The Monterey / Modelo Formation

A natural geologic source in Malibu Creek's northern headwaters is an origin of multiple water quality impairments in the Malibu Creek watershed.

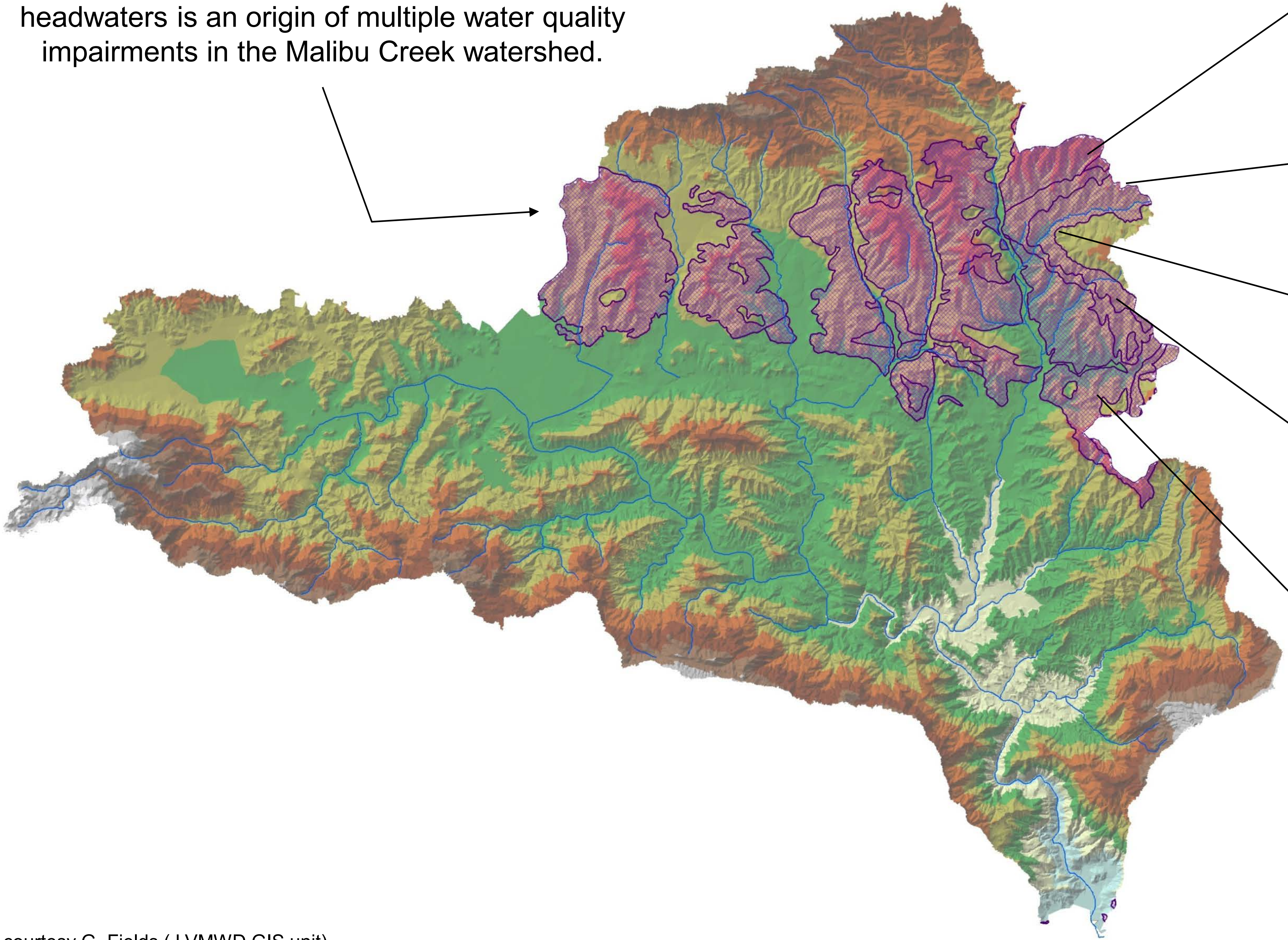
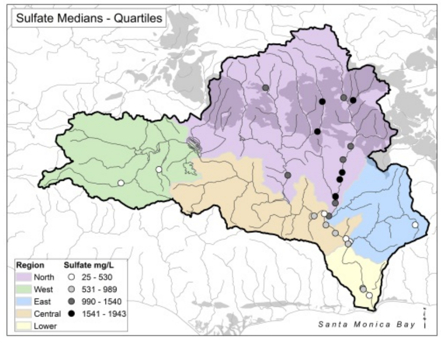
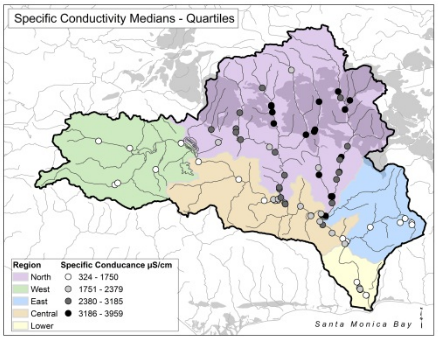
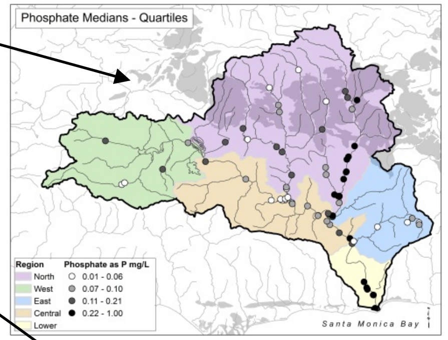
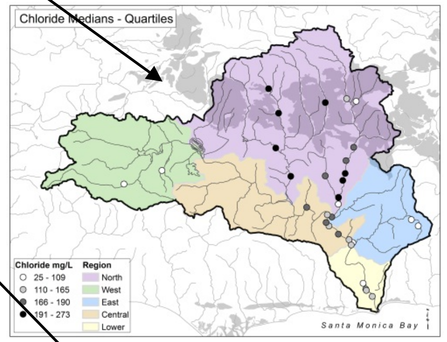


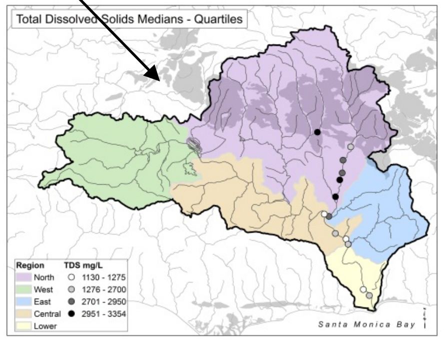
Image courtesy G. Fields (LVMWD GIS unit)











Section 3 - Natural Source Assessment

An analysis of the impacts of the Monterey / Modelo Formation on water quality and aquatic life in the Malibu Creek watershed

The Monterey Formation (M Fm.) is one of California's most important petroleum source rocks, with large offshore and onshore oil and gas deposits throughout the state. It is also a source of potentially hazardous levels of trace metals according to the US Geological Survey's Water Resources Division website on "Hazardous Trace Elements in Petroleum Source Rocks: The Monterey Formation" (USGS 2002). **The U.S.G.S. findings compel a more focused inspection of the impacts of the M Fm. on local water quality and aquatic life, presented in this section.**

Major Findings:

(1) **Extent and impact.** Large exposures of the M Fm. have been mapped in the northern tributaries of Malibu Creek (CA), where high levels of selenium, metals, phosphorus, nitrogen and sulfate were detected even in tributaries draining non-urbanized open space. The M Fm. maintains Malibu Creek at brackish levels (SC 1,500 – 4,000 µS/cm) from its northern headwaters to the sea, impacting the aquatic community across three trophic levels, and rendering the watershed's northern ground and surface waters unfit for human consumption.

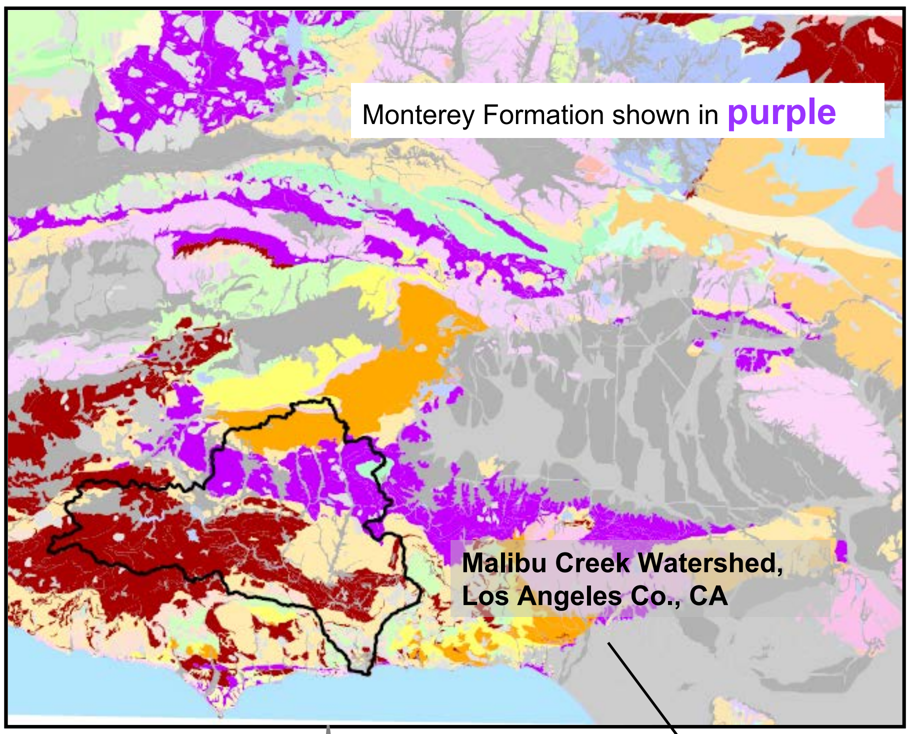
(2) **Comparisons to other streams with similar mineral water quality.** A comparison of major ion concentrations in Malibu Creek and its M Fm. drainages with their levels in over 1,100 other US streams found that Malibu Creek's levels of TDS, SC, sulfate, magnesium, and calcium are extremely unusual, matching those found in non-acidic streams in Pennsylvania, Virginia, and Kentucky downstream of mountain top coal mining. In those streams where benthic macroinvertebrate assessments have been done, these levels of major ions (especially sulfate) are associated with poor benthic macroinvertebrate indices (Pond *et al*., 2008), as they are in Malibu Creek. A review of the scientific literature also found that high TDS and SC levels equivalent to those measured in Malibu Creek also impact benthic diatom algae species composition and abundance (Potopova and Charles, 2003) and fish community species richness and density (Kimmel and Argent, 2008).

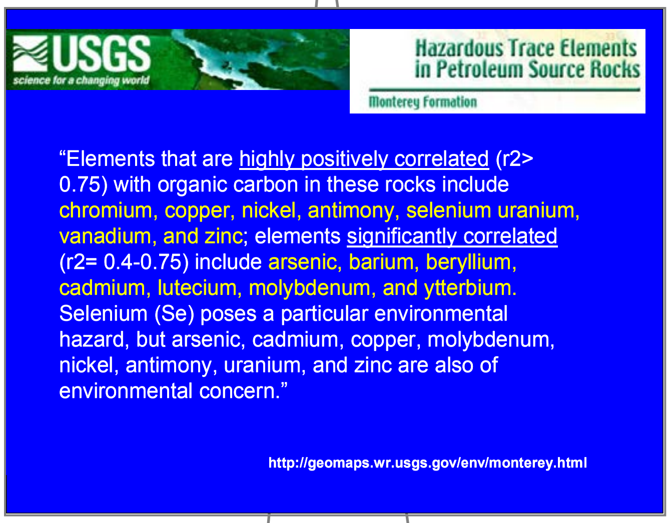
(3) **Comparisons to streams with similar geology.** High background levels of biostimulatory substances (phosphate, nitrate) are shown to be associated with local exposures of M Fm. rock, with effects on algal growth and algal species composition identical to those reported by Biggs (2000) for New Zealand catchments with even modest exposures of similar marine tertiary siltstones and shales. Eutrophic conditions in Malibu Creek and its northern tributaries draining the M Fm. are probably a natural consequence of the watershed's geology, with strong evidence for these conditions from historical water quality data predating the bulk of the watershed's development, including the construction of imported and recycled water distribution systems.

(4) **Public awareness.** None of the historical or current monitoring programs considered local or regional geology, either for site location or parameters tested. No studies of local water quality or aquatic life mention the M Fm. or consider it as an alternative explanation for poor water quality, even in those studies that noted anomalously poor water quality at stations within and immediately downstream of M Fm. rock. None of the water quality regulations or permits we reviewed for this data compilation and assessment appear to have investigated the M Fm. as an alternative natural source of mineral, metal, nutrient, algal or benthic macroinvertebrate impairments, aside from brief references to anomalously high selenium levels in reach 5 of the LA River in the LA river metals TMDL, and potentially high natural nutrient levels in Lake Calabasas in the LA Lakes TMDL. The apparent lack of awareness in the regulatory community of M Fm. impacts on water quality can have ramifications for regulated agencies and communities. This report provides recommendations and guidance for future regulatory actions in watersheds draining significant exposures of the M Fm. rock and contemporaneous stratigraphic and lithologic equivalent units of the Monterey Formation elsewhere in the Los Angeles Region (e.g. Modelo, Point Sal and Puente Formations; Isaacs & Rullkötter, 2001).

Monterey / Modelo Formation impacts on native water quality

(SYNOPSIS)





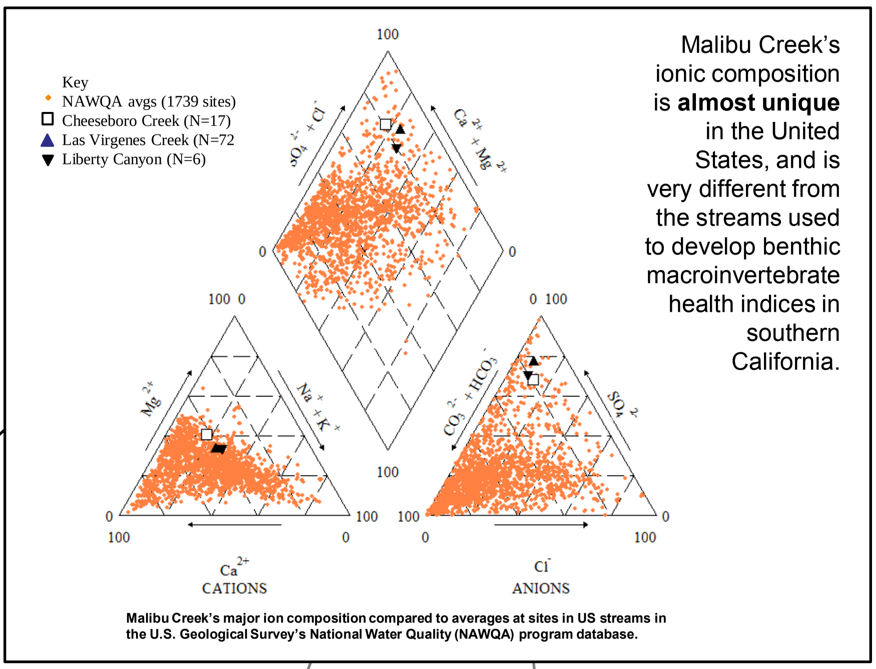
Hazardous Trace Elements in Petroleum Source Rocks

Monterey Formation

"Elements that are <u>highly positively correlated</u> (r2> 0.75) with organic carbon in these rocks include chromium, copper, nickel, antimony, selenium uranium, vanadium, and zinc; elements <u>significantly correlated</u> (r2= 0.4-0.75) include arsenic, barium, beryllium, cadmium, lutecium, molybdenum, and ytterbium. Selenium (Se) poses a particular environmental hazard, but arsenic, cadmium, copper, molybdenum, nickel, antimony, uranium, and zinc are also of environmental concern."

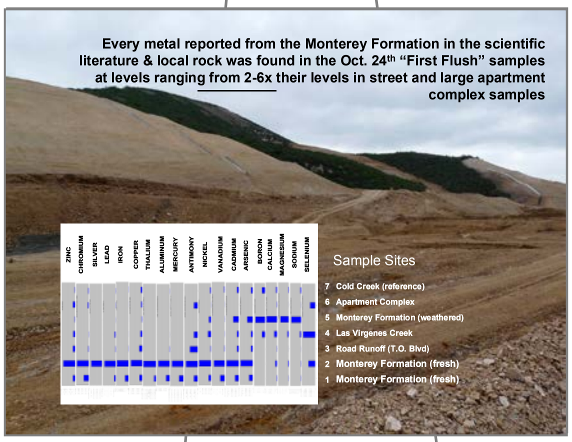
http://geomaps.wr.usgs.gov/env/monterey.html

USGS NAWQA Database



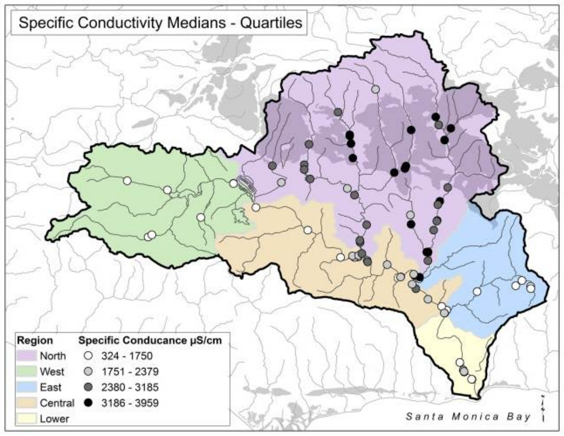
Malibu Creek's ionic composition is **almost unique** in the United States, and is very different from the streams used to develop benthic macroinvertebrate health indices in southern California.

Malibu Creek's major ion composition compared to averages at sites in US streams in the U.S. Geological Survey's National Water Quality (NAWQA) program database.

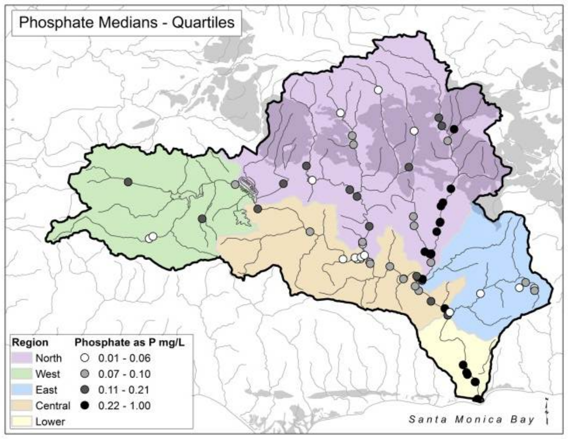


Every metal reported from the Monterey Formation in the scientific literature & local rock was found in the Oct. 24th "First Flush" samples at levels ranging <u>from 2-6x</u> their levels in street and large apartment complex samples

Naturally high metals, selenium



Sulfate levels naturally higher than Basin Plan Objective. Exceedances of US EPA secondary drinking water standards for TDS, SC, sulfate



Phosphorus levels naturally higher than TMDL target

<u>Undrinkable</u> Exceedances of primary & secondary drinking water standards (sulfate, TDS, SC, uranium decay (This research, Neal & Todd (2003)

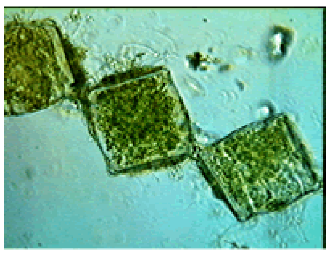
<u>Elevated metals,</u> selenium in fishes, crayfish (ABC Labs (multiple years), Moeller *et al.*, (2003)

<u>Benthic diatom composition impacted</u> for brackish, high sulfate & high magnesium ion favoring species such as Pleurosira laevis ("Malibu muck"). Potapova & Charles (2003)

<u>Impacts on benthic macroinvertebrates</u> from high conductivity (Pond *et al.*, 2008)

<u>Naturally Eutrophic</u> – high algal growth favoring floating mat species (*Cladophora, Rhizoclonium*) (Biggs, 2000)

Steelhead trout



Pleurosira laevis ("predominant diatom in Malibu muck

Dragonfly larva

Impacts on aquatic life and beneficial uses

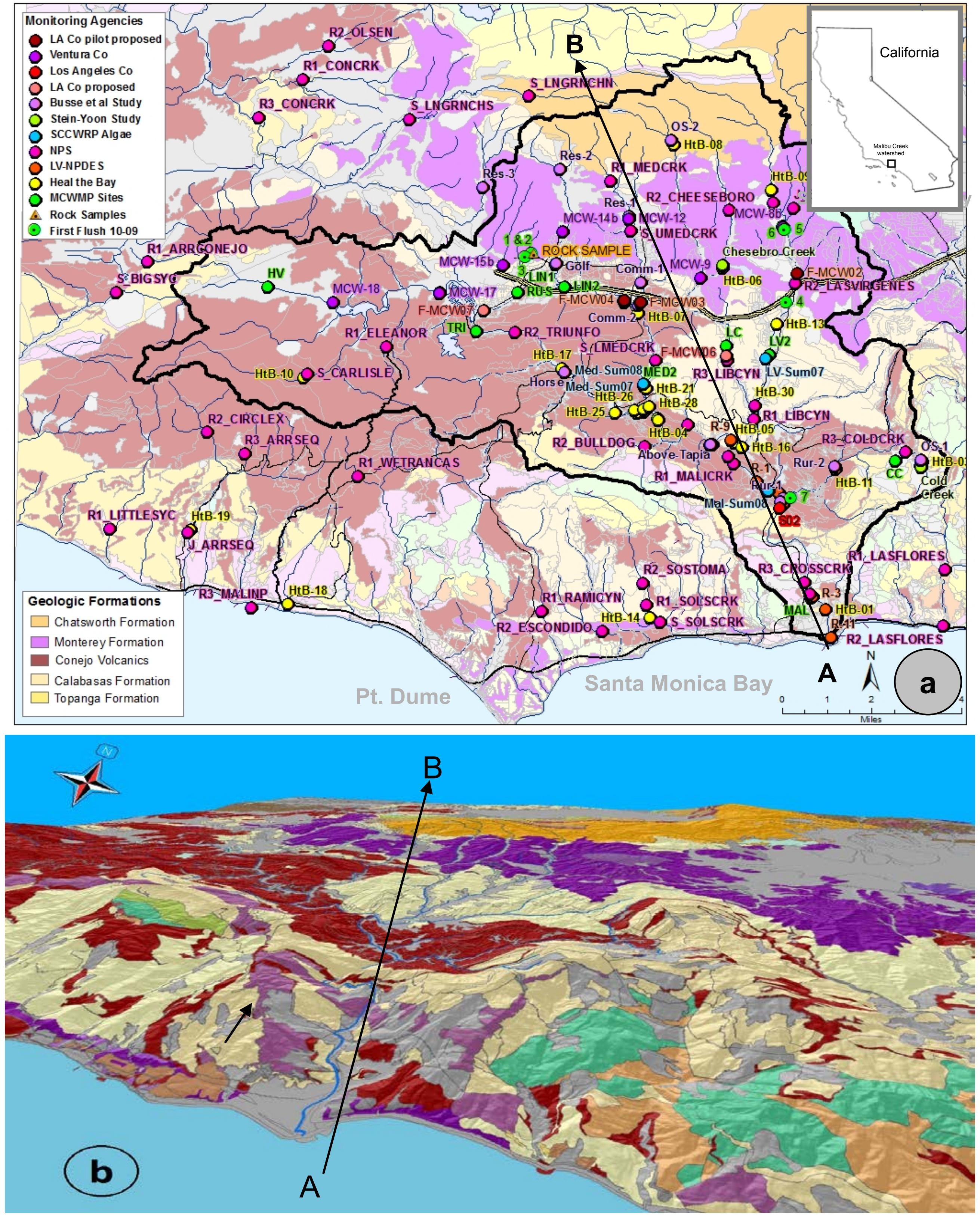
INTRODUCTION

Previous studies of poor water quality in Malibu Creek and its tributary streams have tended to focus on potential anthropogenic sources of pollutants such as septic tank leachate, urban runoff, and discharges from the Tapia Water Reclamation Facility (WRF; Manion & Dillingham, 1989; Ambrose *et al.*, 1995; Ambrose & Orme, 2000; Busse *et al.* 2003; Luce, 2003; Moeller *et al.,* 2003; Luce & Abramson, 2005). Several studies have attempted to quantify anthropogenic pollutant sources and their impact on aquatic life by comparisons to more-natural reference sites in undeveloped areas within the watershed or nearby coastal streams. However, aside from noting that geology can affect water quality, none of these studies included any analysis of local geology or evaluated its effects on their water quality results. A recent regional water quality study by Stein and Yoon (2007) did note differences in native water quality in drainages with sedimentary versus those with igneous or metamorphic rock. However, their study did not investigate differences in water quality between drainages with different *types* of sedimentary rock such as marine and non-marine sedimentary rock, or sedimentary petroleum source rock, all of which have substantial deposits and exposures in the Malibu Creek watershed. Our assessment found clear evidence of sub-standard water quality associated with one geologic formation in particular, the Monterey / Modelo Formation[1], and our review of the scientific literature on this formation found well-documented references to its potential impacts on both ground and surface water quality and aquatic life.

The geology of the Malibu Creek watershed is complex (Fig. 1), with significant exposures of volcanic rock (Conejo Volcanics), and both marine and freshwater Tertiary sedimentary rock represented in various sub-catchments and elevations. Tectonic contact between the North Pacific and North American plates resulted in widespread uplifting, compression and folding of Tertiary-age formations in the watershed (Ingersoll, 2008), and consequently today the youngest sedimentary rock such as the Monterey / Modelo Formation are found at higher elevations (Fig. 1b) that drain into Malibu Creek and sustain creek flows through the dry summer months. This drainage is important in the watershed's arid, Mediterranean climate, because aside from infrequent subtropical summer rainstorms, dry-weather native flows in Malibu Creek from about mid-May through October are derived almost entirely from groundwater drainage and seepage (Hibbs 2010). These flows provide critical habitat for endangered southern steelhead trout (anadromous *Oncorhynchus mykiss)* and arroyo chub (*Gila orcutti), a state fish species of special concern.* Even with these flows, Malibu Creek commonly dries out above Malibu Lagoon in late summer as it emerges from Malibu Canyon and enters the Malibu floodplain. During these late summer low-flow periods, evaporation can further concentrate solutes in isolated pools that serve as dry-weather refugia for the creek's aquatic life. As we report below, this process exacerbates the already unusually high salt content of Malibu creek, which is brackish from its northern tributaries to the sea even in the wet winter months.

Malibu Creek's northern headwaters (e.g. Cheeseboro, Las Virgenes, Lindero, Medea, and Palo Comado Creeks) originate in unincorporated, largely undeveloped foothills in northwest Los Angeles County above the inland cities of Agoura Hills, Calabasas, Thousand Oaks and Westlake Village (a small fraction of the headwaters lie within eastern Ventura County). Malibu Creek is unique in this regard among Santa Monica Mountain coastal streams, penetrating inland beyond the ridgeline of the Santa Monica Mountains, and eventually reaching the foothills north of the US 101 freeway. One consequence of this geography is that,

Fig. 1. (a) Malibu Creek watershed (outlined by heavy black line), showing major geological formations (after Yerkes & Campbell, 2005), major tributaries and adjacent coastal streams, and sample locations coded by agency. See text for site abbreviations (Data Sources & Methods). (b) Oblique view of watershed geology looking upstream Malibu Creek along AB transect in (b), showing relative elevations of major geological formations. Courtesy LVMWD GIS unit (G. Fields).



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[1] Local exposures of the Monterey Formation are also known as the Modelo Formation, and throughout this assessment we refer to it as the Monterey / Modelo Formation. Where we reference studies of the Monterey Formation in other watersheds outside of the Santa Monica Mountains, we drop the locally-used "Modelo" moniker.

unlike smaller adjacent coastal streams that do not penetrate the Santa Monica Mountains, the northern headwaters of Malibu Creek drain a large area underlain by the Miocene-age marine sedimentary Monterey Formation (also referred to in the Santa Monica Mountains as the Modelo Formation after Fritsche, 1993), which runs in an east-west band from Santa Barbara to Orange County, with major exposures in the upper Ventura, Santa Clara, Los Angeles and Santa Ana river basins (http://geomaps.wr.usgs.gov/env/monterey.html).

The Monterey Formation (M Fm.) is well known to the oil industry as the most important petroleum source rock in California, with a total organic carbon (TOC) content ranging from 1-20 percent by weight (Isaacs & Rullkötter, 2001). It also contains phosphatic nodules, and historically it was mined as a commercial source of "soft-rock" phosphorus in Santa Barbara and Orange Counties (S. Jasinsky, pers. Comm.; Morton and Miller, 1981). Fertilizers derived from the M Fm. and other marine phosphatic rock can have elevated levels of arsenic, cadmium, chromium and lead (US EPA, 1999), and the US Geological Survey has issued an on-line alert on the Monterey Formation's potential hazard as a source of selenium and trace metals (http://geomaps.wr.usgs.gov/env/monterey.html). The M Fm.is also commonly enriched in uranium, especially in exposures with high levels of total organic carbon (TOC; see Table 2-4 in Piper & Isaacs, 2001), and groundwater in contact with the M Fm. has been shown to exceed state Maximum Contaminant Levels (MCL) for alpha particle emission in drinking water in the Malibu Creek watershed (Neal & Todd, 2005).

In 1969, a blow-out at a Union Oil platform tapping offshore M Fm. rock in Santa Barbara County resulted in a large spill that washed up on local beaches throughout the Santa Barbara Channel. This event raised public awareness of the potential environmental hazards of offshore drilling and is often cited as a major milestone in the passage of the federal Clean Water Act in 1972 (Clarke and Hemphill, 2002). However, to date the natural impacts of terrestrial exposures of the M Fm. on water quality in southern California inland and coastal streams have received remarkably little attention from water quality regulators and managers despite known hazards for water quality and widespread occurrence through five counties. Sulfate, total dissolved solids (TDS) and selenium concentrations exceed water quality standards in over a dozen water bodies in the greater Los Angeles area alone, yet the Los Angeles Basin Water Quality Control Plan, written in 1994, devotes just three general paragraphs to the region's geologic setting, with no discussion of the widespread occurrence of petroleum source rock or its potential for impairing water quality and aquatic life (LARWQCB, 1994). Confusing the situation further is the fact that virtually all of these substances may also be found in urban runoff, with elevated levels commonly attributed to anthropogenic sources even in those watersheds where the M Fm. and other petroleum source rocks occur. While our specific focus is on the M Fm.'s impacts on water quality and aquatic life in the Malibu Creek watershed, our hope is that water resource managers in other regions will review the geologic setting of their watersheds when assessing exceedances of water quality objectives under the CWA. Attention to geology is especially important in southern California and other arid environments, where dry season evaporation can concentrate already-elevated levels of metals, selenium, sulfate, and biostimulatory substances (e.g. phosphorus and nitrogen) and other compounds that may be enriched in M Fm. and other Tertiary marine sedimentary rock.

Until recently, the influence of the Monterey Formation on surface and groundwater quality was poorly known in the Malibu Creek watershed, especially with respect to uses other than municipal water supply. Water district records (LVMWD) provide some information on historical groundwater quality in early well logs and geotechnical studies from the early 1960's, submitted for district water system design reports for large developments either proposed or constructed. These groundwater quality data, albeit limited to a few constituents such as TDS and sulfate, were collected prior to the importation of State Water Project (SWP) water and ~95 percent of the area's urban development, and are thus helpful in assessing the relative magnitudes of influence on surface water quality from among geologic, imported water and urban runoff influences. Discussions with LVMWD staff and long-time residents indicate that area ranchers and "old timers" were well-aware of sub-standard groundwater quality (recalling individual wells with names like "old stinky"). Water district records show that the poor mineral quality of local groundwater basins was one of the drivers for the formation of a public water district to import SWP water in the mid-1960's. The majority of these early wells produced water with TDS higher than current US EPA secondary standards for taste and odor, and most were abandoned upon the arrival of SWP water.

Through the 1990's, surface water quality monitoring stations in Malibu Creek were limited to the creek's lower reaches, primarily to monitor releases from the Tapia Water Reclamation Facility. Stream flows in these lower reaches are a blend of the creek's three major tributaries (Cold, Las Virgenes and Triunfo Creeks), each draining different geologic formations (Fig. 1). Only in the last decade have water quality time-series data become available from sites in the upper watershed, including sites located entirely within the Monterey Formation and immediately downstream of it. Identification of associations between water quality and geology in the watershed may have also been hindered by the limited availability of geological maps for the watershed until the early 1990's, when Dibblee, the US Geological Society and the Society for Sedimentary Geology published a series of geological maps, field guides and papers for the area (Dibblee & Ehrenspeck, 1990; Dibblee 1992; Fritsche, 1993; Weigand *et al.* 1993), a remarkable accomplishment given the complex geology. These maps and field guides were consulted by the authors in 2008, during an investigation of unusually high salt and phosphorus levels in surface waters sampled well above urban development in the foothills north of the US 101 Freeway. Our review revealed a strong association between the M Fm. and both specific conductivity and phosphorus concentration prompting further investigation into the geochemical character of the Monterey Formation and its effects on downstream water quality and aquatic life.

DATA SOURCES AND METHODS

Geology - maps. (Fig. 1). The location and geographic boundaries of the Monterey Formation and other geologic formations in the Malibu Creek watershed and adjacent coastal basins were identified from the Los Angeles 30' x 60' southern California Quadrangle (Yerkes & Campbell, 2005). Regional geology adjacent to the above quadrangles was determined from the geological maps of the Point Mugu and Triunfo Pass Quadrangles (Map #DF-29) and Camarillo and Newbury Park Quadrangles (Map #DF-28), produced by the Dibblee Geological Foundation in cooperation with the California Department of Conservation (Division of Mines and Geology) and the US Geological Survey from 1990-1993. Also reviewed was a field guide to Middle Tertiary rocks in the Santa Monica Mountains that includes surface exposures of the Monterey Formation in the Malibu Creek watershed along Mulholland Highway between Cornell and Las Virgenes Roads (Weigand *et al.*, 1993). Relatively large numbers of fossil fish otoliths were found by the authors at Stop 7 of this guide. Otoliths are small, high-density bones in fish cranial sensory organs used for balance, also known as "ear stones" or otoliths. Samples were provided to the Los Angeles County Museum of Natural History Ichthyology unit (J. Seigel). Otoliths are common in the Monterey Formation (Isaacs & Rullkötter, 2001 and this research).

Geology – Elemental Composition. The elemental composition of Monterey Formation rocks located outside the Malibu Creek watershed is reported in Table 2.2 of Piper & Isaacs (2001), with samples from Naples Beach, Santa Barbara County. To compare their results with local M Fm. rock within the Malibu Creek watershed, an elemental analysis was performed by LVMWD on four samples of M Fm. rock within the Malibu Creek watershed from a recently graded, cross-sectionally exposed 125-ft. ~ 30° inclined cut of the Monterey Formation at a construction site in Westlake Village immediately north (adjacent) to Thousand Oaks Blvd on 8 October 2009 and 19 February 2010 ("Rock Sample" site in Fig. 1). The grading cut was approximately orthogonal to the bedding plane. Sample 1 was an embedded white nodule with a friable / chalky consistency collected from the stratigraphic middle of the 2009 grading cut. Sample 2 was collected from the base of the cut and consisted of unoxidized black and dark grey rock with very fine packets, fining upwards from fine sands to silts. Sample 3 was collected five stratigraphic feet below the top of the cut, and consisted of oxidized diatomaceous silt, sand and shale, orange-brown in color. Crumbled and examined under low-power microscope, we observed fish otoliths and foraminifera ($CaCO_3$). Sample 4 was a weathered rock taken from the surface above the 2010 grading cut, and was blocky, cemented and sandy, but covered with a white precipitate that fizzed upon contact with HCl. Samples were pulverized and tested via inductively coupled plasma-atomic emission spectrometry (ICP-AES) by Fruit Growers Laboratory Environmental (Santa Paula, CA) for Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Sn, Tl, V and Zn (EPA sample preparation method 3050/analytical method 6010B), Li (EPA 3050/6020), Hg (EPA 7470/245.1), Br, Cl, F, SO_4, NO_3, NO_2 (EPA 9056/300.0), PO_4 (4500-P E/4500P), alkalinity (SM 2320B/WS 51.30), and CN (EPA 9010B/4500CNCE). Inorganic anions were assayed by ion chromatography (EPA 300.00). Total organic carbon (TOC) was assayed (EPA 9060) by ESB Laboratory Services (Riverside, CA); Total Kjeldahl nitrogen (TKN) was assayed (SM 4500-Norg-B M) by Capco Analytical Services (Ventura, CA).

Groundwater Quality. Data on groundwater quality prior to the importation of non-native water were obtained from Staal, Gardner and Dunne, Inc. (1991), who compiled well and well water data from Los Angeles County registered well records dating back to the 1930's. More recent data on groundwater quality within the Monterey Formation in the Malibu Creek watershed were obtained from sentinel test wells along the perimeter of the Calabasas Landfill, collected by the Los Angeles County Sanitation District in compliance with Los Angeles Regional Water Quality Control Board (LARWQCB) Order Nos. 93-062, 89-053, and 00-077 (available from the LARWQCB), reported in Carry (1996). Carry (1996) also provides data on mineral leaching in bench top reactors over a two year period from surface sediments and subsurface bedrock samples in the vicinity of the Los Angeles county landfill within the Monterey, Topanga and Calabasas Formations in the City of Calabasas. Note Carry (1996) and others refer to local Monterey Formation rock as the Modelo Formation.

First rain event – metals. We tested levels of trace metals in surface runoff from both the freshly-exposed grading site and from weathered and ungraded M Fm. rock following the first rain event of the 2009-2010 wet season on October 9th, 2009. Two samples were drawn from puddles at the immediate toe of the same freshly-graded M Fm. exposure sampled for elemental composition in M Fm. rock (see above). A sample of street runoff was also taken from the north gutter along Thousand Oaks Blvd adjacent to this site. We believe this sample represents street runoff: no runoff was observed crossing the perimeter of the grading site, being contained on site and diverted directly to the county storm drain system. All three sampling sites are located in the City of Westlake Village (Fig. 1). We also tested metals in runoff in the Las Virgenes Creek subdrainage on the same day as follows: Sample 1 was taken from surface runoff from an unnamed east tributary of Las Virgenes Creek draining M Fm. rock immediately to the east and upslope of the large apartment complex at the head of Las Virgenes Road (Fig. 1). The sample was taken immediately above the intake to the open trapezoidal Los Angeles County storm water channel located adjacent (east) to the apartment complex. Sample 2 was taken from the west side of the same storm channel from a 6" diameter storm drain daylighting into the larger trapezoidal channel. This drain collects surface runoff from the eastern edge of the apartment complex, but may also include seepage of shallow groundwater from the apartment complex fill material (unknown provenance). Sample 3 was taken mid-thalweg from Las Virgenes Creek approximate 300 m upstream of Agoura Road. Creek flows at this location are a blend of both native and urban runoff, including water from both the Sample 2 and Sample 3 sites described above. Sample 4 was taken from lower Cold Creek approximately ½ mile east of the intersection of Piuma and Malibu Canyon Roads. Flows in Cold Creek at this location include runoff from both undeveloped and urban areas. After adding nitric acid, samples were refrigerated and stored at the Tapia WRF laboratory and transported to Fruit Growers Laboratory (FGL) for metal assays on 17 November 2009. Mercury was not tested as the samples exceeded the permissible hold time of 28 days. Sample preparation followed EPA method 310; assays followed EPA inorganic method 200.7 (Al, Ca, Fe, Mg, K, Na, Sb) or 200.8 (As, Ba, Be, Bo, Cd, Cr, Co, Cu, Pb, Ni, Se, Ag, Th, Va, Zn). Assay QA/QC procedures: ICV - Initial Calibration Verification, analyzed to verify the instrument calibration is within criteria; ICB - Initial Calibration Blank, analyzed to verify the instrument baseline is within criteria; CCV - Continuing Calibration Verification, analyzed to verify the instrument calibration is within criteria; CCB - Continuing Calibration Blank, analyzed to verify the instrument baseline is within criteria; Blank, prepared to verify that the preparation process is not contributing contamination to the samples; LCS - Laboratory Control Standard/Sample, prepared to verify that the preparation process is not affecting analyte recovery; MS - Matrix Spikes - A random sample is spiked with a known amount of analyte. The recoveries are an indication of how that sample matrix affects analyte recovery. MSRPD - MS/MSD Relative Percent Difference (RPD), which provides an indication of precision for the preparation and analysis. All samples conformed to QA/AC procedures except for mercury as noted above.

Surface Water Quality. Publicly-available water quality data were compiled from 51 stations (Fig,1), sampled over the last 20 years by four independent monitoring programs as follows: (1) Long term (25+ year record depending on parameter) surface water quality data collected by the Las Virgenes Municipal Water District (LVMWD, District) for compliance with NPDES Permit No. CA0056014, monitoring and reporting program. Three stations located upstream of Tapia WRF in upper Malibu Creek watershed: Station R1 is located in upper Malibu Creek just above Tapia WRF, R9 is located in upper Malibu Creek below the confluence with Las Virgenes Creek, R6 (no longer monitored) is located in Las Virgenes Creek below the US 101 Freeway. For georeferences, US EPA laboratory and analytical method references and further details see Section VII(1)(A), p. T-18 in Tapia WRF Monitoring and Reporting Program No. CI-4760. (2) Long term (10 year) surface water quality data collected by the Heal the Bay (HtB) Stream Team available at http://www.healthebay.org/streamteam/data/chem/query and http://www.healthebay.org/assets/pdfdocs/streamteam/FieldGuide.pdf (methods). HtB Site 06: N 3780474.360, E 340884.363; HtB Site 07: N 3778803.136, E 3337860.582; HtB Site 08: N 3784968.235, E 339152.078; HtB Site 09: N 3783321.844, E 342649.395; HtB Site 13: N 3778446.110, E 342898.886; HtB Site 17: N 3776789.624, E 335111.025; Universal Transverse Mercator (Projection) Zone 11, North American Datum 1927. (3) Short term (2 yrs) recent surface water quality data collected by the Malibu Creek Watershed Monitoring Program (Rinehart and Medlen, 2006). Data, methods, and Quality Assurance Program Plan available at http://www.cityofcalabasas.com/environmental/water-resources.html or through the City of Calabasas. TDS data reported in that study were calculated by multiplying specific conductivity measured in the field by 0.60 on the recommendation of the Los Angeles Regional Water Quality Control Board (LARWQCB) (Rinehart & Medlen, 2006). However, simultaneous TDS/specific conductivity (SC) measurements of Malibu Creek and Las Virgenes Creek yielded an empirically-derived value of 0.87, which was used to estimate TDS from SC data in this study in the absence of TDS data. Carry (1996) reported an almost-identical ratio (0.86) of TDS/SC from M Fm. leachate in bench top reactors. (4) Short term (2 yrs) recent data on heavy metal and organic pollutants in surface waters of Malibu Creek collected by the LVMWD in compliance with the California Toxics Rule (CTR), available from the LARWQCB (Compliance file No. CI-8059 / CI-4760) or the authors. Our focus on surface water quality was limited to metals, inorganics (e.g. selenium, thallium), SC, sulfate and phosphorus, as M Fm. is known to be potentially enriched in these substances, and because the Los Angeles Region Water Quality Control Plan identifies water quality objectives for these constituents above which impairments occur to human and aquatic life beneficial uses.

<u>CTR testing.</u> Twelve metals, metalloids and inorganic compounds were tested monthly by the LVMWD from mid-2001 through 2002 from LVMWD station R1 (Fig. 1) on upper Malibu Creek below the confluence of Triunfo Creek immediately above the Tapia WRF following the methods specified in the California Toxics Rule (CTR) for inland dischargers (Tapia WRF NPDES permit,1997). Flows at this location are a blend of Triunfo Creek and Las Virgenes Creek, which drain both the Monterey Formation and Conejo Volcanics primarily, along with smaller percentages of the Chatsworth, Calabasas and Sespe Formations (Fig.1). 57 volatile pollutants and 13 pesticides were also tested, but none were detected in any sample above their minimum detection levels (MDL) over the 18 monthly surveys.

<u>Algae and Fish Tissue Elemental Analysis</u>. Five samples of macroalgae (*Cladophora glomerata* or *Rhizoclonium sp.)* were collected by G. Amah, a UCLA doctoral intern in residence at the LVMWD, in October 2000 at three locations in Malibu Creek below its confluence with Las Virgenes Creek (draining large areas of the Monterey Formation) and two locations below the confluence with Cold Creek (no known Monterey Formation drainage). The samples were tested by Wallace Laboratories (El Segundo, CA) for dry-weight tissue elemental composition (details available from authors). Only the results from station R1 are reported here. Fish tissue metal and trace element data were reviewed from the following sources: (1) Malibu Creek Watershed Monitoring Program (Rinehart and Medlen, 2006; Data, methods, and Quality Assurance Program Plan available at http://www.cityofcalabasas.com/environmental/water-resources.html or through the City of Calabasas or the authors). (2) Berry (1979). (3) Aquatic Bioassay and Consulting Laboratories testing for LVMWD Receiving Water Monitoring (1991, 1992 & 1995; available from authors). (4) Moeller *et al.* (1993).

<u>Hydrology</u>. Malibu Creek stream gage data were obtained from Los Angeles County Department of Public Works Water Resources Division (Station F130-R at Lat. 34.078, Long. -118.701) and the US Geological Survey (Station 11105510 – available electronically at http://waterdata.usgs.gov/ca/nwis/uv/?site_no=11105510). Precipitation data for the watershed were obtained from LVMWD's Tapia WRF weather station, located approximately 5 miles upstream of the mouth of Malibu Creek, and from the National Weather Service for the Los Angeles Civic Center (proxy for local rainfall in the absence of local records). These data were used to assess the effects of dilution via rainfall on creek mineral quality, specifically through the proxy of specific conductivity (SC) or as total dissolved solids (TDS), and on concentrations of sulfate, selenium, metals, phosphate and nitrogen, and to identify periods when Malibu Creek flows transition from surface runoff to groundwater drainage from higher elevations in the watershed.

<u>Data compilation - LVMWD Geographic Information System (GIS).</u> Geographic locations for all compiled water quality data were entered into the LVMWD GIS to calculate the percentage of M Fm. and other geologic formations exposed within their respective drainages. Dominant upstream geologic formations were determined visually in a GIS or by comparing area values when it was not obvious what formations had the first and second most surface area upstream from a monitoring point. The percent cover from each geologic formation in each watershed was calculated using geoprocessing tools. One caveat to this method is that the resulting percentages of each geological formation upstream of each sampling point is based on surface exposures; the actual influence of each formation will depend on their relative thicknesses and transmissivity, which are not shown in the geologic plates aside from occasional cross-sectional transects.

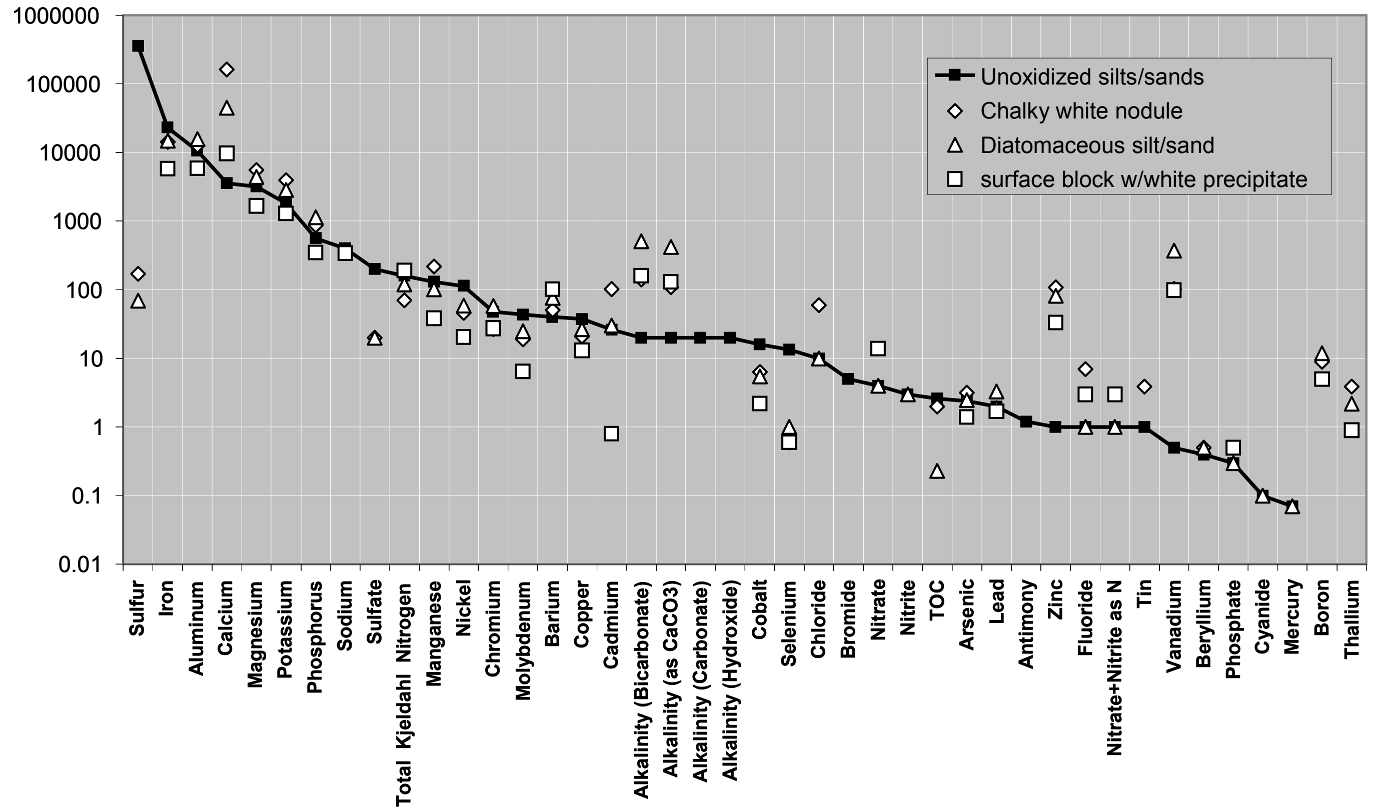
RESULTS

<u>Geology (Fig. 1).</u> The Monterey Formation accounts for 16.4 percent of the Malibu Creek watershed surface area, with higher percentages (33.7 – 56.2% per drainage) in the Creek's northern tributaries above the US 101 Freeway in the headwaters of Las Virgenes, Medea, Palo Comado, Cheeseboro and Lindero Creeks. These tributaries also had the highest levels of specific conductivity and TDS, phosphorus, sulfate, selenium and trace metals (see below). The northern section of the M Fm. in the Malibu Creek watershed extends east and west well beyond the watershed's boundaries into Ventura and Santa Barbara Counties to the west (with Calleguas Creek and the Santa Clara and Ventura Rivers being major drainages with M Fm. rock) and to the east along the northern slope of the Santa Monica Mountains draining to the upper Los Angeles River basin. Smaller exposures of the M Fm. occur in the lower watershed just east of Malibu Lagoon and in small coastal canyons west to Point Dume, including Solstice Creek and possibly Lachusa Creek.

<u>Elemental Composition of M Fm. rock (Figs. 2 & 3).</u> Figure 2 shows the composition of major and minor elements and some other constituents (TKN, sulfate, etc.) of four samples of freshly-exposed (graded) M Fm. rock from the upper watershed north of Thousand Oaks Blvd on undeveloped land in the foothills north of the City of Westlake Village (Fig 1. "Rock Sample" site). Of 34 elements tested, 13 varied across rock samples by 1-2 orders of magnitude in samples deliberately selected on the basis of large visual

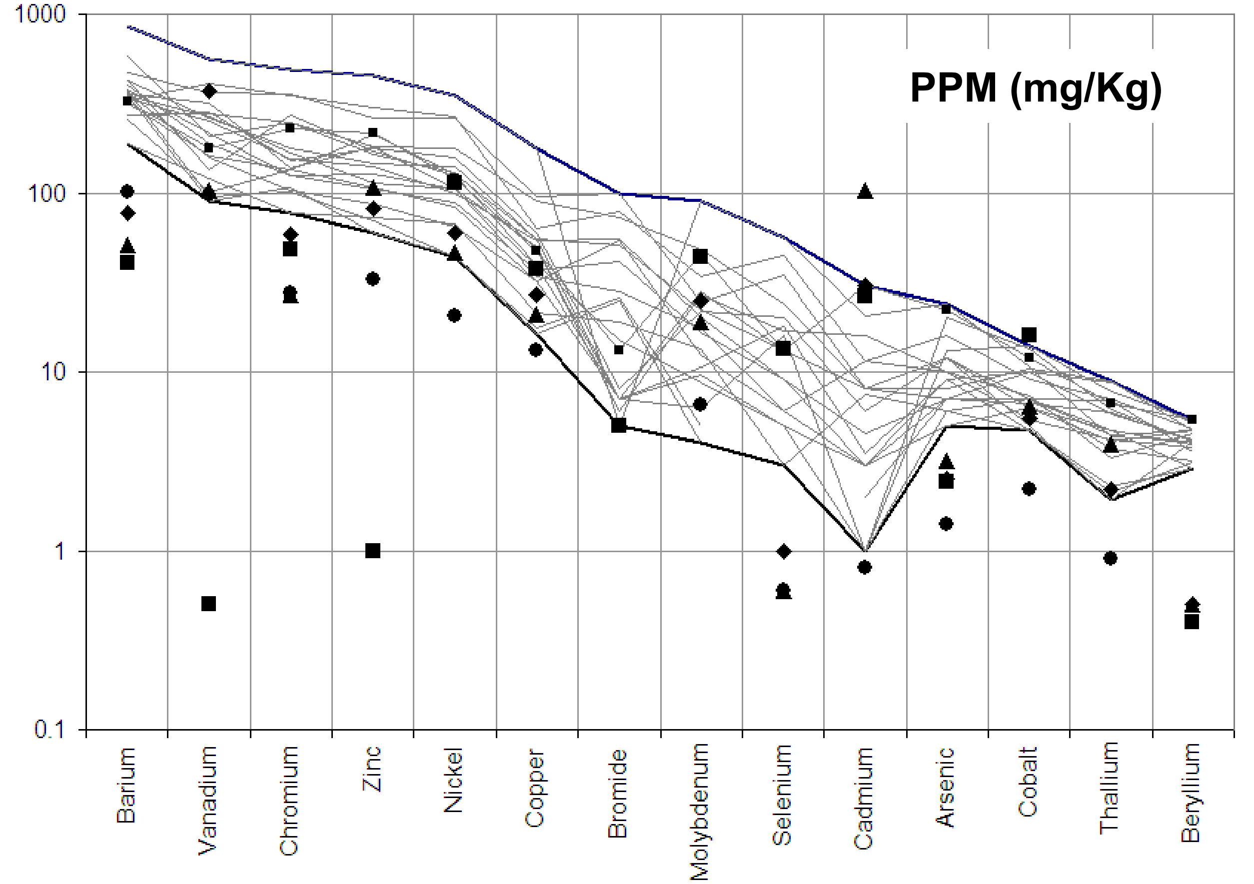
Fig. 2. Composition of unoxidized silts/sands vs oxidized rock in freshly exposed Monterey Formation rock (ppm)

Note 10x-100x differences in sulfur, calcium, sulfate, Cd, alkalinity, Co, Se, chloride, nitrate, TOC, Zn, Fl, Tin, Va, Bo, Th



differences in the field and widely separated stratigraphic sections. Both the magnitude of variation and the elements exhibiting it are consistent with their variability in exposures of the Monterey Formation in Santa Barbara County (Fig. 3, compiled from local data (this research) & Piper and Isaacs, 2001. However, with the exception of cadmium, samples of local M Fm rock tended to be lower in metals than in M Fm. rock sampled in Santa Barbara County, where the M Fm. is actively tapped for petroleum. Isaacs & Rullkötter (2001) used V/Ni ratios to categorize M Fm. rock samples by the estimated oxygen content of their depositional environment with values <0.35, 2-4 and > 6.5 corresponding to oxygen levels of 0.6, 0.15, and 0.05 mg/L dissolved oxygen, respectively. V/Ni ratios in our four samples were 0.004, 2.19, 4.76 and 6.25 over a stratigraphic interval of approximately 125 ft, with the smallest ratio at the base of the exposure and the largest ratios at the top. These results suggest that the depositional history of this exposure may have begun in a shallower, more oxygenated nearshore environment that moved further offshore into deeper, less oxygenated water over geologic timescales. This scenario is consistent with the paleotectonic reconstruction by Ingersoll (2008) for the M Fm. in the Santa Monica Mountains, with implications for the relative amounts of TOC, sulfate and phosphate enrichment in surface exposures of local M Fm. rock (see Discussion).

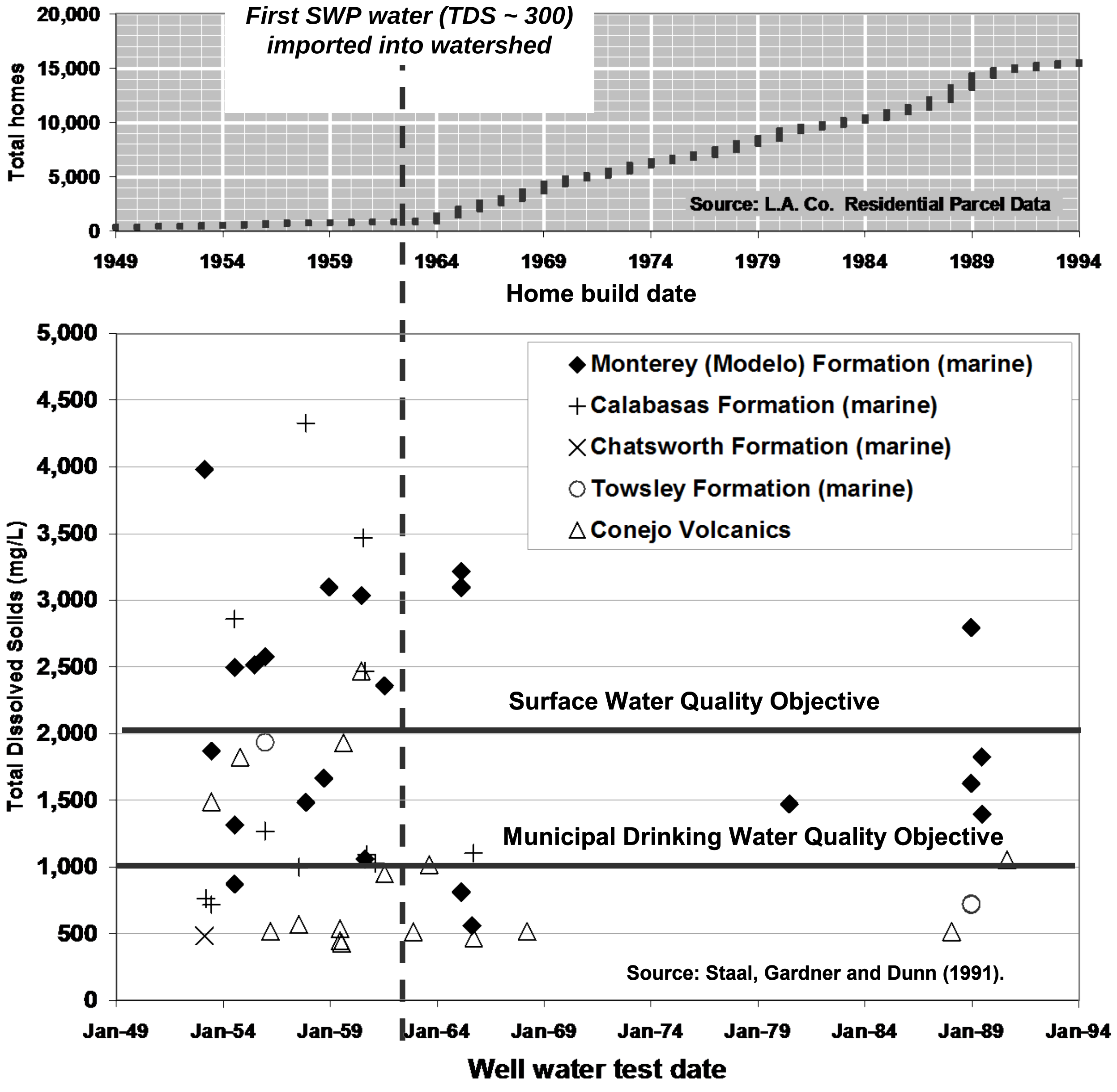
Fig. 3. Trace metal composition (ppm by weight) in MF rock from Malibu Creek watershed (dots) vs Santa Barbara County (lines) from Lion's Head & Naples Reef (from Pipers and Isaacs, 2001)



Dark lines = min. & max values for MF rock from S. Barbara Co., CA. Light grey lines = individual samples from same. Superimposed points = Local MF rock (▲= Chalky white nodules; ●= surface block w/white precipitate; ■ = siltstone; ◊ = diatomaceous silt/sand)

Groundwater Quality (Fig. 4). Historical well records indicate that TDS levels in excess of the 2,000 mg/L state groundwater quality objective were common in wells located within the M Fm., and were sometimes also exceeded in well water sampled from within other marine sedimentary formations and from the Conejo Volcanics. The majority of these samples were tested before the onset of urban development and the arrival of non-native SWP water in the 1960s (upper graph in Fig. 4), and are probably good indicators of native groundwater quality. Fig. 28 in Falco *et al.* (1976) shows the locations of well water exceeding water quality objectives (Los Angeles Region) for sulfates, nitrates, chlorides and TDS. Within the Malibu Creek watershed, 23 of the 27 wells exceeding the sulfate objective were located within M Fm. drainages with an additional four wells in Las Virgenes Creek within two miles downstream of the M Fm. Nitrate objectives were exceeded in 6 of 8 wells; these were also located within M Fm.-dominated drainages. One well with

Fig. 4. High TDS predates urban development & imported water. Total number of residential parcels (above) vs Total Dissolved Solids (TDS) in local well water (below). Lower legend: Well-water geology based on well site surface geology (Yerkes & Campbell, 2005); deeper wells sited close to the mapped margins of geological formations may have tapped other formations at depth.



water in excess of the sulfate objective was located in between Escondido and Ramirez creeks (small coastal streams west of Malibu Creek), where small surface exposures of the M Fm. are shown in Yerkes and Campbell (2005).

The only other information on M Fm.-influenced groundwater we could locate was an unpublished study by the Los Angeles County Sanitation Districts (Carry, 1996) of mineral leaching from native rock samples at the Los Angeles County's Calabasas Landfill. This site is located in the Monterey and Calabasas Formations north of the US 101 Freeway in the headwaters of Cheeseboro, Liberty Canyon, and Las Virgenes Creeks (western tributaries). The purpose of this study was to establish a baseline for natural background levels of potential landfill contaminants in local groundwater upgradient of potential landfill leachate. Tests of groundwater from landfill perimeter and sentinel wells found unusually high levels of compounds known to exist in Tertiary marine shales, suggesting a natural geologic source. To investigate this possibility, 34 pulverized subsurface rock samples from landfill barrier sites and grading exposures were placed in bench top reactors with deionized water, and tested for the resulting levels of leached solutes (e.g. major ions, trace metals, TDS) at monthly intervals for periods of up to 517 days. Comparison of their results with our first rain event testing of M Fm. rock ~ 5 miles west of the landfill is shown in Table 1. Our first rain event data, like those from the County study, show higher concentrations relative to those measured in rain-diluted urban runoff and local streams outside the M Fm. (i.e. Cold Creek), with similar rank order (by magnitude) from freshly exposed M Fm. Rock as were found for most constituents in the County tests. The County report also noted extremely high nitrate levels (>429 mg/L) from one reactor test of M Fm. rock (CA-205), high percentages of anions (2-3%) as nitrate (NO_3) in two others (CA-211, CA-212), and very high levels of Total Kjeldahl Nitrogen (TKN) from reactors CA-204 (120 mg/L TKN) and CA-205 (130 mg/L TKN). TKN levels in the M Fm. reactor tests are consistent with high levels of TKN found in local M Fm. rock (Fig. 2) and elevated NO_3 levels in upper Las Virgenes Creek (> 2 mg/L in from 1984 - 1997, LVMWD site R6 upstream of LVMWD spray fields; data not shown). With the exception of barium, copper and lead, metal concentrations in Carry's reactors after 517 days were higher than those in surface runoff from local M Fm. rock 9 hrs following a rain event in our first rain event tests (below). This result is consistent with the longer contact times in Carry's study, with two caveats: (1) Our first rain event samples of surface runoff from freshly-exposed M Fm. rock (below) undoubtedly also contained an unknown percentage of older groundwater that seeped from the face or base of the exposure during the rain event due to upgradient hydraulic pressure, as well as a "first flush" of surface precipitates; (2) Inspection of Carry's time series figures (Appendix B) shows that reactor solute levels generally equilibrated within ~60 days, suggesting that the lower levels of metals in our first rain event samples (assumed to represent surface runoff from the face of a fresh exposure of M Fm. Rock) are consistent with solute levels in groundwater in contact with M Fm. rock for < 60 days. Regardless, Carry's results demonstrate that local M Fm. rock is capable of generating groundwater with elevated levels of metals, nutrients and major ions consistent with those seen in M Fm.-dominated tributaries, much greater than those present in either urban runoff or native runoff from other formations in the watershed. Levels are similar to runoff in streams impacted by coal mining (Pond *et al.*, 2008 and Table 1).

First rain event results (Table 1, Fig.5). Twelve metals sampled from local M Fm. rock ("Rock Sample" site in Fig. 1) were also tested in runoff immediately downslope of the site approximately six hours after a small storm on October 9th, 2009, the first rain event of the 2009-10 wet season. Comparing their rank order in rock (Fig. 2) with their rank order in runoff (Table 1), the 6 most abundant metals in M Fm. rock were the same as the 6 most abundant metals in runoff from their surfaces. These levels were uniformly higher (as much as an order of magnitude) than those in urban runoff adjacent to the site or from residential parcels located within the M Fm. following the same rain event. This was also true comparing the levels of the same trace metals in two Malibu Creek tributaries with and without M Fm. rock (upper Las Virgenes Creek and lower Cold Creek, respectively). Metals in runoff from freshly exposed M Fm. were also much higher than those in runoff from weathered M Fm. rock, with the notable exception of boron, calcium, magnesium and sodium. Arsenic and cadmium levels were similar in runoff from both weathered and freshly exposed M Fm. rock.

CTR testing (Table 2). Twelve metals, metalloids and inorganics were detected in at least one monthly sample from mid-2001 through 2002 from LVMWD station R1, located about 100 m upstream of the Tapia Wastewater Reclamation Facility discharge. Also tested were 57 volatile pollutants and 13 pesticides, but none were detected in any sample above their minimum detection levels (MDL) over the 18 monthly surveys. In general, the most abundant metals (e.g. zinc, copper, nickel, chromium III, cadmium, lead, silver) and inorganics (e.g. selenium, antimony) in any given month were also the most-frequently detected throughout the 18 month sampling. Their concentrations were uniformly less than their concentrations in undiluted "first rain event" surface runoff from M Fm. rock following the first rainstorm of the 2009-10 wet season in 2009. Their concentrations were also uniformly more than those measured in 2009 from lower Cold Creek (no known M Fm. exposures). Their relative abundances in lower Malibu Creek generally mirrored their relative abundance in freshly-exposed M Fm. rock in the upper watershed above the 101

Table 1. First rinse results – metals and inorganics (all mg/L) in surficial runoff from MF rock in comparison to urban runoff, tributaries in both MF-drained and non-MF drained tributaries following October 9th 2009 rain event (columns 2-8), streams impacted by coal mining (column 9; mean values from Ponds et. al. 2008), and MF leachate in benchtop reactors (Cary, 1996). Highest values for each metal in first rinse tests are shown in **bold**. Blank cells = Not detected above PQL. nd = no data. See Data Sources for methods & site locations.

All values mg/L	Monterey formation surficial runoff			Urban runoff within MF		Creek		Coal mining impacted streams (Pond et. al. 2008)	MF leachate (Appendix A in Cary, 1996)	
	fresh exposure		weathered	T.O. blvd	Apartment complex	Las Virgenes Creek (MF)	Cold Creek (min MF)			
Site No.	1	2	5	3	6	4	7		min	max
Calcium	15	53	**318**	10	13	87	35	137.5	317	840
Iron	13	**40.3**	0.27	1.84	0.48	0.49	1.56	0.276	0.6	139
Zinc	0.08	**0.39**	0.02	0.08	0.08	0.07	0.02	0.01	0.77	22
Aluminum	11.4	**34.5**	0.03	1.72	0.28	0.36	0.93	0.096	4.6	123
Magnesium	6	19	**191**	2	2	30	13	122	17	577
Sodium	12	13	**392**	3	5	52	39	12.6	54	447
Potassium	2	12	**16**	2	2	7	4	9.9	2	18.7
Barium	0.0441	**0.378**	0.0277	0.0149	0.018	0.022	0.01	0.041	0.014	0.23
Vanadium	0.088	**0.205**	0.007	0.012	0.004	0.006	0.015	nd	nd	nd
Nickel	0.025	**0.111**	0.022	0.007	0.003	0.031	0.011	0.014	3	13
Copper	0.018	**0.068**	0.004	0.019	0.007	0.012	0.01	0.003	0.03	0.06
Chromium	0.028	**0.065**		0.004	0.006	0.002	0.004	nd	0.037	0.16
Cobalt	0.0033	**0.0319**	0.0033	0.0012	0.0004	0.0015	0.0015	nd	nd	nd
Cadmium	0.0035	**0.0215**	0.0002	0.0008		0.0015		nd	0.093	3.4
Lead	0.0032	**0.0212**	0.0004	0.0011	0.0007	0.0022	0.0007	0.0012	0.002	0.005
Arsenic	0.004	**0.013**	0.006	0.002		0.002	0.002	nd	0.003	0.06
Selenium		0.004			0.003	**0.007**		0.011	0.020	1.400
Beryllium	0.0004	**0.0032**						nd	nd	nd
Antimony	0.001	**0.003**		0.002	0.001	0.001		nd	nd	nd
Thallium	0.0003	**0.0017**						nd	nd	nd
Boron	0.001	0.001		0.001	0.001			nd	0.24	1.6
Tin								nd	nd	nd
Silver		**0.001**						nd	<0.01	0.011

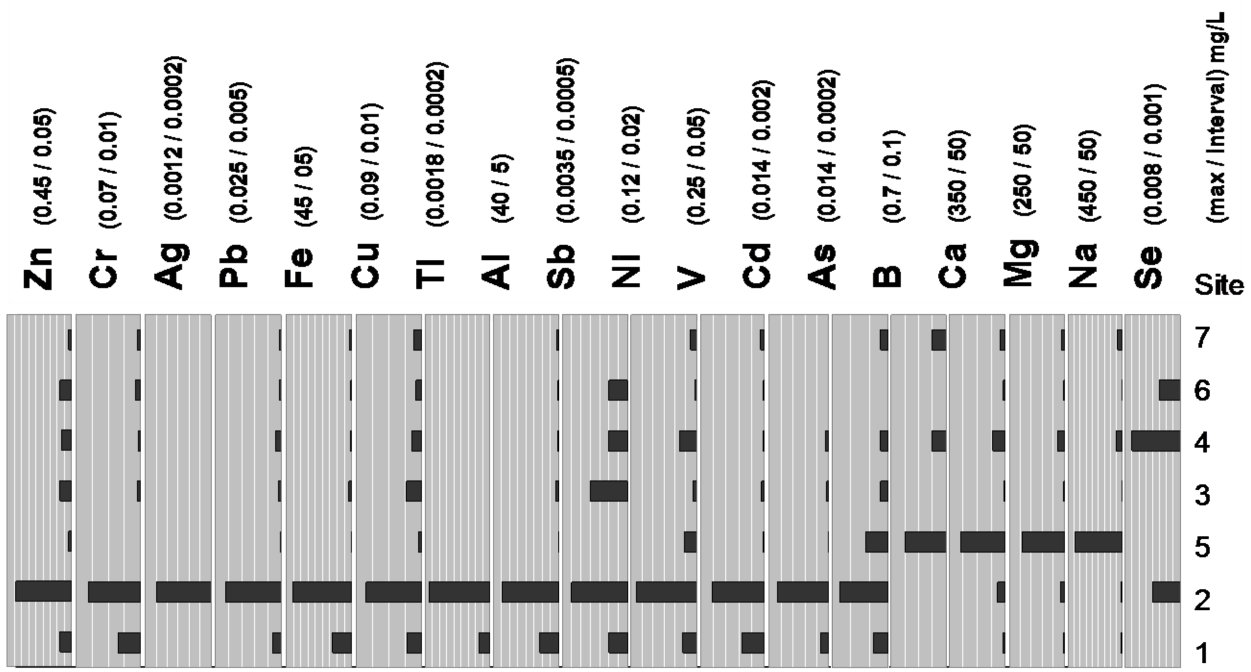


Fig. 5 . Relative abundances of metals and trace elements in surficial runoff from various sites and landuse ~6 hrs following 10/14/09 rain event (mg/L). All results in mg/L, but note scale varies by element (max value & grid line interval shown in parentheses). Sites: 1 & 2 = Freshly exposed MF runoff; 3 = Street runoff adjacent Site 2; 4 = Las Virgenes Creek downstream of sites 2 & 3; 5 = weathered MF runoff; 6 = Residential runoff adjacent Site 5; 7 = Cold Creek reference site (outside MF).

freeway, just east of the Los Angeles County line ("rock sample" site in Fig. 1). Maximum concentrations of most but not all metals in the lower creek generally occurred in late summer prior to the onset of wet weather, when flows consist almost entirely of groundwater baseflow (data in **bold** in Table 2). Conversely, the frequency of non-detection tended to peak in spring during the latter half of the wet season (Nov – May), when dilution from winter rains is greatest.

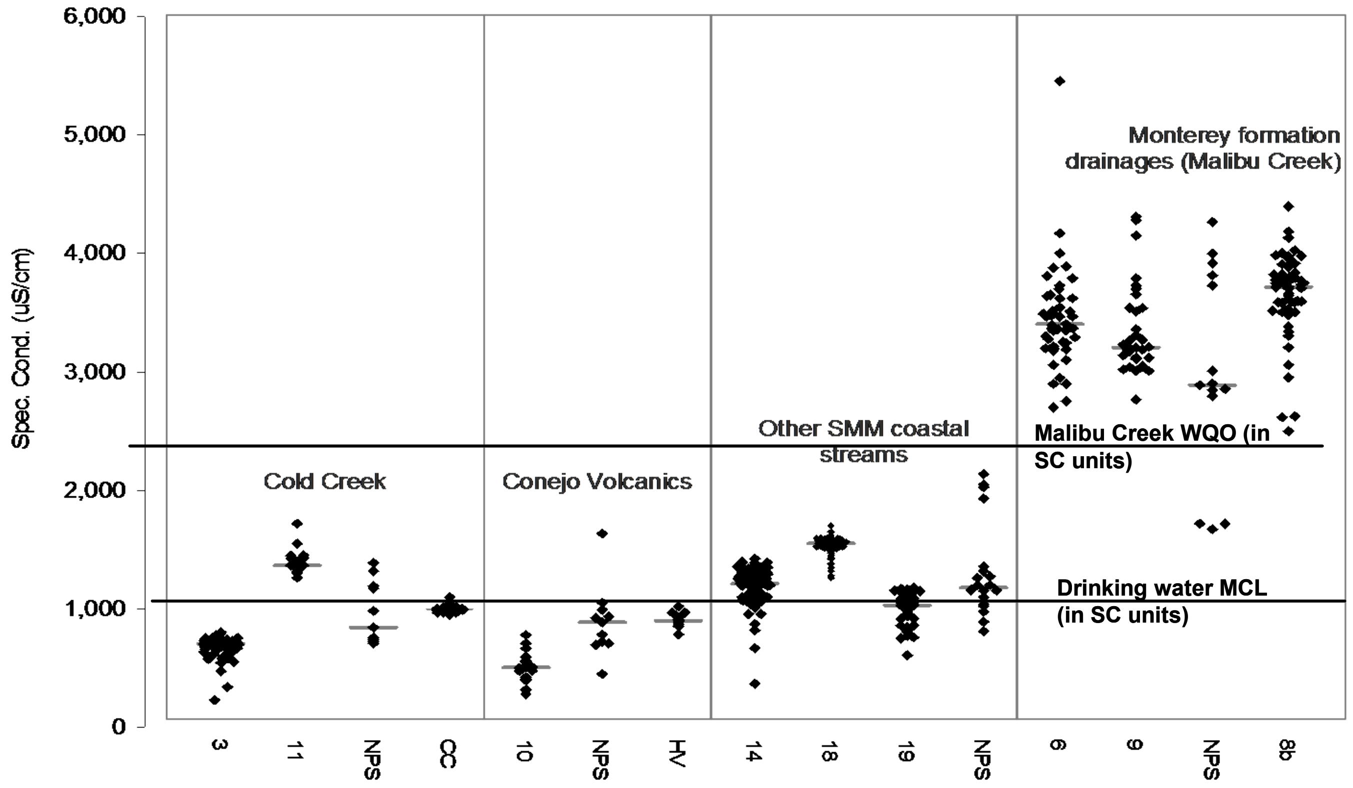
Table 2. Metals (mg/L) in upper Malibu Creek below Triunfo Creek confluence (LVMWD CTR Site R1). Highest annual values for each metal shown in **bold**. Blank cells = Not detected above MDL. See Data Sources for methods & site location.

CTR (inorganics, mg/L)	2001						2002											
	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Thallium																		
Mercury																		
Silver			**0.9**	0.62														
Arsenic	2.1			**3**													**3**	
Lead				0.9	**1.5**		0.7						**3.6**				1.5	2
Cadmium			0.2	0.7	**0.8**	0.3		0.4	0.3		0.3		**0.5**			0.3		0.4
Antimony				**0.9**	0.8	0.6	0.8	0.6	0.7		0.6	0.7		0.6		0.8		0.8
Selenium	11	11		**13**	7	10		10	10	6	8	11	7	7	10	10	**12**	6
Chromium-III			1.2	2	**3**	1	1	1	**3**	2	1	1	1	2	1	1	**3**	1
Nickel	6.8	7.3		8	**10**	6	5	6	**11**	9	5	5	5	7	7	8	10	8
Zinc	3.6	22	2.8	**39**	30	20	40	10	20	20	10	10	10	10	10	20	**60**	20
Copper	2.7	**11.1**	1.2	4	11	4	5	4	7	5	5	4	6	4	4	13	**21**	14
pH	8.1	8	8	7.9	8.2	8	8.2	8.3	8.4	8.1	7.8	8	7.8	7.8	7.8	7.8	7.9	7.8
Hardness (mg/L as CaC03)	1475	1190	1300	1350	1140	1084	1044	1064	1039	1098	1186	1245	1315	1390	1460	1490	1480	1150

Specific conductivity (SC) (Figs. 6-8). Malibu Creek specific conductivity was the highest of any measured among Santa Monica Mountain (SMM) coastal streams. It was brackish year-round (SC > 1,500 µS/cm; Masters and Ela, 2007) over the 1998 – 2009 period of record from its highest northern tributaries in the foothills north of the 101 freeway to its lower reaches in the City of Malibu, except during large rain events, when SC fell to ~1,200 µS/cm (Fig. 6). Average SC from 1998 to 2009 ranged from ~3,300 µS/cm in the creek's northern headwaters (range 2,150 - 5,200 µS/cm at HtB stations 6-9, Lindero Creek station 1 (LIN1), Medea Creek station 1 (MED1), Liberty Canyon Creek station 1(LC)) to ~1,890 µS/cm (range 1,090 to 3,690) in the lower creek about ½ mile above Malibu Lagoon (station 1 in Fig. 1). Even during three large rain events in February 2001, 2005 and 2009, SC in Malibu Creek did not fall below 1,200 µS/cm at any station (Fig. 7). Two tributaries to Malibu Creek, Carlisle Creek and upper Cold Creek (located on the western and eastern limits of the watershed, respectively) are exceptions to the high SC levels and large seasonal variation_found in other tributaries to Malibu Creek. They drain areas with no known exposures of the M Fm. (Fig. 1). Carlisle Creek's drainage consists almost entirely of Conejo Volcanics with average SC of 510 µS/cm (range 272 – 780). Mean SC in upper Cold Creek (which drains primarily the Conejo Volcanics and Topanga Canyon and Calabasas Formations) was 686 µS/cm (range 230 – 762) from 1998 -2009. Cold Creek SC was similar to SC in Arroyo Sesquit Creek, a small coastal drainage with no known Monterey Formation exposures, where mean SC during 1998 – 2009 was 989 µS/cm (range 752 – 1,162). Mean SC was higher in two other SMM creeks (Lachusa and Solstice Creeks) that drain some M Fm. rock.

There is a strong seasonal component to SC in Malibu Creek, peaking at the end of the dry season in any given year. From 1998 to 2009, SC in the lower reaches below Rindge Dam peaked in Sept – early November at between 2,200 to 2,700 µS/cm, depending on the year. Late summer SC levels in the upper creek and its northern tributaries was significantly higher than SC in non-M Fm. tributaries (T-test, 0.05

Fig. 6. Specific conductivity (µs/cm) in Malibu Creek watershed and adjacent Santa Monica Mountain coastal streams by drainage geology. Median SC shown by cross (+). See Fig. 1 for site locations and data provenance. Drinking water MCL (1,000 mg/L TDS) and Malibu Creek Water Quality Objective (WQO) (2,000 mg/L TDS) were converted to SC by dividing TDS by empirically-derived 0.86; See text, Data Sources, Surface Water Quality.



rejection criteria), with peak values >3,500 µS/cm. For comparison, SC in municipal potable and recycled water in the watershed rarely exceeds about 300 and 800 µS/cm, respectively (LVMWD records). An unusual exception to the seasonal trend was observed in the winter of 1999, when SC rose abruptly to very high levels at three stations in Medea, Palo Comado and upper Las Virgenes Creeks following a very small rain event (Fig. 7). This rise in SC immediately following a small rain event was also recorded in 2009 in a small eastern tributary to Las Virgenes Creek following the Oct. 9th, rain event during the first rain event testing.

Fig. 7. Specific Conductivity (µS/cm) (a) vs rain events in Malibu Creek and major tributaries (b). Rain events = spikes in gaged streamflows (R-107) shown in (b). SC in lower Malibu Creek below its confluence with Cold Creek is inbetween the higher SC from MF-fed northern tributaries and lower SC in Cold Creek (minimal MF drainage). Note drop in Cold Creek SC following three large rain events in 2001, 2004 and 2008, and increase in SC in Malibu Creek & MF-fed tributaries following very small rain events in the dry winter of 1999.

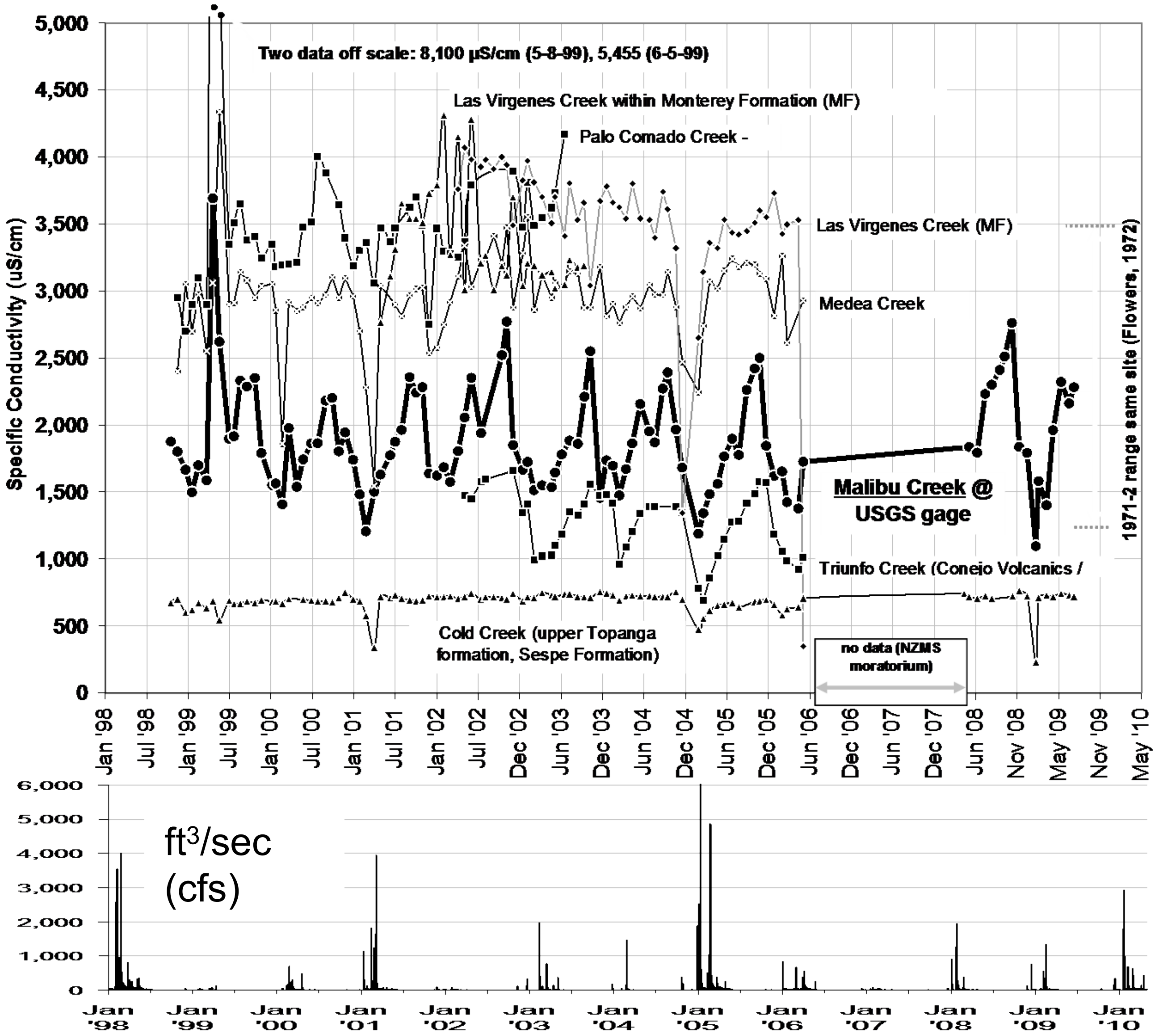
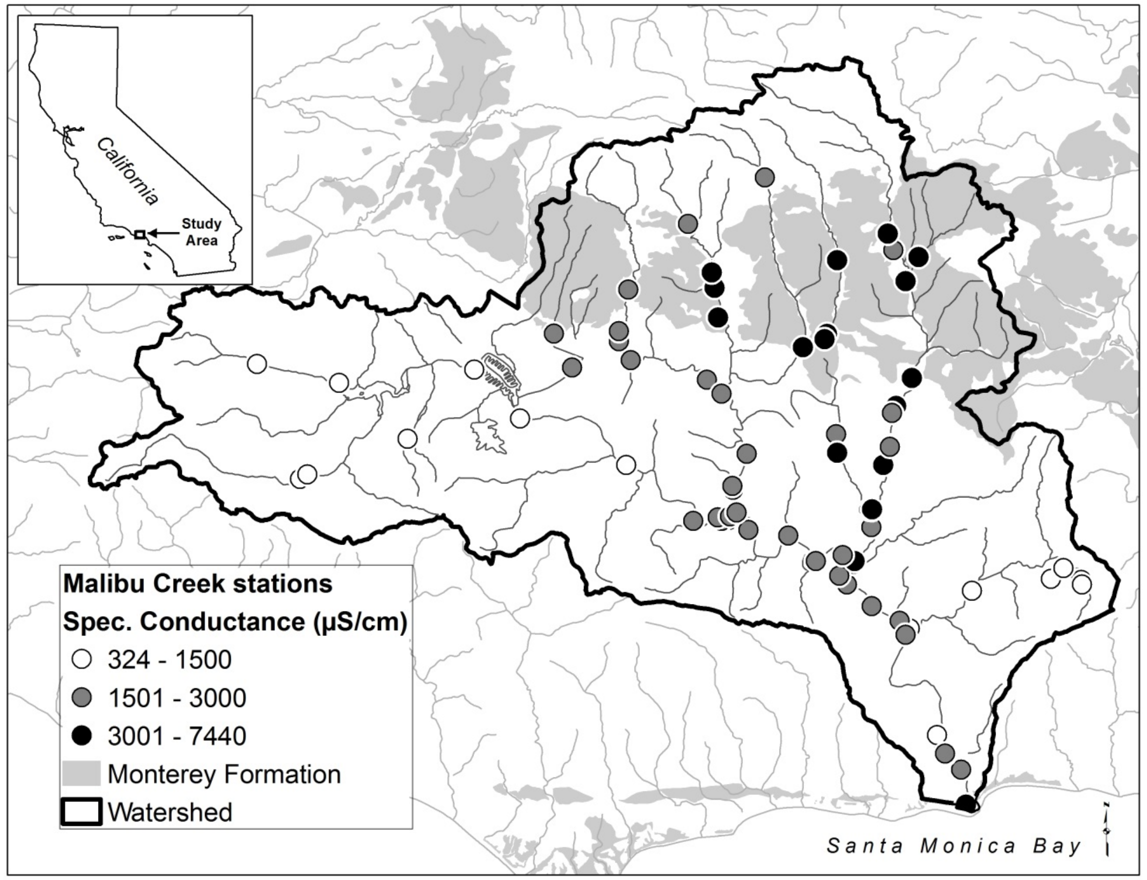
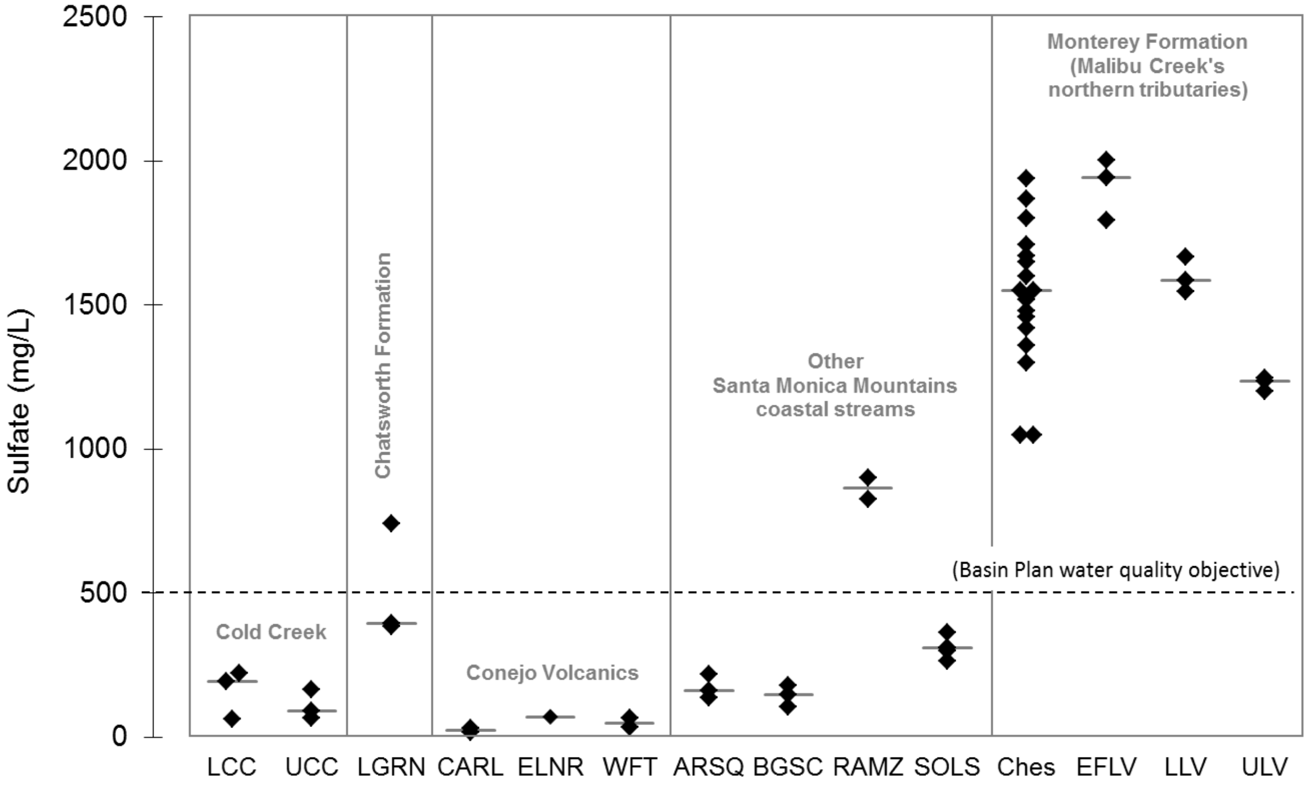


Fig. 8. Average Specific Conductivity (µS/cm) in Malibu Creek and major tributaries in relation to MF rock, 1998 - 2009. Note low SC in east and west subdrainages (= Cold Creek and Carlise Creek, respectively) with minimal MF rock. See Fig. 1 for station ID's



Sulfate (SO_4) (Figs. 9 & 10). Sulfate levels in the Malibu Creek watershed generally mirrored SC values with respect to seasonal trends and associations with drainage geology (Fig. 9). All Malibu Creek tributaries draining the M Fm. exceeded the Los Angeles Region Water Quality Control Plan (Basin Plan) of 500 mg/L; none of the tributaries without M Fm. rock did. The lower reaches of Malibu Creek (receiving both M Fm. and non-M Fm. drainage) oscillated seasonally (not shown) from about 350 mg/L in the wet season, rising to levels >1,000 mg/L by late summer. The only available time series data on major ion composition in surface waters (Fig. 10) was for Cheeseboro Creek, a northern Malibu Creek tributary draining the Monterey and Calabasas Formations. These data were collected by the Los Angeles County Sanitation Districts from 1999 (one sample) and from 2002 – 2009. Sulfate levels in these samples were very high, constituting 68% - 72% of the total major anions and 43% - 55% of the TDS, which ranged from 2127 - 4048 mg/L. Calcium and magnesium constituted the large majority of the cations, each being about 45% of the total. For comparison, the concentration of sulfate, calcium and magnesium in this M Fm. dominated creek is over an order of magnitude higher than that found in imported SWP water. The major ions in SWP are sodium and chloride, levels of which in Cheeseboro Creek were less than 8% of TDS.

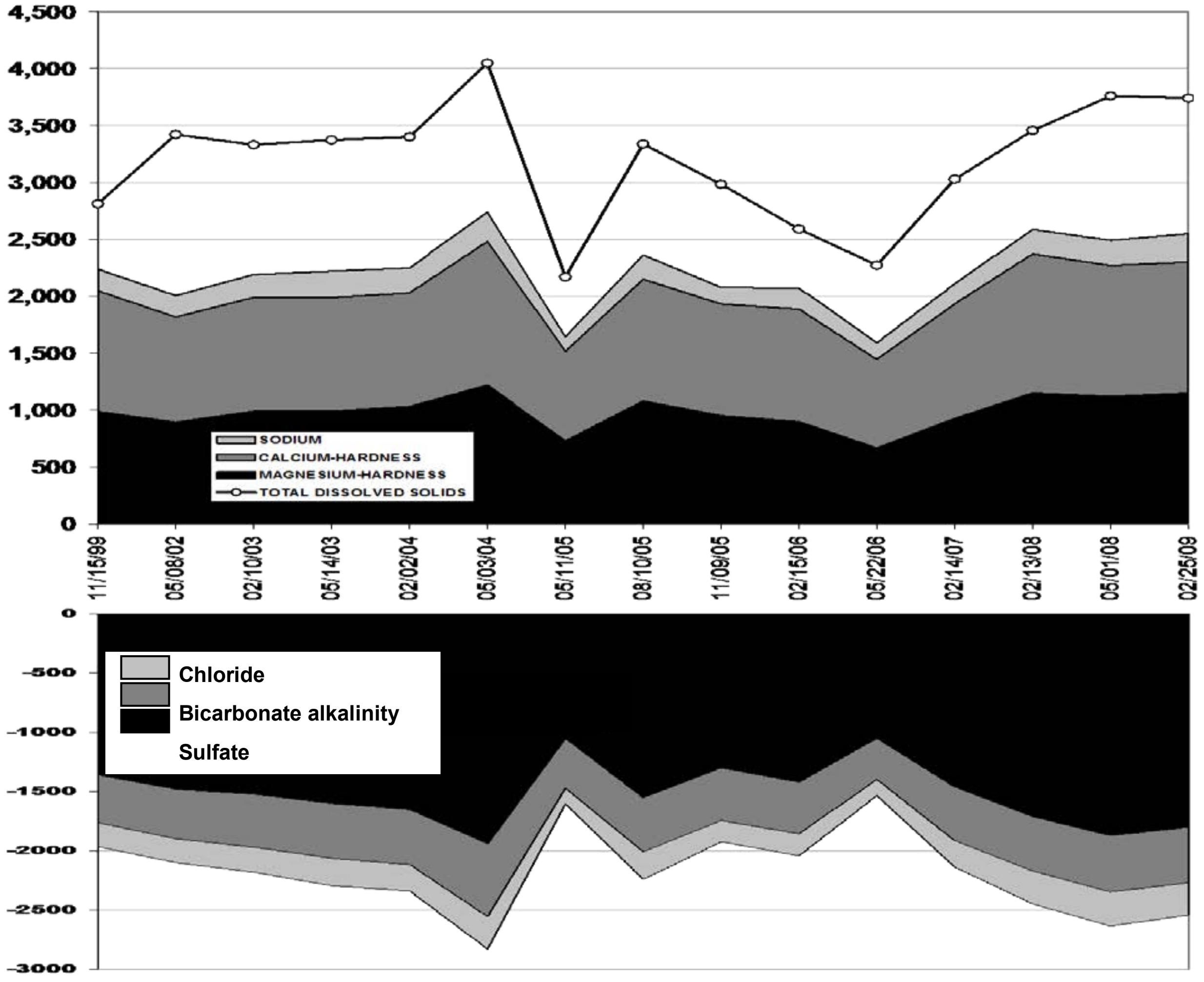
Fig. 9. Sulfate (mg/L)in Malibu Creek and its tributary streams and adjacent Santa Monica Mountain coastal streams by drainage geology. Bars = median value. See Fig. 1 for sample locations and text (Data Sources) for stream abbreviations and data provenance.



Phosphorus (P) (Fig. 11). As for sulfate, phosphorus levels in the Malibu Creek watershed generally mirrored SC values with respect to seasonal trends and associations with drainage geology. Malibu Creek tributaries within the M Fm. such as upper Las Virgenes Creek and Medea, Palo Comado and Cheeseboro Creeks consistently exceeded the 0.1 mg/L summertime phosphorus target established by the US EPA, including sites located in undeveloped State and National Park Service lands. EPA phosphorus targets were also usually exceeded in Malibu Creek and those tributaries and stream reaches located outside of the M Fm. but receiving significant volumes of water from M Fm. drainages (e.g. lower Las Virgenes Creek, Triunfo Creek). In contrast, exceedances of the TMDL target rarely occurred in adjacent coastal streams or Malibu Creek tributaries located outside the M Fm. (e.g. Cold Creek, Carlisle Creek). Those coastal streams where the TMDL target was exceeded had mapped exposures of M Fm. rock (Fig.1).

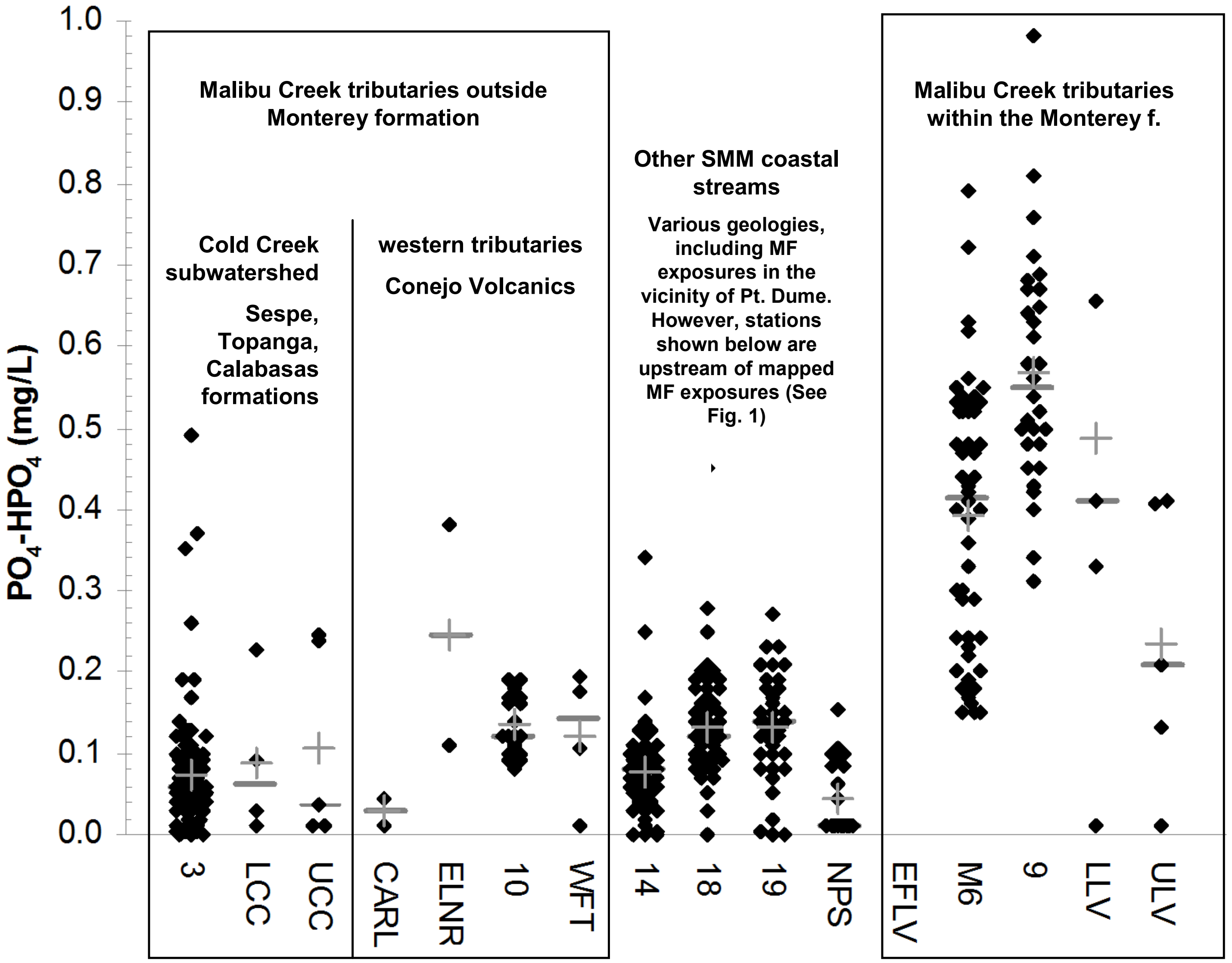
Algae and Fish Tissue Elemental Analysis. The earliest studies of metals in Malibu Creek fishes focused on potential impacts from discharges from the Tapia WRF by comparing their levels in downstream fishes with simultaneous collections upstream of the Tapia discharge (Berry, 1979; ABC Labs, 1991, 1992 & 1995; Moeller *et al.* 2003). One consequence of this study design is that stations upstream of Tapia receive significant volumes of water from M Fm.-drained northern tributaries, and so provide some information its potential downstream effects on the fish species that constitute the creek's highest instream trophic levels. Moeller *et al.* (1993) found that silver,

Fig. 10 . TDS (line in upper graph), major cations (above) & anions (below) in Cheseboro Creek, northern tributary to Malibu Creek draining MF rock (mg/L). Data courtesy Los Angeles County Dept. Public Works (O. Galang). See Fig. 1 for site location.



chromium, copper, lead and selenium in fishes sampled above the treatment facility discharge were consistently higher than those below in these studies and, as for instream concentrations (Table 1), their relative abundance in fish tissue generally mirrored their abundance in local M Fm. rock and M Fm. surface runoff better than their relative abundances in street and residential urban runoff (Table 1, Fig. 3). As for aquatic macroinvertebrate metrics (lower in high SC sites), Aquatic Bioassay Consulting Laboratories (1992) found that, with the exception of copper, all detected metals in fathead minnows (*Pimephales promelas)* were higher above the Tapia WRF than below, as was SC and water hardness measured on the date sampled (Oct. 22, 1992). Thus the release of treated, recycled SWP with lower to non-detectable levels of metals is apparent in the metal content of upstream versus downstream fathead minnows separated by less than 700 m. An interesting anomaly in their results along with those of Berry (1979) and Aquatic Bioassay Consulting Laboratories (1991, 1993, 1995) was the non-detection of nickel (Ni). This result was unexpected given the elevated levels of Ni in M Fm. rock (Fig. 3), groundwater (Table 1) and M Fm.-drained tributaries (Fig. 5) that constitute a major

Fig. 11. Phosphate (mg/L) in Malibu Creek tributary streams and adjacent Santa Monica Mountain coastal streams by drainage geology. Bars = median value. Cross (+) mean value. See Fig. 1 for sample locations and text (Data Sources, Surface Water Quality) for data provenance. TMDL summer target (April 15 - Nov. 15) shown by dotted line. Results for east fork Las Virgenes creek (EFLV) are off-scale (1.85, 2.97, 3.83, 4.24, 5.03,; mean = 3.58).



fraction of stream flows at this site. However, Rinehart and Medlen (2006) found Ni levels of 0.06 and 0.17 ppb wet weight, respectively, in common carp and green sunfish sampled further downstream in Malibu Creek (Site R3 in Fig. 1) in 2005. They also found higher levels of Ni and other metals (As, Cd, Cr, Cu, Pb, Hg, Se, Ag & Zn) in arroyo chub, fathead minnow and green sunfish in M Fm.-drained tributaries sampled further upstream (i.e. upper Las Virgenes, Lindero and Medea Creeks), consistent with their higher levels in M Fm.-drained versus non M Fm.-drained tributary streams (Table 1).

DISCUSSION

The observation that a watershed's geology can influence its surface and groundwater quality is one of the oldest recorded principles of hydrology (Karaji, 1000). However, it is only within the last decade that geologically relevant water quality data such as specific conductivity (SC), major and minor ion composition, TDS, and metals have been compiled for streams and rivers across eco-region scales through the US Geological Survey National Water Quality Assessment (http://water.usgs.gov/nawqa/about.html). These data have quickly proven their utility across multiple trophic levels and taxonomic categories as predictors of species composition and community structure.

In benthic freshwater algal diatoms, for example, Potapova and Charles (2003) found that SC and the relative abundances of major ions (HCO^{-}_{3} + CO^{2-}_{3}, Cl^{-}, SO^{2-}_{4}, $Ca^{2+,}$ $Mg^{2+,}$ Na^{+}, K^{+}) explained a statistically significant amount of variance in the species composition of 3,239 benthic diatom samples from 1,109 US rivers, with additional subgroups sorting on various combinations of these parameters, such as the proportion of individual cations and anions, and the ratio of monovalent to divalent cations. They also identified ranges and optimal values for these parameters for 191 diatom taxa, noting their potential utility as indicator values in water quality assessments. We found good agreement with their upper SC and major ion ranges and benthic diatom abundance and species composition in Malibu Creek. SC in lower Malibu Creek below the Los Angeles County gaging station oscillates seasonally between ~1,200 µS/cm after winter rain events, to ~ 2,300 – 2,700 in the late summer (Fig. 7). This range is optimal for *Pleurosira laevis* (Potapova & Charles, 2003), a cosmopolitan species of diatom that favors brackish waters (El-Awamri, 2008). In Malibu creek this species numerically dominates the benthic diatom community in summer. It also favors waters with extremely high levels of magnesium (Mg), Chloride (Cl) and potassium (K) (*ibid.*), which are also present in very high levels in the Malibu Creek watershed in M Fm.-drained tributaries (Fig. 10 & Table 1). Anaerobic conditions in stream sediments underneath *Pleurosira*-dominated algal mats are common in Malibu Creek in the summer (authors' pers. obs.), and high sulfate levels (also from M Fm.-drained tributaries; Fig. 9) appear to favor sulfate-reducing bacteria that decompose organic detritus from the overlying algal mat, producing metabolic H_2S gas. Disturbing this layer releases this sulfurous gas at concentrations easily sensible to fieldworkers (Dagit *et al.*, 2009). Aside from *Pleurosira,* nine other genera of benthic diatoms have been identified in Malibu Creek (i.e. *Melosira, Nitzchia, Navicula, Achnanthes, Cocconeis, Gomphonema, Gyrosigma, synedra, Fragillaria;* Chapman, 1980), and while they were not identified to species, all nine genera include one or more species favoring high SC streams with high levels of HCO^{-}_{3} + CO^{2-}_{3}, Cl^{-}, SO^{2-}_{4}, $Ca^{2+,}$ $Mg^{2+,}$ Na^{+}, and K^{+} (Potapova & Charles, 2003).

Turning to stream macroalgae, in New Zealand, Biggs (2000) found a similar relationship between SC, algal biomass and algal species composition in freshwater periphyton and macrophytes, with *Cladophora glomerata* and *Rhizoclonium*-dominated algal communities favoring high SC habitats (mean SC 3100 and 2700, respectively). In Malibu Creek these two cosmopolitan algal species form large, floating algal mats every summer, coinciding with the period when SC rises to the same range observed in streams dominated by these algae in New Zealand (Fig. 7). Noting the relevance of geology to his findings, Biggs observed that the presence of high-SC, nutrient-rich Tertiary marine siltstones in New Zealand streams might preclude efforts to control nuisance algal growth in those watersheds where they occur. In Malibu Creek the high SC (Fig. 6), phosphate-rich (Fig. 2, 11) water from Tertiary marine M Fm. sustains both SC and phosphate concentrations downstream at levels that are optimal for these species, and as in *Cladophora* and *Rhizoclonium* dominated New Zealand streams, these naturally optimal conditions will likely frustrate efforts to limit their growth in Malibu Creek to levels acceptable to the public, especially in the summer when SC peaks. *Cladophora* and *Rhizoclonium* mats remain common in the lower creek every summer (except for a short mid-summer decline in *Cladophora* when stream temperatures exceed 22-24C) despite termination of flows from the Tapia WRF for seven months beginning April 15th each year since 1999 (CH2M Hill, 2000, and pers. obs. RDO). No mention of the Monterey Formation or its impacts on SC (Figs. 6-8) or phosphorus levels (Fig. 11) in Malibu Creek is found in the US EPA Nutrient Total Maximum Daily Load (TMDL) regulations or technical support documents, which used a national guidance target of 0.1 mg/L phosphate in establishing a summertime numeric phosphorus target for Malibu Creek (US EPA, 2000). Average phosphate levels in M Fm.-dominated tributaries to Malibu Creek consistently exceed the 0.1 mg/L target (range from 0.41 to 1.62 mg/L), and exceedances are also common in Malibu Creek and other coastal drainages where M Fm. rock occurs (Figs. 1 & 11).

Unusually high SC and phosphate levels in Malibu Creek's northern tributaries have been noted in several studies (Busse *et al.*, 2003; Luce, 2003; Luce & Abramson, 2005; Stein & Yoon, 2007), all of which attempted to use monitoring sites upstream of urban development in these creeks as natural reference sites for the lower watershed, but had difficulty reconciling their results with those from upper Cold Creek, an eastern tributary to Malibu Creek that is also commonly used as a natural reference site for the lower watershed. Our research reconciles their findings by demonstrating that high levels of SC and phosphate (along with sulfate, selenium and many metals) are clearly associated with large exposures of M Fm. rock in the northern tributaries, versus little to no M Fm. rock in upper Cold Creek or Malibu Creek's western tributaries (e.g. Carlisle Creek). In their regional natural sources study, Stein and Yoon (2007) noted higher SC and P levels in reference sites dominated by sedimentary rock in comparison with igneous rock, but did not sort these sites according to the percentage of M Fm. or other petroleum source rock in their respective drainages.

Moving from algae to aquatic invertebrates, a large body of literature has linked macroinvertebrate species assemblages with the ionic composition of the streams they inhabit (reviewed by Goodfellow *et al.*, 2000), with significant impacts on aquatic macroinvertebrates in watersheds draining petroleum source rocks or coal (Pond *et al.* 2008). These findings are potentially important in a regulatory context in southern California, where petroleum source rock is abundant and where aquatic macroinvertebrate assessments have recently been added to water quality testing required of municipal wastewater treatment facilities. The utility of this approach in Malibu Creek rests on the ability to separate the effects of human impacts from natural controls on water quality, which may be difficult absent more detailed information on the effects of local geology on water quality generally, and petroleum source rock in particular.

In Malibu Creek, for example, Luce (2003) found SC was negatively correlated to all benthic macroinvertebrate (BMI) metrics, except percent dominant species (significant positive relationship) and percent filterers (no significant relationship). She also noted that her natural reference sites R6 and R9 (both located in the M Fm.) had higher SC than her other reference sites, slightly higher diatom cover, and lower values of taxa richness, EPT richness, EPT index, sensitive EPT index, percent intolerant species and percent shredders, especially at site R9. She attributed elevated SC and phosphate levels at these sites to geologic or unknown groundwater inputs to the creek, noting (Luce & Abramson, 2005) that these sites were downstream from the Los Angeles county landfill and an abandoned nursery, respectively. However, Carry (1996) demonstrated that high SC and phosphate levels in the vicinity of the landfill are associated with M Fm. rock (summarized in our groundwater results), and potential groundwater inputs of phosphate from a nursery abandoned over 40 years ago (LVMWD records) cannot account for elevated levels of phosphate (along with other constituents enriched in M Fm. rock) in adjacent tributaries within the M Fm. M Fm. rock in other California counties has been mined for phosphorus (see Introduction), and together with our ground and surface water quality results from M Fm.-drained tributaries we believe the simplest explanation for elevated phosphate, sulfate, metals and SC in Malibu Creek's headwaters is drainage from the M Fm.

Very poor BMI metrics in the Malibu Creek watershed were also associated with all high SC sites in macroinvertebrate bioassessments performed by the Aquatic Bioassay and Consulting Laboratories (ABC Labs, 2007). In this survey, the best BMI scores (southern California Index of Biological Integrity, IBI) occurred at two sites (LVMWD R2 & R13) where high upstream SC water (> 3,000 μS/cm) from M Fm.-drained tributaries is diluted by treated SWP wastewater from the Tapia WRF (SC 470 – 630 μS/cm), and low SC water from Cold Creek (SC ~ 1,270 μS/cm), yielding the creek's lowest SC of between 1,200 μS/cm (spring) and – 2,300 μS/cm (late summer) (Fig. 7). Likewise, in 2005 the only site in Malibu Creek receiving a "fair" southern California macroinvertebrate IBI score was in the lower watershed (Site R4 in Fig. 1) in the spring, before SC rapidly rose above 1,700 μS/cm and well before it peaked at 2,500 μS/cm in late summer (Fig. 7), when its IBI rating fell to "poor." Reviewing the development of the southern California IBI for benthic macroinvertebrates (Ode *et al.*, 2005) it does not appear that differences in IBI metrics were examined between reference watersheds with and without petroleum source rock such as the M Fm. (versus watersheds with and without sedimentary rock in general). However, in US EPA sponsored research on the effects of mountaintop coal mining on downstream water quality and macroinvertebrates in West Virginia streams, Pond *et al.* (2008) found statistically-significant negative correlations between all eight indices of macroinvertebrate community health and concentrations of sulfate (mean 696, max 1520 mg/L in their study), selenium (mean 0.011, max 0.037 mg/L) and various metals (e.g. Ca, Cl, Mg K, Na) at levels equal to or less than those measured from M Fm. in the Malibu Creek watershed (Table 1, Fig. 10). Thus, for these constituents, water quality in runoff from the M Fm. in the Malibu Creek watershed is comparable to that in streams impacted by drainage from coal mining in West Virginia, and might be expected to have similar impacts on their respective macroinvertebrate communities. These levels may also favor invasive macroinvertebrates adapted to these conditions, out-competing colonization by native species less adapted to high mineral waters from adjacent creeks or nearby watersheds. Herbst (2008), for example, recently demonstrated that low specific conductivity (SC < 200 μS/cm) and low calcium concentrations limit growth and survival of the invasive New Zealand mudsnail (*Potamopyrgus antipodarum)* in the upper Owens River (CA), which may explain its success in high conductivity and high calcium (600 – 1000 mg/L; Fig. 10) northern headwaters to Malibu Creek, where it first became established before colonizing downstream sites (Abramson, 2009).

Alternatively, its recent establishment in upper Cold Creek (~750 µS/cm; Fig. 7) suggests that this species is capable of propagating even in in moderately low SC streams in the Santa Monica Mountains.

With respect to aquatic vertebrates, geologic controls on water quality influence the distribution and abundance of many freshwater fishes, especially mineral water quality parameters such as SC, Total Dissolved Solids (TDS) total hardness, sulfate and metals (Stevenson *et al.*, 1974; Matthews *et al.*, 1992; Kimmel and Argent, 2008). The latter study by Kimmel and Argent, 2008 allows a comparison of these parameters between runoff from the M Fm. in Malibu Creek and runoff from coal mining in Arkansas streams. For example, their SC threshold of 3,000–3,500 µS/cm for impairment to fish communities is commonly exceeded in the Malibu Creek watershed, especially in the creek's M Fm.-drained northern tributaries (Figs. 6 & 7). Conversely, geologic influences on water quality may moderate the effects of some pollutants on aquatic life. Acute toxicity in fathead minnows (*Pimephales promelas)* for cadmium, copper, lead, nickel and zinc is reduced in so-called "hard" waters enriched in sulfate, calcium and magnesium (Brix *et al.*, 2004; Pascoe *et al.*, 1986) to levels common in Malibu Creek's M Fm.-drained northern tributaries (Fig. 10). Sulfate levels >1,000 mg/L, also common in the creek's northern tributaries, have also been shown to reduce acute selenium toxicity in fathead minnows by 50 percent relative to water with 100 mg/L SO_4^{2-} (Brix *et al.*, 2004). This benefit, in turn, may be counterbalanced by increased toxicity from hydrogen sulfide gas (H_2S) de-gassing from anaerobic stream sediments, where it originates as a metabolic by-product of sulfate-reducing bacteria. In stream water H_2S is toxic to brown trout fry at 7 µg/L (Reynolds & Haines, 1980), and Dare *et al.* (2001) found concentrations as low as 0.13 µg/L sufficient to prevent the upstream passage of rainbow trout (*O. mykiss*). High sulfate levels > 1,000 mg/L and H_2S emission from stream sediments are common in Malibu Creek (Dagit *et al.*, 2009), especially in the summer when peak sulfate levels coincide with higher temperature-dependent microbial metabolic rates. These conditions also favor the microbial-mediated conversion of mercury to more toxic methyl-mercury, while reducing acute toxicity from selenate, a form of selenium (Brix *et al.*, 2004). Integrating these effects into testable outcomes for Malibu Creek's fishes is beyond the scope of this study, except for the observation that Malibu Creek, while apparently viable habitat for a number of non-native temperate and warmwater fishes (i.e. largemouth bass, green sunfish, fathead minnow, bullhead catfish), is apparently viable habitat for only one native fish species of state Special Concern (arroyo chub, *Gila orcutti*) and one native federally-endangered anadromous fish (southern steelhead rainbow trout, *O. mykiss*). Thus an alternative approach to assessing the collective effect of M Fm.-drained metals and sulfate in the Malibu Creek watershed may be to compare their levels with their toxicity in other native southern California fishes unrecorded from Malibu Creek, on the expectation that the levels of these substances in Malibu Creek would impair them. Cohen *et al.* (2001) measured trace metals in fish and invertebrates in Malibu Lagoon, finding them generally lower than those in Mugu Lagoon and the Ballona Creek estuary. However, both of these estuaries also drain petroleum source rock, underscoring the need to consider drainage geology along with urban runoff and other human sources. The Ballona Creek and estuary in particular were historically important for petroleum production, and the Environmental Impact Report for the restoration of the wetlands there reports that native methane gas remains a nuisance in the area today and must be removed in some locations to avoid an explosion hazard (SMBRC, 2010).

In summary, our findings overall demonstrate the Monterey Formation's influence on surface and groundwater quality and aquatic life across three tropic levels in the Malibu Creek watershed. These effects include background nutrient levels in excess of current regulatory objectives, persistent benthic and floating algal mats, brackish levels of salts throughout Malibu creek and its northern tributaries, poor to very poor macroinvertebrate metrics, levels of As, Ag, Cd, Cr, Ni, Pb and Se in fishes that exceed human health levels for consumption, and surface and groundwater in the northern watershed that is unfit for human consumption due to elevated sulfate, TDS and radioactivity (groundwater in some locations). In retrospect, however, our findings merely underscore Karaji's observation over a thousand years ago that the geology of a watershed can have a major impact on the suitability of its streams and groundwater for human uses and aquatic life.

Particularly in southern California, where both urban development and petroleum source rock are common, it is important that water quality regulators and managers alike investigate the elemental and mineral composition of major geologic formations in their watersheds when attempting to determine the causes of water quality impairments to public health and aquatic life. Meeting the regulatory targets for metals in the Los Angeles River watershed alone is estimated to cost $1.15 billion dollars, yet an inspection of the supporting documents for these targets finds little analysis of geologic sources besides one reference to anomalously high selenium levels in Reach 5 of the upper watershed, attributed to marine shales (EDAW, 2003). Casual inspection of state geological maps finds significant exposures of petroleum source rock throughout the Los Angeles River basin. Their influence relative to other natural and human impacts in the basin may merit further study.