monitoring well cluster contains five 2 in. (5 cm) nested piezometers installed within a 17.5 in. (44 cm) borehole. These wells are referred to herein by their state well numbers 16S/2W-18J3 through J7 with the shallowest well being J7, which has its 20-ft-long (6 m) well screen set in the base of the MVA at 20 ft (6 m) above mean sea level (amsl) and penetrating the Friars Formation. Thus, SDAQ-J7 provides a mixed sample of MVA and Friars Formation Groundwater, including tritium from the Quaternary sediments and high TDS (1,900 mg/L) from the Friars Formation, as shown in Figure 12.

In addition to sampling the SDAQ multi-level well, the USGS analyzed samples from several other wells in Mission Valley, including that of the River Walk Golf Course number 2 well ("RWGC2"), which is further down Mission Valley (see Figure 1). Both RWGC2 and SDAQ J7 have relatively high salinity, with RWGC2 (TDS ~3,579 mg/L) being higher than J7 (TDS ~1,840 mg/L), compared with those shown in Table 8. The proximity of the RWGC2 well to the San Diego River Floodway (0.5 mile, 800 m) and the typical extraction rates of irrigation wells suggest that the high salinity in this well is due to modern seawater intrusion.

The Groundwater Quality Monitoring Act (California, 2001) initiated the Groundwater Ambient Monitoring and Assessment (GAMA) Priority Basin Project "to assess and monitor the quality of groundwater in California. (Wright and Belitz, 2011, p. 2)" Wright and Belitz (2011, p. 1) indicated that the "GAMA San Diego study was designed to provide a statistically robust assessment of untreated-groundwater quality within the primary aquifer systems." One of the four primary aquifer systems tested is identified as "Alluvial Basins," which would include aquifer systems such as the San Diego River alluvial basin that contains the MVA. The USGS sampled a total of 17 alluvial basin wells in 2004, including two public water-supply wells in the San Diego River Valley farther upstream from Qualcomm Stadium. The range of measured GWQ parameters in these 17 wells is presented in Table 8. The rationale for including in this article groundwater samples from alluvial wells collected by the USGS outside the valley, i.e., Table 8, but within the San Diego Drainages Hydrogeological Province (Wright and Belitz, 2011), is that they are derived from sediments of similar geochemical nature to the alluvial sediments within the valley and thus are representative of GWQ within the valley.

Table 9 presents data from two City of San Diego monitoring wells that were installed and sampled in 2011. These monitoring wells are situated down gradient of the SDAQ multi-level well but in the MVA and were, at the time of sampling, at the leading edge of a plume of contaminated groundwater containing the gasoline additive methyl tertiary-butyl ether (MTBE) and its biodegradation product tertiary-butyl alcohol (TBA). Since these samples were collected, the TBA and TDS concentrations have

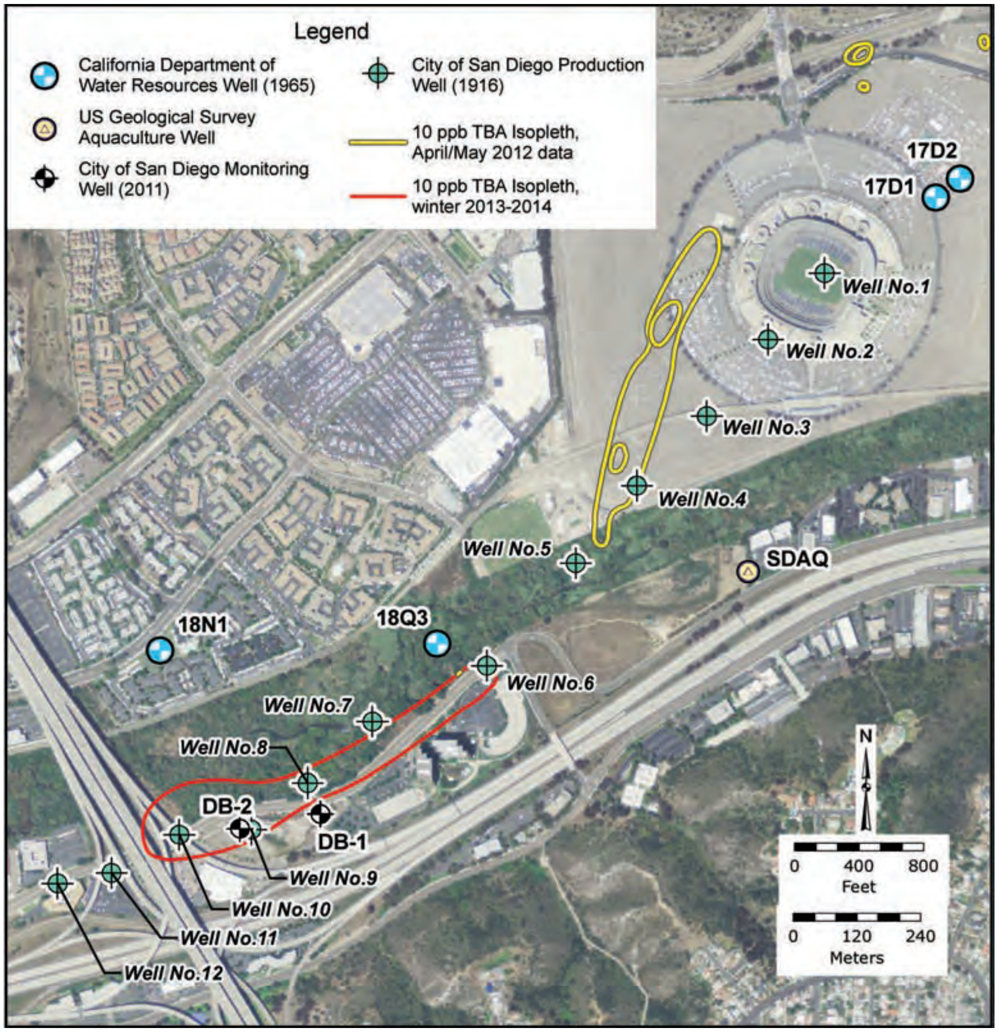


Figure 10. Historic pre-WWII MVA water-supply well field, DWR wells mentioned in text, and recent DB monitoring wells. The TBA plume precisely traces the paleochannel because of its high permeability contrast with the surrounding Friars Formation and the release of gasoline directly into the paleochannel at the MVT (NE corner of figure).

risen in this part of the MVA; thus, no more recent data from these wells are included in this assessment.

These five data sets (Tables 5 to 9) contain increasingly large analyte lists from a limited number of water-supply and monitoring wells in the Lower San Diego River Valley. We now apply several methods of hydrogeochemical analysis in order to identify the origin and evolution of the groundwater in the valley. However, no single well has been continually sampled in the 100 year period since the 1915 USGS analysis shown in Table 5. Samples from the MVA prior to its contamination by the MVT gasoline releases of 1987–1991 are limited to just the 1919 USGS (Table 5) and 1965 DWR (Table 6) data sets. Thus, we will compare data from this valley with that from elsewhere in the San Diego hydrogeologic region as collected, analyzed, and compiled by the USGS (Wright et al., 2005; Wright and Belitz, 2011; Anders et al., 2014; and Anders et al., in review).

Stable Water Isotopes

Measurements of the stable water isotopes ^{18}O and deuterium (^{2}H) provide information on the origin the groundwaters in the valley. Stable water isotope data in this paper are reported in per mil (‰) compared to Vienna Standard Mean Ocean Water (VSMOW), i.e., $\delta^{18}O$ and $\delta^{2}H$, and shown in Figure 13 for July and October 2014. USGS San Diego River sampling locations in the lower valley are shown on Figure 1, while groundwater sampling was conducted with the completion of the city's monitoring well network shown in Figure 14.

The San Diego River water samples (open triangles) represent storm runoff during five events in

Table 7. *Groundwater quality data of wells in the Lower San Diego River Valley wells sampled by the USGS (from Anders et al., in review).*

	Well		
Parameter (Unit)	SDAQ-J7	SDAQ-J7	RWGC-2
Screen elevation (ft a.m.s.l.)	20	20	−50 to −80
Sample date	Aug 2010	May 2005	Jan 2004
Temperature (°C)	24.5	22	21
pH (pH units)	7.0 (field)	7.1	7.1 (field)
Dissolved oxygen (mg/L)	2.1	0.5	0.7
Specific electrical conductance (μS/cm)	2,950 (field)	3,000	4,600 (field)
Total dissolved solids, residue (mg/L)	1,930	1,840	2,813
Alkalinity (mg/L $CaCO_3$)	294	340	755
Sodium (mg/L)	300	301	644
Potassium (mg/L)	2.6	3.9	11.2
Calcium (mg/L)	221	219	303
Magnesium (mg/L)	71.1	75	137
Iron (mg/L)	0.524	0.92	2.43
Manganese (mg/L)	2.79	3.05	3.25
Chloride (mg/L)	742	631	1061
Sulfate (mg/L)	224	237	477
Bicarbonate (mg/L)	338	414.4	852
Nitrate-N (mg/L)	<0.04	0.022	<0.06
Boron (mg/L)	0.22	0.23	0.359
Arsenic (mg/L)	0.0026	0.00713	0.0118
Dissolved organic carbon (mg/L)	4.0	No sample	No sample
Oxygen-18, $\delta^{18}O$ (‰)	−5.2	−5.58	−5.5
Deuterium, $\delta^{2}H$ (‰)	−40	−41.1	−37
Tritium, ^{3}H (tritium units)	5.8	5.6	2.9
SI $CaCO_3$, calcite	0.2	0.33	0.7
SI $Fe(OH)_3$, iron hydroxide	<0.0	2.0	<0.0
SI MnO_2, pyrolusite	<0.0	−10.19	−10.47
Na/Cl ratio (mmol/L)	0.62	0.74	0.94
Cl/Br ratio (mmol/L)	814	661	644

Note: SI indicates the saturation index of the sample, where 0.0 indicates equilibrium with the mineral, negative values indicate mineral dissolution, and positive values indicate precipitation. SI and bicarbonate values were calculated by PHREEQC (Parkhurst and Appelo, 1999). Estimated Eh = +100 mV for all samples. a.m.s.l., above mean sea level.

2004–2010, which was obtained from the USGS National Water Information Database for the three locations shown in Figure 1. These samples fall on or about the global meteoric water line (GMWL), although two plot to the right of the GMWL. Such a displacement is often considered evidence of evaporation prior to sampling (Clark and Fritz, 1997); however, it appears that here it reflects the annual or seasonal variability in the isotopic character of the winter rains (Williams and Rodoni, 1997).

The groundwater samples are mainly from city monitoring wells (DB series) and multi-level wells (Einarson and Cherry, 2002) identified as MW-1, MW-2, and MW-3 and shown in Figure 14 as "MVA MW-2 MW-3" or "MVA MW-1" for that well in Murphy Canyon. These are within the MVA paleochannel, except for the deepest sampling port in each case, which was installed in the Friars Formation just beneath the paleochannel gravels; these are identified as "Friars MW-1-2-3." A few samples are included from the USGS database (Anders et al., in review), e.g., those from SDAQ, RWGC 2, and the Mission (see Figure 1 for locations).

Groundwater stable isotopes from the MVA (diamond-shaped data) fall on or around a "GW correlation" line, in which the most depleted samples (i.e., most negative) are from furthest up Murphy Canyon at multi-level well MW-1 (see Figure 14). The shallow SDAQ J7 sample also plots on this GW correlation line, as do MW-2 and MW-3 samples from the MVA. These samples appear to indicate that the MVA, i.e., both the paleochannel beneath Qualcomm Stadium and that beneath the main channel of the river (DB data), is recharged by discrete storm runoff events producing the unique spatial pattern in the MVA shown in Figure 13. It is also possible that this pattern in some way reflects the infiltration of irrigation at various golf courses above the stadium and the DB site and perhaps infrastructure leaks.

More data are required to resolve this uncertainty, because the runoff data and the groundwater data are from different times; consequently, it is difficult to

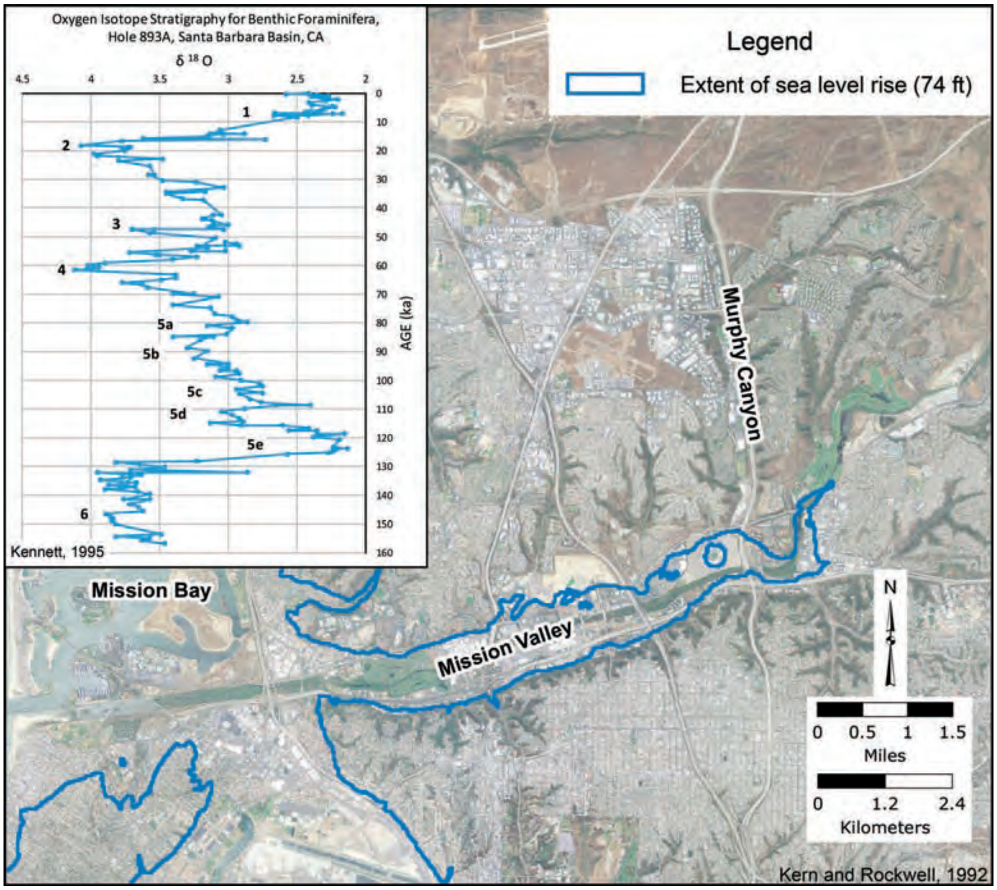


Figure 11. The 74 ft (23 m) a.m.s.l. topographic contour showing the marine inundation of the San Diego River Valley, approximately 120,000 years before present. The inset shows the marine isotope stages ($\delta^{18}O$) for benthic foraminifers in Hole 893A, Santa Barbara Basin, against age (ka) from Kennett (1995). Substage 5e represents the last interglacial at 120 ka for which the marine invasion is shown in this figure.

define reliable end points for mixing calculations. Nevertheless, a comparison of hydraulic heads in SDAQ J7 with the stage height of the river shows evidence of recharge of the shallow alluvium by winter storms, which is not the same as recharge of the MVA. The recharge of the MVA appears to occur at discrete times and localities that cannot be identified with our present data and monitoring well locations.

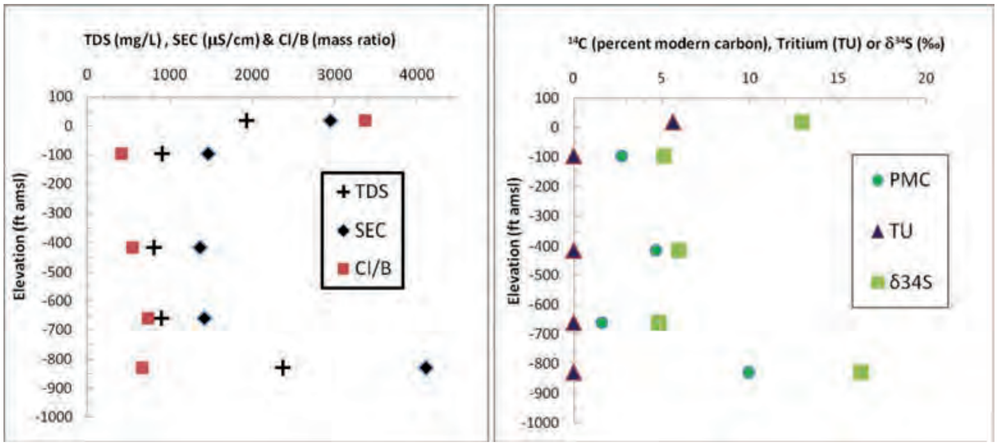


Figure 12. (Left) Variation of TDS (mg/L), specific electrical conductance (µS/cm), and chloride/boron mass ratio for the depth profile of the USGS SDAQ multi-depth monitoring well, August 2010. (Right) Isotopic data for ^{14}C in percent modern carbon (PMC), for tritium in tritium units (TU), and sulfate-sulfur isotope ratio in per mil (‰). Both the Cl/B ratio and $\delta^{34}SO_4$ show trends towards the seawater values of 4,300 and 21‰, respectively, with elevation. The uppermost data are for sample SDAQ J7.

Those groundwater samples from sampling ports located in the Friars Formation (yellow circles) appear to be a mixture of MVA and deep bedrock groundwaters but have low TDS values (~1,200 mg/L), rather than Friars Formation groundwaters, which exhibited higher salinity from the inundation of the valley. It appears that low TDS groundwater present beneath the Quaternary/Friars contact may discharge upwards into the MVA from the deeper Eocene sedimentary bedrock (see TDS data in Figure 12).

Thus, the paleochannels appear to be acting as focused linear discharge areas through which the regional groundwater flow system discharges into the MVA under the artesian conditions noted above. This has resulted in the deepest sampling ports from MW-1, MW-2, and MW-3 plotting midway between the deep SDAQ samples and the DB samples on Figure 13.

Impacts of the MVT Gasoline Release on Groundwater Quality

An additional complication has been posed by the presence of high TDS concentrations induced by the biodegradation of the very large gasoline leak (~200,000 gallons or ~800 m^3) that occurred in 1987–1991 at the MVT. The MVT is situated (see Figure 1) at the neck of Murphy Canyon, which allowed the gasoline to directly penetrate the MVA gravels and for the dissolved phase contamination—principally MTBE, which biodegraded to TBA—to be transported throughout the MVA to the DB monitoring wells. The TBA plume shown in Figure 10 exactly traces the MVA paleochannel due to its very high permeability relative to the Friars Formation.

Biodegradation of the gasoline within this plume resulted in an increase in TDS due to the production of protons caused by the hydrolysis of the dissolved carbon dioxide, i.e., $CO_2 + H_2O = H_2CO_3 = H^+ + HCO_3^-$. The acid produced attacks mineral surfaces (see Bennett et al., 1993; Borden et al., 1995; and McMahon et al., 1995), thus causing their dissolution and an increase in TDS. Such biodegradation-induced TDS may be identified by the simultaneous occurrence of fuel hydrocarbons in the groundwater sample, e.g., MTBE and TBA. For this reason, we have restricted our analysis of groundwater freshening to samples collected by DWR prior to the construction of the MVT in 1963 and gasoline releases.

Freshening Process and Its Effect on the Mission Valley Aquifer

We have defined the MVA as the Pleistocene (LGM) paleochannel deposit underlying both the Qualcomm Stadium and the Lower San Diego River Valley (see section on "Pleistocene Paleochannels"). Because of the cutting and filling of the paleochannel during the Pleistocene lowstand of the sea level, the Eocene sediments, which were inundated by seawater during the last interglacial, now surround the MVA paleochannel throughout its length as shown in Figure 9.

The hydrogeochemical consequence of this Pleistocene aquifer (i.e., MVA) being embedded in an Eocene aquitard is that the aquifer acts as a natural hydraulic drain throughout the valley. When the city began to extract groundwater from the MVA in 1914 (Fay, 1914), the natural process of freshening the Eocene sedimentary rock was enhanced through induced seepage to the MVA, causing the MVA to become somewhat brackish while the Eocene sediments underwent freshening. This process of drainage via the MVA and freshening of the Eocene sediments was accelerated by the heavy pumping that occurred during the remediation of the MTBE/TBA plume that migrated from the MVT to the DB monitoring wells shown in Figure 1. Not only was brackish water induced to flow into the MVA by this pumping, but also the groundwater became more brackish (i.e., higher TDS) due to the effects of the bioremediation of the gasoline released from the MVT (see above).

Head measurements in SDAQ indicate a strong upward hydraulic gradient across the Friars Formation into the Quaternary sediments. This gradient produces an artesian head, exhibited by the piezometers beneath the Quaternary/Friars contact being ~10–15 ft (3–5 m) above ground surface. Thus, SDAQ monitors hydraulic head and GWQ in a regional groundwater discharge area being recharged in the Peninsular Range to the east. The Friars Formation, a poorly indurated sandstone with 20 percent clay-sized particles, is regarded as an aquitard ($K < 1E{-}05$ m/s) in the valley. By contrast, the Pleistocene sands and gravels of the MVA have much higher hydraulic conductivities ($K > 1E{-}04$ m/s). The MVA acts hydraulically as a line sink through the center of the Friars Formation such that Friars' groundwater has slowly drained into the MVA naturally or has been induced to seep more rapidly by groundwater extraction in the MVA.

Depth profiles of TDS, specific electrical conductance, chloride/boron ratios, ^{14}C, tritium and sulfur isotopic values ($\delta^{34}SO_4$), and specific electrical conductance (SEC) for SDAQ are presented in Figure 12. The non-detect tritium results in the lower four ports (J3 through J6) of the SDAQ piezometers indicate the groundwater was recharged before 1953. The uppermost port, J7, had small amounts of tritium (near 6 TUs), which suggests some groundwater recharge occurred after 1953. The ^{14}C results in the

Table 8. *Ranges of results for the parameters determined for the alluvial wells in the San Diego Hydrogeologic Province as part of the GAMA Project (Wright et al., 2005).*

Groundwater Quality Parameter (Unit)	Range in Alluvial Basin Wells
Dissolved oxygen (mg/L)	0.1–5.5
pH (standard units, field measured)	6.8–7.5
Specific conductance (µS/cm @ 25°C, field)	805–2,787
Total hardness (mg/L as $CaCO_3$)	201–922
Alkalinity (mg/L as $CaCO_3$)	133–300
Nitrate + nitrite (mg/L as N)	0.04–9.14
Dissolved organic carbon (mg/L)	0.4–2.1
Major ions in ppm	
TDS (residue on evaporation, mg/L)	685–1,800
Calcium (mg/L)	43–234
Magnesium (mg/L)	22.5–81.6
Potassium (mg/L)	2.51–9.1
Sodium (mg/L)	68–295
Bromide (mg/L)	0.17–1.74
Chloride (mg/L)	113–540
Sulfate (mg/L)	61.7–421
Trace elements in ppb	
Arsenic (µg/L)	0.5–2.0
Barium (µg/L)	21–144
Boron (µg/L)	51–228
Iron (µg/L)	4–2,120
Manganese (µg/L)	0.1–492
Strontium (µg/L)	409–1,130
Uranium (µg/L)	0.46–7.91

lower four ports (< 10 pmc) indicates the groundwater is relatively old and has not been recently recharged.

We note that SEC, TDS, and the chloride/boron ratio indicate a clear trend in the upper 300 ft (100 m) towards a more saline shallow groundwater at the Friars/Quaternary contact (i.e., J7, 12 m or 40 ft bgs), which is confirmed by a similar trend in the sulfur isotope data towards the seawater $\delta^{34}SO_4$ value of 21‰ (Clark and Fritz, 1997, p. 140). Sulfate-sulfur isotope results are reported relative to the Vienna Canyon Diablo Troilite.

We associate these features with the marine inundation of 120 ka, which, we propose, produced the brackish groundwaters of the Friars Formation. In this hypothesis, the high TDS at the Friars/Quaternary contact reflects inundation of the Friars Formation by seawater during the last interglacial (see Figure 11) of 120 ka, when there was a sufficiently high head of seawater (specific gravity = 1.02) to sink through the Quaternary sediments and be trapped at the Friars/Quaternary contact. This trapping is clearly evident in the resistivity and gamma logs from the SDAQ well construction diagram (Figure 9H; Aqua Culture Monitoring Well, http://ca.water.usgs.gov/projects/sandiego/wells/summary.html).

Table 9. *Groundwater quality data for the city's DB monitoring wells near the intersection of Interstate routes I-8 and I-805.*

Parameter (Unit)	Well	
	DB-1	DB-2
Screen elevation (ft amsl)	+6 to −14	4.5 to −20.5
Sample date	Apr-11	Jun-11
Temperature (°C)	—	—
pH (pH units)	7.7 (lab)	7.1 (lab)
Dissolved oxygen (mg/L)	—	—
Specific electrical conductance (µS/cm)	2,710 (lab)	2,650 (lab)
Total dissolved solids (mg/L)	1,540	1,640
Alkalinity (mg/L $CaCO_3$)	416	325
Sodium (mg/L)	233	263
Potassium (mg/L)	—	—
Calcium (mg/L)	160	172
Magnesium (mg/L)	67.6	62.1
Iron (mg/L)	4.11	7.83
Manganese (mg/L)	1.66	2.61
Chloride (mg/L)	545	555
Sulfate (mg/L)	203	212
Bicarbonate (mg/L)	472	374
Nitrate-N (mg/L)	<0.05	0.14
Arsenic (mg/L)	<0.002	<0.002
SI $CaCO_3$, calcite	0.9	0.3
SI $FeCO_3$, siderite	1.4	1.1
SI $MnCO_3$, rhodochrosite	1.2	0.8
SI $Fe(OH)_3$, iron hydroxide	<0.0	<0.0
SI MnO_2, pyrolusite	<0.0	<0.0
Na/Cl	0.66	0.73

Note: See Figure 1 for locations. SI indicates the saturation index of the sample, where 0.0 indicates equilibrium with the mineral, negative values indicate mineral dissolution, and positive values indicate precipitation.

In this assessment, we use ionic ratios and concentrations, as well as the stable water isotopes discussed above (Figure 13), to elucidate processes affecting the observed patterns of GWQ. The relationships between bromide and chloride (Davis et al., 1998), as well as sodium and chloride (see Appelo, 1994; Ravenscroft and McArthur, 2004; Andersen et al., 2005; and chapter 6 in Appelo and Postma, 2005), are common tools used to identify freshening of brackish aquifers.

Bromide and chloride both have high aqueous solubilities, and their movement in brackish or fresh groundwater is considered to be conservative (Davis et al., 1998). Their relationship (in mg/L) is shown in Figure 15, although the DWR (1965) data cannot be shown because bromide was not analyzed by DWR. The seawater ratio of Cl:Br is 284 (by mass) based on the seawater concentrations shown in Hem (1985). The ratio was developed for the range of Cl shown in the figure. The data from the MVA and the USGS GAMA wells plot on or slightly below the seawater ratio line and suggest there is a seawater Cl:Br component in the groundwater.

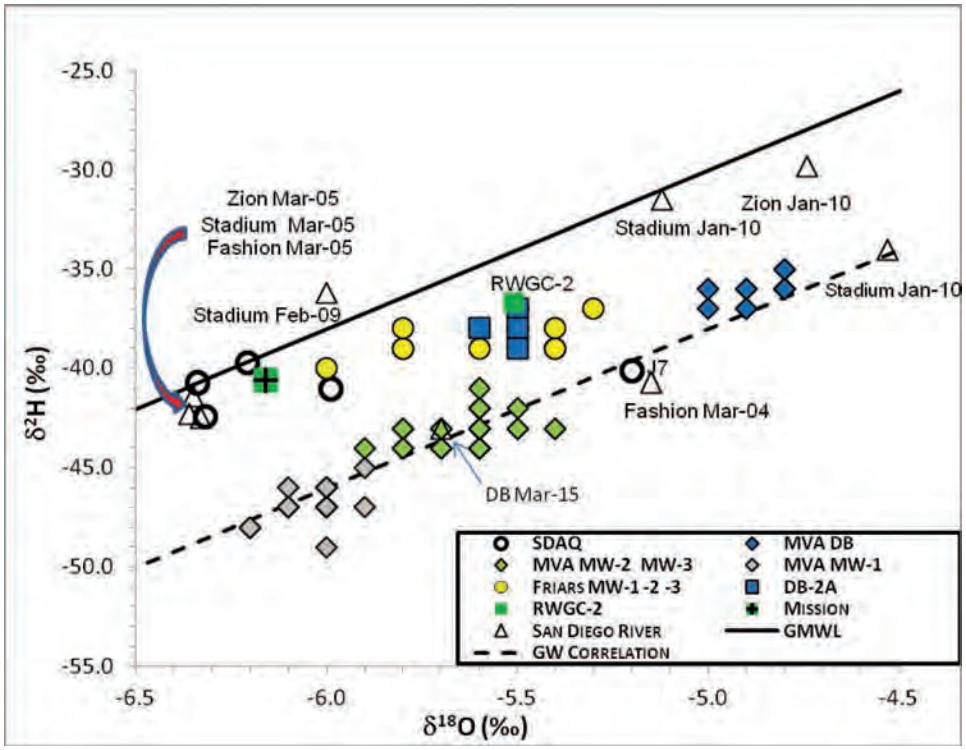


Figure 13. Stable water isotopes in the Lower San Diego River Valley. The groundwater data from city monitoring wells (DB-2A, MVA at DB, Friars GW, MVA Qualcomm, and MW-1) are from July and October 2014. The USGS SDAQ data are from 2010, while the USGS data from the River Walk Golf Course (RWGC2) and that from the Mission wells are from 2005. River water samples are USGS data from 2004–2010, with one collected in March 2015 at the DB site (identified as DB Mar-15); sampling locations are shown in Figure 1.

Figures 16 through 18 present evidence of groundwater within the Lower San Diego River Valley being freshened over the past 20,000 years. The exception is well 18Q3, which was installed in the MVA (see Figure 10); the paleochannel aquifer acts as the drain for the Eocene sediments and thus becomes increasingly saline over time. Ellis and Lee's (1919) composite sample is used to represent the freshwater end member, i.e., background conditions.

Figure 16 shows the sodium and chloride concentrations for the DWR, SDAQ, RWGC2, and DB samples. A two-component mixing line is shown between seawater from Hem (1985; Na = 10,500 mg/L, Cl = 19,000 mg/L) and the Ellis and Lee (1919) sample (Na = 54 mg/L and Cl = 85 mg/L). Ravenscroft and McArthur (2004) and Anders et al. (2014) have used a similar graphical technique to identify aquifers that are being either freshened or salinized.

Figure 16 shows that 5D1, 18Q3, and 17D1 plot on the mixing line and have a seawater signature. The data points above this line include SDAQ J3, J4, J5, J6, and the Murphy Canyon 5M1 and 5N1 wells, representing brackish water that is being freshened, which has resulted in an increase in the Na concentration relative to Cl. The data points below the line represent groundwater that is being influenced by the addition of more saline water. RWGC2 shows relatively less evidence of freshening, which is consistent with the likelihood that it is undergoing modern seawater intrusion that comprises about 5 percent of the sample. Those samples close to the freshwater end member, the Ellis and Lee (1919) sample, indicate that freshening is well advanced. 18Q3 reflects saline seepage into the MVA and is thus more saline than would otherwise be expected.

Freshening of seawater-inundated sediments is also apparent in Figure 17, which presents evidence of the cation exchange processes that are to be expected, such as the replacement of seawater sodium in the Eocene sedimentary rock by freshwater calcium (Appelo, 1994):

$$^1/_2Ca^{2+} + Na-X \rightarrow {}^1/_2Ca-X_2 + Na^+$$

where X represents the ion exchanger, such as clay minerals or other oxide surfaces in the sediments, i.e., desorption of Na from marine-inundated sediments by freshwater Ca.

The mixing line in Figure 17 is drawn with seawater data from Hem (1985; Ca = 410 mg/L) and from the Ellis and Lee (1919) results (Ca = 57 mg/L). Data points that lie below the mixing line are indicative of

Figure 14. Location of monitoring wells used for stable isotope sampling.

freshwater flushing, and data points that lie above the mixing line are indicative of marine inundation (Ravenscroft and McArthur, 2004) and brackish water flushing. Sample RWGC2, which contains ~5 percent modern seawater, represents a saline end member of the freshening process, while the Ellis and Lee (1919) sample represents the freshwater end member. Very generally, the freshening process of the Eocene sediments progresses from RWGC2 towards 18Q3, which represents saline drainage within the MVA.

Similarly, Figure 18 illustrates the reaction involving the desorption of the borate anion in Eocene sediments by freshwater bicarbonate:

$$HCO_3^- + B(OH)_4 - X = B(OH)_4^- + HCO_3 - X$$

As Ravenscroft and McArthur (2004, p. 1428) noted of freshwater flushing of seawater from alluvium in coastal Bangladesh "desorption of B during freshwater flushing occurs in response to lowering of pH and ionic strength, equilibrium re-adjustment, and, possibly, competitive exchange with HCO_3/CO_3." They concluded that "enrichment of both Na and B results from desorption from mineral surfaces in response to flushing by fresh groundwater of previously saline aquifers." A comparison of Figures 16 and 18 shows some similarity in Na and B desorption in the relationship of samples 17D1 and 18N1 to 18Q3.

DISCUSSION: BACKGROUND, BASELINE, AND AMBIENT GWQ

"Background" and "baseline" are adjectives used to describe the GWQ prior to anthropogenic development that might affect the chemical composition of groundwater. We believe that the following terms are consistent with North American usage:

- *Background* describes the pristine GWQ derived from natural geological, biological, or atmospheric

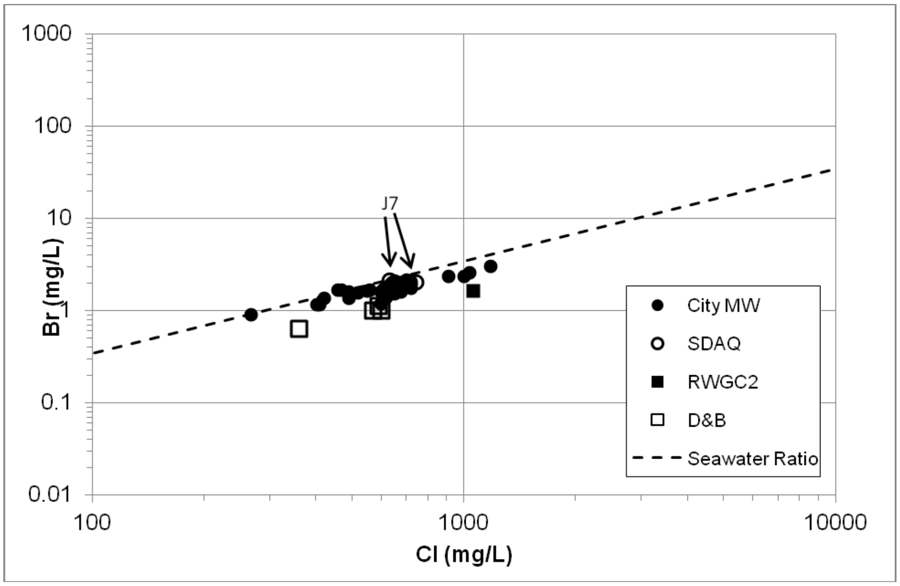


Figure 15. Relationship of chloride to bromide in groundwater samples from the Lower San Diego River Valley (city MWs, SDAQ, RWGC2, and D&B).

sources in the absence of identifiable anthropogenic influences (see Langmuir, 1997, p. 304), whereas

- *baseline* describes the GWQ at the beginning of monitoring and prior to some anticipated event, e.g., "pre-drilling" before hydraulic fracturing (e.g., API, 2009, p. 20; Sloto, 2013).

Baseline GWQ results may include effects of human activities, e.g., coliform bacteria from septic tanks or nitrate from fertilizer applications, although these analytes may or may not be reported. It is noteworthy that European usage of "background" and "baseline" is exactly the opposite of North American usage (see Edmunds and Shand, 2008).

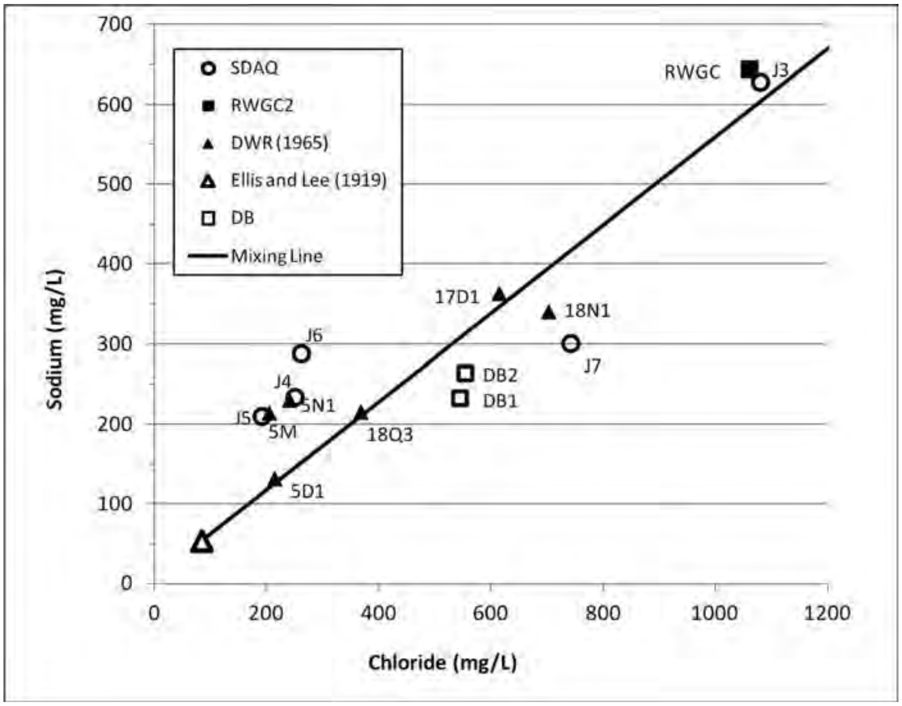


Figure 16. Relationship of chloride to sodium in groundwater samples from the Lower San Diego River Valley from prior to biodegradation-induced elevation of total dissolved solids.

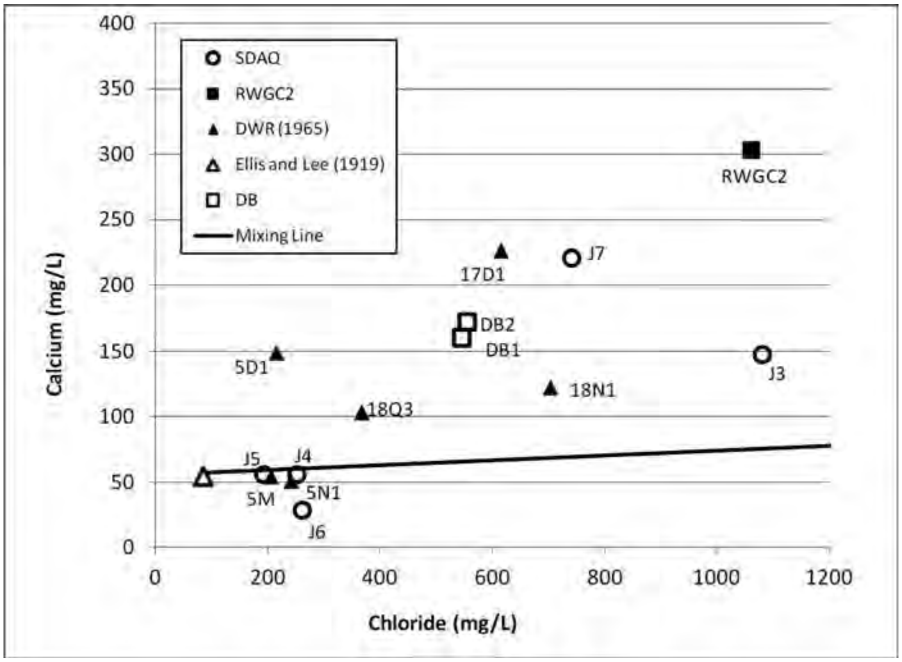


Figure 17. Calcium and chloride concentrations in the Lower San Diego River Valley prior to biodegradation-induced elevation of total dissolved solids. The solid line is a mixing line between the background sample of Ellis and Lee (1919) and seawater.

In addition, some institutions such as the USGS use a third term:

- *Ambient* GWQ is that GWQ measured at some time and place without any assumption being made as to anthropogenic influences.

The USGS (2013, p. 1) states that the California Groundwater Ambient Monitoring and Assessment (GAMA) Program will not only "establish baseline groundwater quality for comparison with future conditions" but will also "identify emerging constitu-

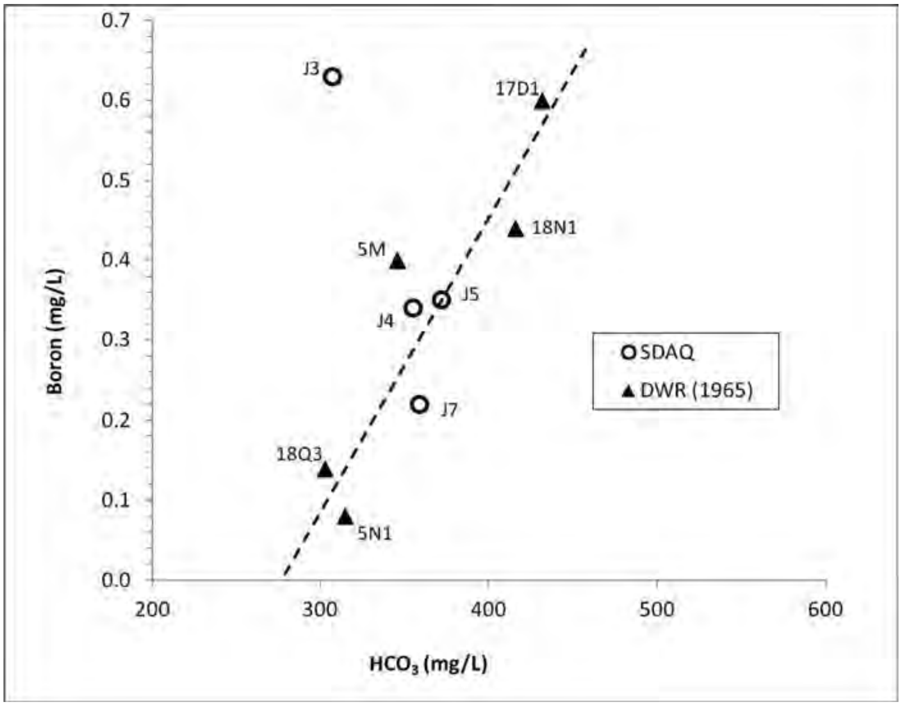


Figure 18. Evidence of freshwater bicarbonate exchange for seawater boron in the DWR (1965) and SDAQ J7 (2010) data caused by aquifer "freshening," i.e., displacement of brackish groundwater by freshwater recharge. The simple linear regression indicates that, if RWGC2 is excluded, 81 percent of the variance is explained by this ion-exchange reaction. DB boron values were not available for 2011.

ents in groundwater." Thus, "baseline" and "ambient" GWQ can indicate the same GWQ; the first term merely indicates that it is the GWQ measured prior to some event that may affect it. Our purpose is identify the particular meaning of each term with respect to the groundwater samples considered in Tables 5 through 9.

The 1915 USGS analysis shown in Table 5 is that of a fresh groundwater with relatively low TDS (<400 mg/L) and trace quantities of iron and 1.0 mg/L of nitrate, indicating an oxygenated groundwater. The common occurrence of dissolved oxygen (DO) and nitrate is discussed by Appelo and Postma (2005, pp. 458–464) and by Langmuir (1997, p. 418); it is also well documented in the technical literature (e.g., Jackson et al., 1990). The data in Table 5 represent what is referred to for regulatory purposes as "background water quality conditions" (San Diego RWQCB, 2005).

Tables 6 and 9 represent subsequent sampling of the MVA over approximately 100 years following the USGS sampling event of 1915. Table 6 data were collected during 1955–1965 by DWR, by which time (1959) the city well field shown in Figure 10 had been abandoned and the wells destroyed, although 18Q3 was sampled before abandonment (see DWR, 1959, p. B-20). Table 9 represents data collected during 2011 from the city's pilot well field (DB-1 and DB-2), which at the time was beginning to show evidence of increased contamination (TDS, MTBE, and TBA) that we associate with the MVT gasoline release of 1987–1991. Therefore, these three sets of data as represented by Tables 5, 6, and 9 provide (1) background GWQ data (i.e., the 1915 USGS sampling in Table 5) and (2) two sets of supplemental analyses representing the evolution of GWQ in the MVA approximately 45 and 96 years later.

The background GWQ of the MVA that emerges from these studies suggests that the MVA groundwater in 1915 was rather typical of alluvial aquifers found throughout the U.S. Southwest, i.e., aquifer sediments derived from plutonic rocks producing a sediment rich in feldspars and silica ("felsic"). In his study of the Southwestern alluvial basins, F.N. Robertson (1991, p. C-16) of the USGS commented that "The basin-fill sediments were transported into the basin and deposited under oxidizing conditions." Robertson's model identifies groundwater in the recharge area as a calcium-bicarbonate water with pH = 7.2, DO ranging from 3 to 7 mg/L, and a mean and standard deviation of TDS = 495 ± 68 mg/L. The major geochemical reactions in the recharge areas according to Robertson (1991, p. C86) are: (1) generation of carbonic acid in the recharge area from the dissolution of soil-zone carbon dioxide, including plant respiration, in the recharging groundwater ($CO_2 + H_2O = H_2CO_3$), producing an acidic groundwater (pH ~ 6); (2) weathering of feldspars and ferromagnesian minerals; (3) dissolution of carbonate minerals; and (4) formation of montmorillonite clay and iron oxides.

Table 5, showing the USGS 1915 analysis, is an accurate representation of groundwater acquired through Robertson's three processes and indicates a TDS ~ 400 mg/L and the presence of DO. These two parameters—TDS and DO—concisely define the major ion and redox state in the background GWQ of the MVA. Even after WWII, DWR (1967, p. 10) stated in its final report on the San Diego region that "[i]n general, ground water from the continental Pleistocene sediments has a TDS concentration falling within 200 to 600 ppm." The background GWQ of the Friars Formation is unknown, but 17D1 and 17D2 had TDS ~ 2,000 mg/L in the 1960s (Table 4).

The baseline GWQ in the MVA prior to urban development of the valley in the 1960s is represented by sample 18Q3 in Table 6, which is similar to the USGS GAMA data shown in Table 8. This high-quality groundwater existed in the MVA until contamination from the MVT caused its deterioration, although some deterioration may have been caused by agricultural development in the area now occupied by the Qualcomm Stadium, e.g., the low nitrate concentrations in Table 6. Groundwater extraction by the city prior to WWII would have caused brackish water inflow into the MVA from the adjacent Friars Formation and is likely the reason for the increase in TDS from ~400 mg/L in 1915 to ~1,100 mg/L in 1955. In addition, the pavement surrounding Qualcomm Stadium would have decreased the infiltration of DO and low-TDS recharge to the MVA after the mid-1960s. Consequently, urban development of Mission Valley in the 1960s led to further deterioration of the MVA prior to the release of fuels from the MVT.

Because knowledge of the MVA used by the city faded from memory after WWII, the perception of relatively high TDS concentrations in the Mission Valley groundwaters developed. This was likely the result of a review of the DWR reports that failed to discriminate between the Pleistocene MVA and Eocene formations, where TDS concentrations ranged up to 3,485 mg/L. The mean and standard deviation of 75 TDS samples reported by DWR (1965) were 1,694 ± 723 mg/L, i.e., about the same as in the present city monitoring well DB-2 (Table 9).

Of particular interest is that all three samples collected and analyzed by DWR (1959) from the present Qualcomm Stadium area shown in Table 6 (17D1, 17D2, and 18Q3) contained measurable dissolved nitrate. As noted above (Appelo and

Postma, 2005, pp. 458–464; Langmuir, 1997, p. 418; Jackson et al., 1990), the presence of nitrate indicates the probable presence of DO in these groundwaters at that time prior to urban development.

The USGS GAMA data (Table 8) indicate the ambient GWQ in coastal southern California alluvial aquifers that were *not* affected by the marine invasion during the last interglacial. All six USGS GAMA wells contained some DO, although their mean was only 1.6 mg/L. The 1955 DWR sample from 18Q3 also appears to have contained DO because of the presence of nitrate in the sample. The six Alluvial Basin wells sampled by the USGS during its GAMA survey shown in Table 8 had a mean TDS concentration of only 1,021 mg/L, which is similar to that reported for 18Q3 (1,105 mg/L) in 1955 (DWR, 1965) and displayed in Table 6.

The ranges in Table 8 provide guidance as to what might be considered reasonable present-day concentrations within MVA groundwaters. That is, values beyond the ranges reported are likely due to either (1) poor sampling technique, such as incorporation of sub-micron fines, resulting in erroneous concentrations, or (2) contamination, e.g., the migration of the uncaptured plume of MTBE, TBA, and TDS from the MVT gasoline releases.

In 2005, the San Diego Regional Water Quality Control Board (San Diego RWQCB, 2005, p. 3) ordered that the gasoline contamination from the gasoline tank farm (MVT; see Figure 1) that was contaminating the MVA should be remediated "to attain background water quality conditions" by the end of 2013. The board defined these background conditions as "the concentrations or measures of constituents or indicator parameters in water or soil that have not been affected by waste constituents/pollutants from the Site"; i.e., from the MVT. However, it has been long established (Bennett et al., 1993; Borden et al., 1995; and McMahon et al., 1995) that *all* inorganic constituents are affected by the intrinsic bioremediation such as that which has occurred within that part of the MVA contaminated by the gasoline components. This is because the oxidation of hydrocarbons produces carbon dioxide, which causes a chain of hydrogeochemical processes: It dissolves in water and thus lowers the pH by forming carbonic acid, causing dissolution of aquifer minerals and raising TDS concentrations. Similarly, the dissolved hydrocarbons change the redox state by reducing DO, nitrate, and sulfate and causing the reductive dissolution of iron and manganese oxides on aquifer minerals. Thus, this definition of background GWQ by the regulator is based on a false assumption; i.e., there is no effect of intrinsic biodegradation of organic hydrocarbons on the concentrations of inorganic groundwater constituents, and the Board's definition of background conditions is therefore incorrect.

The attainment of "background water quality conditions" could theoretically be associated with the attainment of the 1915 GWQ measured by the USGS (Ellis and Lee, 1919), i.e., TDS ~ 400 mg/L and presence of DO, which is the real background GWQ. However, this would likely require the recharge of distilled water to the aquifer but recharge of any water—treated or not—has been continually rejected by the owner of the MVT and by the board in recent years. The attainment of the baseline GWQ, represented by 18Q3 (TDS ~ 1,100 mg/L, DO present) measured in 1955, prior to the development of the MVT, is however practical given today's desalinization technology. It should be noted that the DWR (1965, pp. 42–43) advised the San Diego RWQCB that the Eocene sediments of the valley were brackish and that "the most practical way to alleviate the problem of post-nate [i.e., brackish] water seepage is to increase the relative head of ground waters by means of ground water recharge of Mission San Diego Basin" (i.e., the Lower San Diego River Valley).

SUMMARY AND CONCLUSIONS

In order to explain the current pattern of GWQ in the Lower San Diego Valley, we have reconstructed the likely Quaternary evolution beginning with the last interglacial about 120,000 years ago. Pleistocene sea-level fluctuations have caused periodic incision of Lower San Diego River channels and inundation by rising seas. From water-well data, we have identified channels that developed during the LGM that cut into the Eocene and early Quaternary sediments. This channel probably extended far offshore relative to the present coastline as it graded to a lowered base (sea) level about 17,000 years ago, similar to other major coastal rivers in southern California. These gravels became the principal hydraulic unit in the city's pre-WWII groundwater supply—the MVA.

We hypothesize that the inundation of the Eocene sediments, such as the Friars Formation, by these shallow seas during the last interglacial is recorded in the brackish GWQ of water wells completed in the valley sediments, with the exception of those wells completed in the gravel paleochannel(s) that date to the LGM, during which the MVA was deposited. However, groundwater extraction from MVA wells has induced brackish groundwater flow into the MVA from the adjacent Friars Formation sediments, and biodegradation-induced natural attenuation of hydrocarbons has further raised TDS concentrations.

Several lines of evidence support this hypothesis:

- Abbott's (1999, pp. 202–203) popular history of regional geology illustrates the marine invasion of 120 ka, confirms the geographic extent of the invasion, and outlines the same causes of sea-level rise since the LGM and tectonic uplift over ~120,000 years.
- Similar gravel aquifers to the MVA were laid down in all the major southern Californian valleys following the LGM; recent drilling evidence from the MVA has confirmed this.
- The USGS 1915 sampling of the GWQ in the MVA showed clearly that the aquifer had low TDS and was oxygenated prior to the beginning of large-scale municipal extraction.
- Numerous water-supply wells sampled by DWR in the 1950s, i.e., prior to urbanization of the valley, indicate TDS concentrations varying from 700 to 3,500 mg/L; the lower TDS values were associated with the alluvial gravel aquifer.
- DWR also concluded in the 1960s that marine waters explained the brackish GWQ of the Lower San Diego River Valley and that artificial recharge of water was necessary to keep the TDS concentrations low.
- The USGS SDAQ (Aquaculture) multi-depth monitoring well in the valley records this brackish water (TDS ~ 2,000 mg/L) at the contact of the Quaternary and Eocene sediments.

We conclude that the confusion concerning the GWQ in the valley is due to a loss of institutional memory of documentation and a failure to re-visit the excellent work of the DWR in the 1950s and 1960s conducted for the present San Diego Regional Water Quality Control Board. While new information is always helpful, it does not negate the bountiful data readily available in the published literature. Restoration of the MVA as a municipal water supply is being planned. Evidence of storm runoff recharge events is apparent in stable water isotope data from new monitoring wells; however, the nature of the recharge process is uncertain because of limited data at present. High residual TDS concentrations will require a significant water-treatment initiative to make MVA groundwaters suitable for public consumption in the area of the pre-WWII city well field.

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