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Historical Data Evaluation of Aluminum in the Ventura River, Santa Clara River, and Calleguas Creek Watersheds

Prepared for:

Ventura Countywide Stormwater Quality Management Program

Prepared by:

LARRY WALKER ASSOCIATES

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Executive Summary

The total aluminum concentrations observed by the Ventura Countywide Stormwater Quality Management Program (VCSQMP) in Ventura County surface waters and urban runoff during wet weather events routinely exceed the Title 22 Drinking Water Primary Maximum Concentration Level (MCL) cited in the Los Angeles Region Water Quality Control Plan (Basin Plan). Such exceedances have been observed since early 2004, when VCSQMP began analyzing for aluminum in its routine water quality monitoring.

To investigate the high concentrations of total aluminum identified in urban runoff and surface waters in Ventura County, primarily during storm events, VCSQMP conducted a historical data evaluation, and initiated new monitoring during the 2013/14 monitoring season.

The majority (74.2 percent) of all wet weather water quality samples collected by the VCSQMP exceed the Title 22 Primary MCL for total aluminum of 1,000 µg/L. However, upstream from anthropogenic activities 100% of wet weather samples exceeded the objective. In comparison, concentrations of total aluminum in dry weather samples appear to be a much smaller issue, with approximately six percent of samples exceeding the Title 22 Primary MCL.

Required to protect municipal and domestic supply (MUN) beneficial uses of receiving waters, the VCSQMP is investigating the geospatial and seasonal trends in aluminum concentrations measured in the Ventura River, Santa Clara River, and Calleguas Creek watersheds. A better understanding of the major sources and factors contributing to elevated aluminum concentrations is needed to identify potential solutions. As aluminum occurs naturally in soils and sediments and is the most abundant metal in the earth's crust it is suspected that naturally occurring aluminum is the primary source, and sampling was designed to confirm this hypothesis.

Data evaluation for total aluminum is ongoing and includes surface water quality samples and soil samples. Data sources include the Ventura Countywide Stormwater Monitoring Program, Calleguas Creek Watershed Total Maximum Daily Load (TMDL) Compliance Monitoring Program (CCWTMP), Surface Water Ambient Monitoring Program (SWAMP), Southern California Stormwater Monitoring Coalition, and the Southern California Bight Monitoring Program. Recent monitoring was also performed on river sediments and on wet weather flows from pristine upstream areas in the three watersheds and included in this analysis.

A summary of the main conclusions of this evaluation are provided below.

- Wet weather exceedance rates of the Title 22 Primary MCL were greater than 50% for eleven of the fourteen individual VCSQMP monitoring sites. The three exceptions included the current mass emission station in the Ventura River Watershed, the City of Fillmore's major outfall, and the Port Hueneme major outfall.
- Average and median total aluminum concentrations measured in the Santa Clara River and Calleguas Creek watersheds were noticeably higher than those observed for the Ventura River watershed and the Port Hueneme major outfall that discharges to the Pacific Ocean.
- Agricultural discharges contribute higher levels of total aluminum to receiving waters than urban discharges (based on the CCCWTMP data set, which distinguished between runoff from different land use types).

- For dry weather monitoring, publically owned treatment works (POTWs) contribute very little total aluminum to surface waters (also based on the CCCWTMP data set). During wet weather events, POTW discharges are not monitored.
- Within the Calleguas Creek Watershed, upstream agricultural land use discharges appear to appreciably influence surface water total aluminum concentrations measured downstream of such discharges within a subwatershed.
- Correlation analyses of total aluminum and TSS, and total aluminum and flow:
    - Measured total aluminum and TSS concentrations were strongly correlated for both wet weather and combined dry and wet weather data.
    - Measured water column aluminum concentrations were more dependent on the amount of solids suspended in the water column than the flow transporting the aluminum and TSS (based on total aluminum concentrations at the mass emission sites correlating more strongly with TSS than with flow).
- Review of soils data in the three watersheds:
    - The total aluminum measured in water quality samples appears to be derived from the erosion of soil (based on the consistency between the average mass of total aluminum per mass of TSS in the water column and the range of total aluminum soil concentrations in Ventura County; and on the high correlation between total aluminum and TSS concentrations measured in VCSQMP water quality samples).
- Data gaps in historical monitoring and additional monitoring:
    - Data gaps were identified for upstream portions of the three watersheds where sediment and runoff is little influenced by anthropogenic activities. Monitoring was initiated at new upstream locations in each of the three watersheds in December 2013 and February 2014 to help fill this gap.
    - Natural background sites were monitored for water (December 2013 and February 2014) and sediment (December 2013) and data showed that upstream locations in each of the three watersheds also possess elevated water column and sediment aluminum concentrations. Wet weather aluminum at these background sites was seen from 19,000 µg/L to 250,000 µg/L.
    - Limited stormwater runoff data collected from parking lots at the Ventura County Government Center in February and March 2014 also revealed elevated aluminum and TSS concentrations in half of the samples collected, even so these were much lower than the natural background with the highest concentration being only 2,100 µg/L.

The exceedingly high level of total aluminum detected in runoff from undeveloped areas suggests that wet weather aluminum will routinely exceed water quality objectives regardless of Permittee efforts. Since high background concentrations of aluminum appear to be a primary source contributing to the routine water quality objective exceedances observed in Ventura County surface waters, VCSQMP will need to discuss with the Los Angeles Regional Board the implementation of an appropriate regulatory mechanism (e.g., reference stream/antidegradation approach; natural source exclusion approach; water-effects ratio approach; or high-flow suspension of beneficial use) that would limit the Copermittees' liability for controlling such background concentrations. As part of the effort to provide support in selecting a possible regulatory off-ramp and to otherwise develop a sound scientific approach for managing the elevated concentrations of aluminum measured in urban runoff, VCSQMP will need to continue

evaluating historical and new aluminum data collected in the three watersheds, in particular, from monitoring locations that represent land uses little affected by human activities.

Introduction

In Ventura County, aluminum has been identified in high concentrations during storm events in both urban runoff and in the rivers and streams of the County. Aluminum that naturally occurs in soils and sediments in the region has the potential to become mobilized in stormwater runoff during wet weather events. Pollutant generating activities in urban areas can also contribute to aluminum concentrations measured in the runoff. The Ventura County Watershed Protection District is the Principal Permittee for the Ventura Countywide Stormwater Quality Management Program (VCSQMP or Program). As Principal Permittee they are responsible for the monitoring and reporting under the MS4 NPDES Permit. The VCSQMP added aluminum to the suite of trace metals it analyzes as part of its routine wet and dry weather water quality monitoring in Ventura County beginning in February 2004. Since that time, the VCSQMP has routinely observed total aluminum concentrations in wet weather stormwater runoff samples that exceed the Title 22 Primary Maximum Concentration Level (MCL) for total aluminum of 1000 µg/L that is incorporated by reference into the Water Quality Control Plan, Los Angeles Region (Basin Plan). The Title 22 Primary MCL exists to protect the municipal and domestic supply (MUN) beneficial use designated for all surface water bodies in California. Total aluminum concentrations in wet weather environmental water quality samples collected by the VCSQMP exceed the Title 22 Primary MCL for total aluminum in greater than 74 percent of samples. By comparison, total aluminum concentrations in dry weather environmental water quality samples exceed the Title 22 Primary MCL for the metal in slightly less than 6 percent of the samples collected. The VCSQMP reports these exceedances of water quality standards in its annual monitoring reports and in post-event water quality monitoring summaries provided to the Regional Water Quality Control Board, Los Angeles Region (Regional Water Board).

The VCSQMP is currently reviewing total aluminum concentrations in its water quality samples, those collected by the Calleguas Creek Watershed Total Maximum Daily Load (TMDL) Compliance Monitoring Program (CCWTMP), and aluminum levels measured in the local geology to gain a better understanding of the geospatial and seasonal aluminum concentrations observed in the surface waters of the Ventura River, Calleguas Creek, and Santa Clara River watersheds. This evaluation of historical aluminum data, along with an assessment of additional data to be collected by the Ventura Countywide Stormwater Monitoring Program, the CCWTMP, and the Southern California Coastal Water Research Project (SCCWRP), are intended to provide the VCSQMP with insight into the major sources of aluminum – naturally occurring and anthropogenic – that contribute to the elevated aluminum concentrations primarily measured in wet weather water quality samples.

Total aluminum data evaluated in this report were collected by the Ventura Countywide Stormwater Monitoring Program, the CCWTMP (as part of the Calleguas Creek Metals and Selenium TMDL), and other sources. Available data were compiled, reviewed, and analyzed to identify geographical and/or seasonal trends in the three watersheds of interest: Ventura River, Calleguas Creek, and Santa Clara River. Total aluminum concentrations were characterized by watershed and season to determine if any aluminum "hot spots" exist among the current locations monitored by the VCSQMP and the CCWTMP during either the wet or dry season. Relationships between co-occurring total aluminum and total suspended solids concentrations

measured in surface waters and between total aluminum and flow were also evaluated. In addition, an area map showing aluminum soil concentrations measured in the three watersheds was generated to inform the VCSQMP of the potential for sediments upstream and downstream of urban areas to contribute to observed surface water total aluminum concentrations. Finally, locations where future monitoring efforts could prove useful in determining the extent of anthropogenic contributions to observed aluminum concentrations in surface waters were identified.

The National Pollutant Discharge Elimination System (NPDES) Permit for Ventura County's Municipal Separate Storm Sewer System (MS4), for which the VCSQMP is the Principal Permittee, requires the Copermittees[1] to reduce aluminum in stormwater discharges within their respective jurisdictions through the implementation of best management practices (BMPs). Current BMPs employed by Copermittees, including Enhanced Construction BMP Implementation, illicit discharge screening, and industrial and commercial inspections, have not resulted in noticeable decreases in wet weather aluminum concentrations in recent years. In addition to considering additional BMPs to reduce aluminum concentrations in wet and dry weather flows, the VCSQMP is performing the current evaluation to determine if naturally occurring aluminum levels in the native geology of Ventura County support the use of a regulatory mechanism or "off ramp" (e.g., reference stream/antidegradation approach; natural source exclusion approach; water-effects ratio approach; or high-flow suspension of beneficial use) that would limit the Copermittees' liability for controlling high background concentrations of aluminum. The VCSQMP will use the information contained in this report and that generated by future aluminum assessment efforts carried out by itself and others, along with guidance provided by the Regional Water Board to craft a prudent approach to managing the elevated concentrations of aluminum observed in Ventura County surface waters.

HISTORICAL DATA EVALUATION BACKGROUND

Aluminum is the most abundant metal in the earth's crust and is widely distributed (DHHS, 2008). The metal is very reactive and is never found as the free metal in nature. It is found combined with other elements, most commonly with oxygen, silicon, and fluorine. These chemical compounds are commonly found in soil, minerals (e.g., sapphires, rubies, and turquoise), rocks (especially, igneous rocks), and clays (DHHS, 2008). Aluminum occurs naturally in soil, water, and air. High levels of aluminum in the environment can potentially occur with the mining and processing of aluminum ores or in the production of metal, alloys, and associated compounds. Small amounts of aluminum are released into the environment from coal-fired power plants and incinerators (DHHS, 2008). Agriculture can contribute aluminum to surface waters through aluminum-laden sediment contained in its runoff. Based on a limited data set for treated wastewater effluent, it appears that publically owned treatment works (POTWs) in the Calleguas Creek Watershed are minor contributors of aluminum to surface waters (CCWTMP, unpublished data, August 2008 – May 2013). Most aluminum-containing compounds do not dissolve to a large extent in water unless the water is acidic or very alkaline. On average, the VCSQMP's wet weather dissolved aluminum results comprise less than 2 percent of the concentration measured in the total fraction of any given water quality sample

[1] The Copermittees currently covered under the NPDES MS4 permit include the County of Ventura, and the cities of Camarillo, Fillmore, Moorpark, Ojai, Oxnard, Port Hueneme, San Buenaventura (Ventura), Santa Paula, Simi Valley, and Thousand Oaks.

analyzed, supporting the assertion that very little aluminum in wet weather water quality samples exists in the dissolved form. In contrast, just over 12 percent of the aluminum measured in dry weather water quality samples, on average, is present in the dissolved fraction.

STUDY AREA

The Study area includes the Ventura River, Calleguas Creek, and Santa Clara River watersheds. These watersheds and the various water quality monitoring stations monitored by the VCSQMP are listed in **Table 1** and shown in **Figure 1**. The various TMDL monitoring sites monitored by the CCWTMP are listed in **Table 2** and shown in **Figure 2**. Because the County's NPDES stormwater monitoring program was generally designed to assess the impact of urban and other land uses on receiving water quality, the VCSQMP has not historically monitored locations in the upper parts of the Ventura River, Santa Clara River, and Calleguas Creek watersheds that would experience little to no anthropogenic impacts.

Table 1: Current and Historical Sampling Locations Monitored for Aluminum by the Ventura Countywide Stormwater Monitoring Program.

Site ID[1]	Site Description	Latitude	Longitude
Ventura River Watershed			
MO-MEI	Major outfall	34.44554	-119.29
MO-OJA	Major outfall	34.44474	-119.241
ME-VR	Mass emission	34.35194	-119.307
ME-VR2	Mass emission	34.34305	-119.299
Santa Clara River			
MO-FIL	Major outfall	34.40459	-118.931
MO-SPA	Major outfall	34.34861	-119.056
ME-SCR	Mass emission	34.29917	-119.107
R-1	Residential land use	34.25861	-119.195
I-2	Industrial land use	34.24917	-119.228
MO-VEN	Major outfall	34.24356	-119.195
MO-OXN	Major outfall	34.23614	-119.184
Calleguas Creek			
MO-MPK	Major outfall	34.27905	-118.905
MO-SIM	Major outfall	34.2721	-118.784
W-3	Receiving water	34.26583	-119.093
MO-CAM	Major outfall	34.21952	-119.066
MO-THO	Major outfall	34.21331	-118.921
ME-CC	Mass emission	34.17917	-119.039
A-1	Agricultural land use	34.17051	-119.095
W-4	Receiving water	34.17045	-119.095
Pacific Ocean			
MO-HUE	Major outfall	34.14081	-119.188

1. Site IDs within watersheds are listed in upstream to downstream order.

Stations currently monitored by the VCSQMP are shown in bold type.

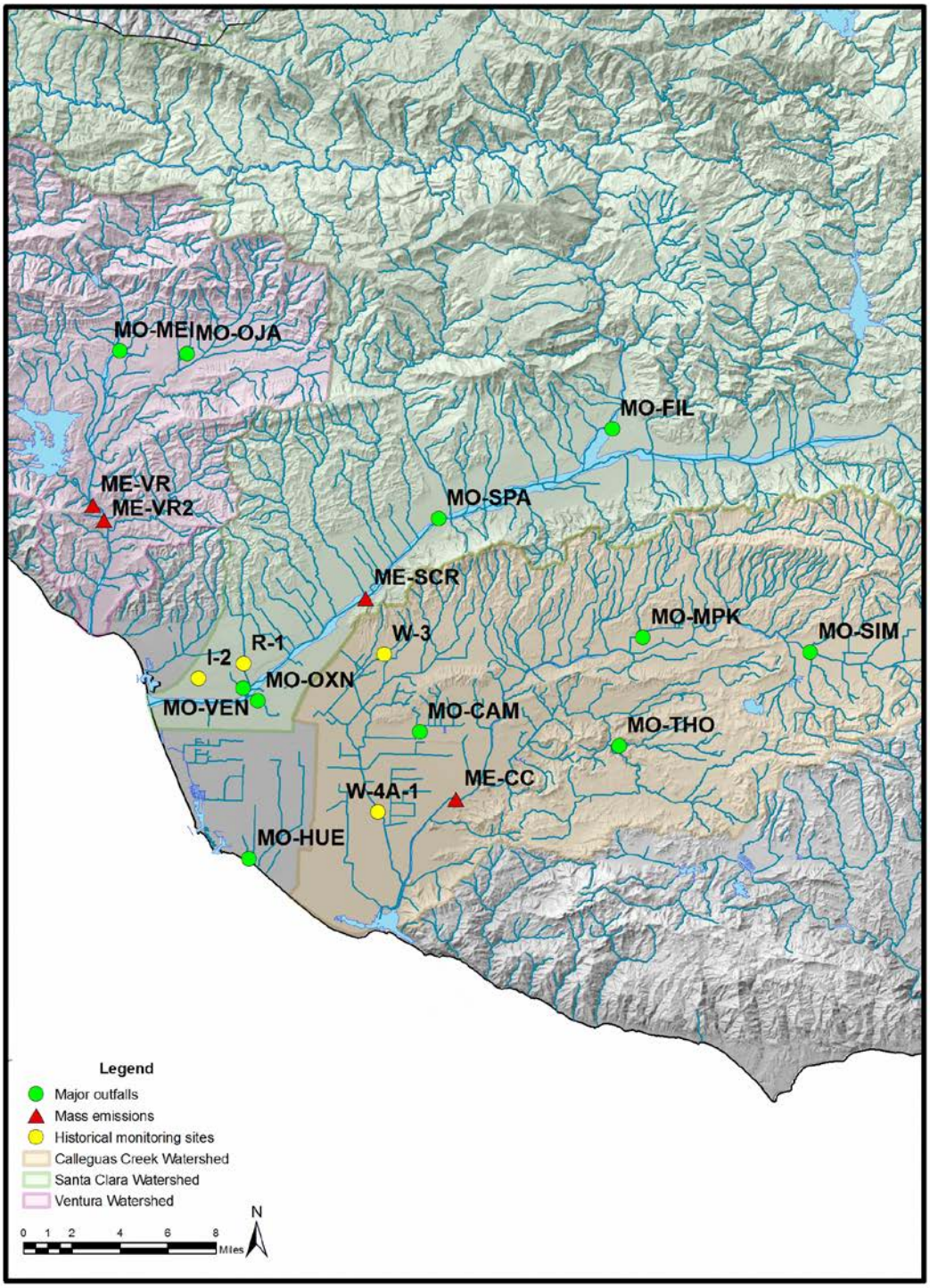

Figure 1: Stormwater NPDES Monitoring Locations in the Ventura River, Santa Clara River, and Calleguas Creek Watersheds.

Table 2: Sampling Locations Monitored for Aluminum by the Calleguas Creek Watershed TMDL Compliance Monitoring Program.

Subwatershed[(1)]	Site ID	Site Description	Latitude	Longitude
Arroyo Simi	D_SIMI	POTW Effluent	34.2814	-118.815
Conejo	D_GERRY	Agriculture land use	34.2359	-118.95
	D_ADOLF	Urban land use	34.2148	-118.995
	D_HILL	POTW Effluent	34.2131	-118.925
Calleguas	D_CAMA	POTW Effluent	34.1938	-119.002
	UNIV	Receiving Water	34.1793	-119.039
	D_BROOM	Agriculture land use	34.14335	-119.071
	PCH	Receiving Water	34.1119	-119.082
Revolon Slough	D_SANTV	Agriculture land use	34.24267	-119.114
	VENTRA	Urban land use	34.2161	-119.068
	D_WOOD	Agriculture land use	34.1707	-119.096
	WOOD	Receiving Water	34.1703	-119.095
Mugu Lagoon	ODDS	Agriculture land use	34.13951	-119.118
	SG_74	Receiving Water	34.10125	-119.096
	RR_BR	Receiving Water	34.109	-119.092
	BPT_15	Receiving Water	34.10545	-119.093
	BPT_14	Receiving Water	34.10455	-119.117
	BPT_6	Receiving Water	34.10255	-119.109
	BPT_3	Receiving Water	34.1023	-119.091

1. Subwatersheds and Site IDs are listed in upstream to downstream order.

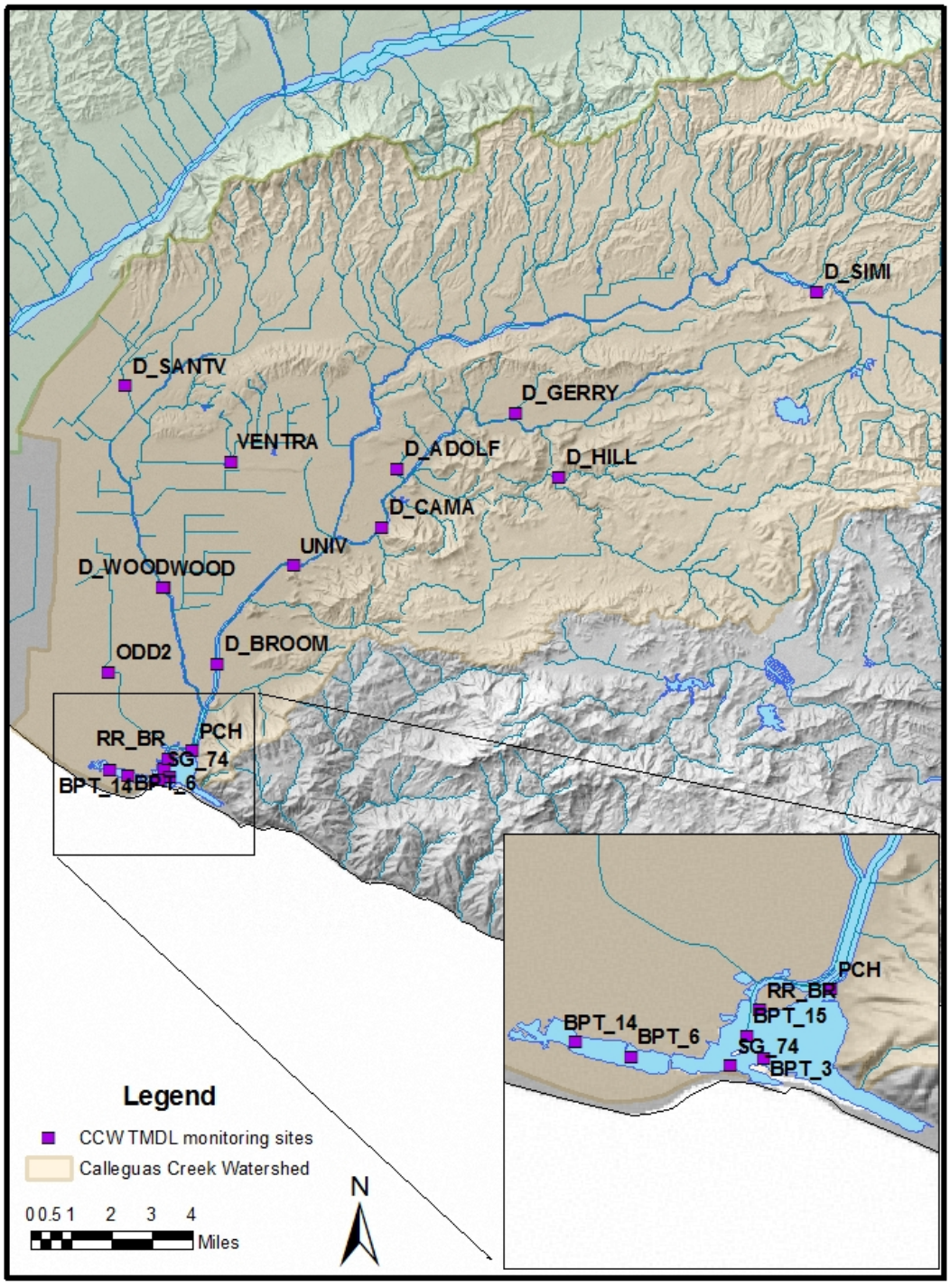

Figure 2: Calleguas Creek Watershed TMDL Compliance Monitoring Program Sampling Location.

Analysis of Historical Data

Total aluminum data evaluated in this report were collected by the Ventura Countywide Stormwater Monitoring Program, the Calleguas Creek TMDL Compliance Monitoring Program, and other sources (CCWTMP). The data were compiled, reviewed, and analyzed by watershed and season or "event type" (i.e., wet or dry season data) to identify geographical and/or seasonal trends in the watersheds. Wet season monitoring typically occurs from October through March, whereas dry season monitoring typically occurs from April through June. In addition, the data were analyzed to determine locations where future monitoring efforts could prove useful in filling existing data gaps and helping to determine the extent of natural and anthropogenic contributions of aluminum in the three subject watersheds. The recommendations for future aluminum monitoring within the three watersheds are not intended to expressly lead to a particular regulatory off ramp, but rather to provide support in making a decision to select an appropriate off ramp.

SOURCES OF DATA

Total aluminum data evaluated in this report were obtained from the following sources:

- Total aluminum data measured in surface waters were obtained from the VCSQMP and the CCWTMP;
- Total aluminum data measured in major outfalls were obtained from the VCSQMP;
- Total aluminum data measured in POTW treated effluent were obtained from the CCWTMP;
- Total aluminum data measured in soils were obtained from the California Environmental Data Exchange Network. Data obtained from the CEDEN Database were collected by the Surface Water Ambient Monitoring Program (SWAMP), the Southern California Stormwater Monitoring Coalition, and the Southern California Bight Monitoring Program.
- In addition, total suspended solids (TSS) and flow data collected at VCSQMP monitoring sites along with total aluminum data were also evaluated to determine the strength of any correlations that may exist between total aluminum and TSS and total aluminum and flow.

It should be noted that the total aluminum data collected by the CCWTMP as part of the Calleguas Creek Metals and Selenium TMDL is not routinely published in the Program's Annual Monitoring Reports because the TMDL only addresses copper, mercury, nickel, zinc, and selenium, the parameters for which the TMDL specifies interim load and waste load allocations. There are no such allocations in the TMDL for aluminum, and therefore, the CCWTMP does not report aluminum data in its annual monitoring reports.

HISTORICAL DATA EVALUATION RESULTS

Between Watershed Comparisons

Total aluminum data collected during dry weather and wet weather monitoring events were separated for comparison between watersheds and statistical analyses were performed. Summary statistics calculated for dry and wet weather monitoring events by watershed (Calleguas Creek, Santa Clara River, Ventura River, and Pacific Ocean) and sampling program (the Program and CCWTMP) are presented in **Table 3** and **Table 4**, respectively. It should be noted that the watershed described as the Pacific Ocean includes only a single Program monitoring location, the Port Hueneme major outfall, that drains to the Pacific Ocean. When this report references the three watersheds monitored by the VCSQMP, the watersheds referred to are the Calleguas Creek, Santa Clara River, and Ventura River watersheds.

Table 3: Summary Statistics by Watershed for Dry Weather Total Aluminum Concentrations Measured by the Program and CCWTMP.

	Dry (µg/L)					
Watershed	**N**	**Median**	**Mean**	**Std Dev**	**Min**	**Max**
Calleguas Creek	29	65	221	589	5	3,170
Santa Clara River	29	57	366	826	3	3,800
Ventura River	25	13	81	204	1	932
Pacific Ocean	3	34	38	15	26	55
CCWTMP(1)	328	105	210	352	3	2,849

1. Data collected in the Calleguas Creek Watershed by the CCWTPM; all other data listed are collected by the Program in the watershed specified.

Summary statistics calculated for total aluminum concentrations measured during dry weather in the three watersheds monitored by the VCSQMP (Ventura River, Santa Clara River, and Calleguas Creek) fall within a similar range, as shown in **Table 3**. A review of the data used to calculate the summary statistics showed that concentrations were higher between 2004 and 2007, then decreased in 2008-2009, and then were followed by a slight increase at some sites during the period 2011 to 2013. Starting in 2010, additional sites (major outfalls) were monitored in each watershed, while other sites were retired from monitoring. Monitoring data from the major outfall sites added to the overall data variability observed within a watershed, and show differences among locations within and between watersheds.

The average dry weather total aluminum concentrations measured in the Ventura River, Calleguas Creek, and Santa Clara River watersheds were 81 µg/L, 221 µg/L, and 366 µg/L, respectively. The median values for the three watersheds were 13 µg/L, 65 µg/L and 57 µg/L, respectively, which indicates that the average values for Calleguas Creek and the Santa Clara River were influenced by a few high concentrations (likely those measured during the early monitoring years). The average, minimum, and maximum dry weather total aluminum concentrations calculated for the Calleguas Creek Watershed using data collected by the CCWTMP are comparable to those summary statistics calculated for the watershed using data collected by the VCSQMP.

Table 4: Summary Statistics by Watershed for Wet Weather Total Aluminum Concentrations Measured by the Program and CCWTMP.

	Wet (µg/L)					
Watershed	**N**	**Median**	**Mean**	**Std Dev**	**Min**	**Max**
Calleguas Creek	89	4,233	6,636	8,228	190	55,500
Santa Clara River	79	2,405	7,311	14,974	22	79,000
Ventura River	56	1,400	3,064	5,360	5	30,300
Pacific Ocean	9	500	562	2,94	230	1,100
CCWTMP(1)	88	2,525	8,204	17,446	50	134,049

1. Data collected in the Calleguas Creek Watershed by the CCWTPM; all other data listed are collected by the Program in the watershed specified.

Summary statistics calculated for total aluminum concentrations measured during wet weather in the three watersheds are shown in **Table 4.** Similar to the summary statistics calculated for dry weather monitoring events, total aluminum concentrations measured in the Santa Clara River Watershed show the highest average concentration and the greatest variability. Total aluminum concentrations were frequently measured above the Title 22 Primary MCL for total aluminum of 1000 µg/L at all monitoring sites in all three watersheds during wet weather events except between 2007 and late 2009 in the Ventura River Watershed. During this period, only a single total aluminum concentration in the Ventura River Watershed was measured above the Title 22 Primary MCL. Overall, wet weather total aluminum concentrations below 1000 µg/L were most frequently measured in the Ventura River watershed.

The average wet weather total aluminum concentrations measured in the Ventura River, Calleguas Creek, and Santa Clara River watersheds were 3064 µg/L, 6636 µg/L, and 7311 µg/L, respectively. The median values were 1400 µg/L, 4233 µg/L, and 2405 µg/L, respectively. The mean total aluminum concentration calculated for the Santa Clara River Watershed was higher than those calculated for the Ventura River and Calleguas Creek watersheds, whereas the highest median concentration was calculated from data collected in the Calleguas Creek Watershed. The average, standard deviation, mininum, and maximum wet weather total aluminum concentrations calculated for the Calleguas Creek Watershed using data collected by the CCWTMP are all greater than those summary statistics calculated for the watershed using data collected by the VCSQMP.

Figure 3 provides box-and-whisker plots by watershed of all total aluminum data collected during dry and wet monitoring events that were considered when calculating the summary statistics shown in **Table 3** and **Table 4**, respectively. The box-and-whisker plots show the distribution of total aluminum concentrations measured in each watershed. Data points above the upper whisker represent those values that fall outside of the following calculated value:

Upper whisker value = 3rd quartile + 1.5 * the interquartile range
(the difference between the 1st and 3rd quartile is called the interquartile range)

This graphical representation of the data lends itself to easy visualization of the greater variability of the total aluminum data collected by the CCWTMP in the Calleguas Creek

Watershed as compared to the data collected by the VCSQMP in the watershed; this is true for data collected during both dry and wet monitoring events. The greater variability of the CCWTMP data set might be explained by the fact that this monitoring program focuses on pollutant contributions from a variety of sources, including agriculture, POTWs, urban inputs, along with receiving water monitoring which is used to characterize all pollutant inputs to the subwatershed.

Table 5 shows the dry and wet weather environmental data percent exceedances of the Title 22 Primary MCL for total aluminum of 1000 µg/L for each watershed. The data show that the percent exceedances observed for the Calleguas Creek Watershed during dry weather monitoring are similar for the Program (3.4%) and CCWTMP (4.0%) monitoring programs. The Program wet weather data show a greater percent exceedance of the water quality objective for the Calleguas Creek Watershed (89.9%) than do wet weather data collected in the watershed by CCWTMP (76.1%).

Table 5: Calculated Percent Exceedances of the Title 22 Primary MCL for Total Aluminum by Event Type and Watershed for Data Collected by the VCSQMP and CCWTMP.

		Dry Weather		Wet Weather	
Monitoring Program	**Watershed**	**Total Samples (n)**	**% Exceedance**	**Total Samples (n)**	**% Exceedance**
VCSQMP	Calleguas Creek	29	3.4	89	89.9
	Santa Clara River	29	13.8	79	77.2
	Ventura River	25	0.0	56	55.4
	Pacific Ocean	3	0.0	9	11.1
	All Watersheds	86	5.8	233	74.2
CCWTMP	Calleguas Creek	328	4.0	88	76.1

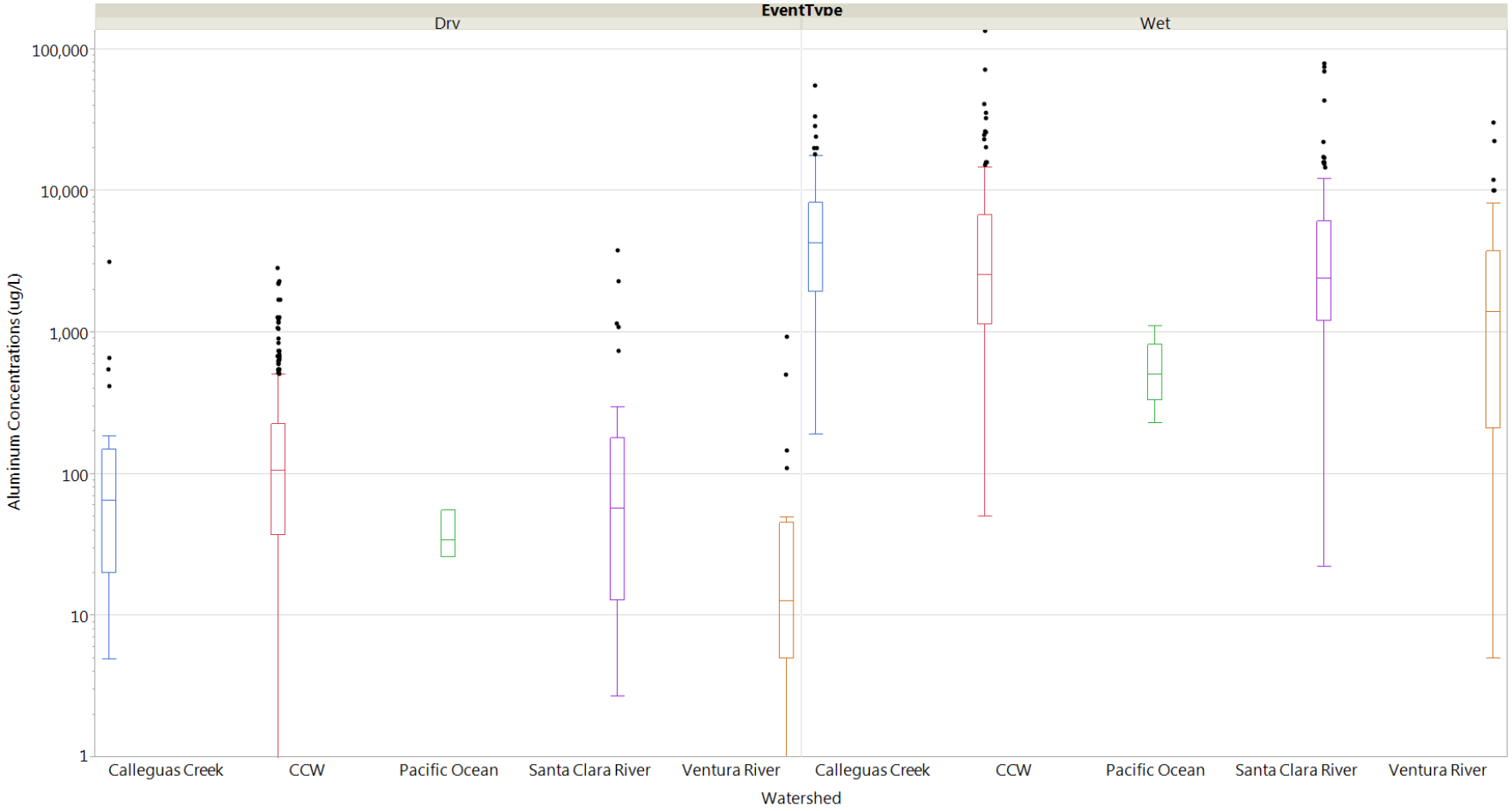

Figure 3: Comparison by Watershed of Total Aluminum Concentrations Measured during Dry and Wet Weather Monitoring Events. (All plotted data collected by VCSQMP except for Calleguas Creek Watershed "CCW" data collected by the CCWTMP)

Within Watershed Comparisons

Ventura River

As shown in the top graph of **Figure 4**, dry weather total aluminum concentrations in the Ventura River Watershed have not exceeded the 1000 µg/L Title 22 Primary MCL for total aluminum between 2004 and 2013. Wet weather total aluminum concentrations are typically much higher than dry weather concentrations, often rising above the Title 22 Primary MCL, as seen in the bottom graph of **Figure 4**. Wet weather total aluminum concentrations at major outfall sites MO-MEI and MO-OJA consistently exceeded the Title 22 Primary MCL during the period monitored (2010-2013). The range of total aluminum concentrations measured at mass emission site ME-VR(2) appears to have narrowed over time, with a wider range of concentrations observed between 2004 and 2009, and a narrower range observed between 2010 and 2013. The cause of this narrowing of the observed variability of total aluminum concentrations at ME-VR2 in recent years in unknown, but could be linked to reduced flows measured at the site during this period. The difference between the total aluminum data collected at ME-VR and ME-VR2 was more pronounced during wet weather events, with no total aluminum results exceeding the Title 22 Primary MCL at site ME-VR2 after 2010.

Santa Clara River

As shown in the top graph of **Figure 5**, only dry weather total aluminum concentrations measured at the Santa Clara River mass emission site (ME-SCR) have exceeded the Title 22 Primary MCL for total aluminum of 1000 µg/L. Dry weather total aluminum concentrations measured at all major outfalls (MO-FIL, MO-SPA, MO-VEN, MO-OXN) monitored in the Santa Clara River Watershed exist below the Title 22 Primary MCL. Wet weather total aluminum concentrations measured in the Santa Clara River Watershed were regularly higher than dry weather concentrations observed between 2004 and 2013, as seen in the bottom graph of **Figure 5.** Samples collected from mass emission site ME-SCR exceeded the Title 22 Primary MCL of 1000 µg/L frequently during wet weather monitoring events. The handful of wet weather total aluminum concentrations measured at historical (i.e., no longer monitored) land use sites I-2 (industrial) and R-1 (residential) are similar to average concentrations observed at the mass emission site ME-SCR. Wet weather total aluminum monitoring results measured at three of the major outfalls (MO-SPA, MO-VEN, MO-OXN) in the watershed site exceeded the Title 22 Primary MCL regularly. The major outfall representing urban discharges from the City of Fillmore, MO-FIL, tended to have lower wet weather total aluminum concentrations than the other major outfalls located in the watershed, and has exceeded the water quality objective for total aluminum infrequently from 2010 to 2013.

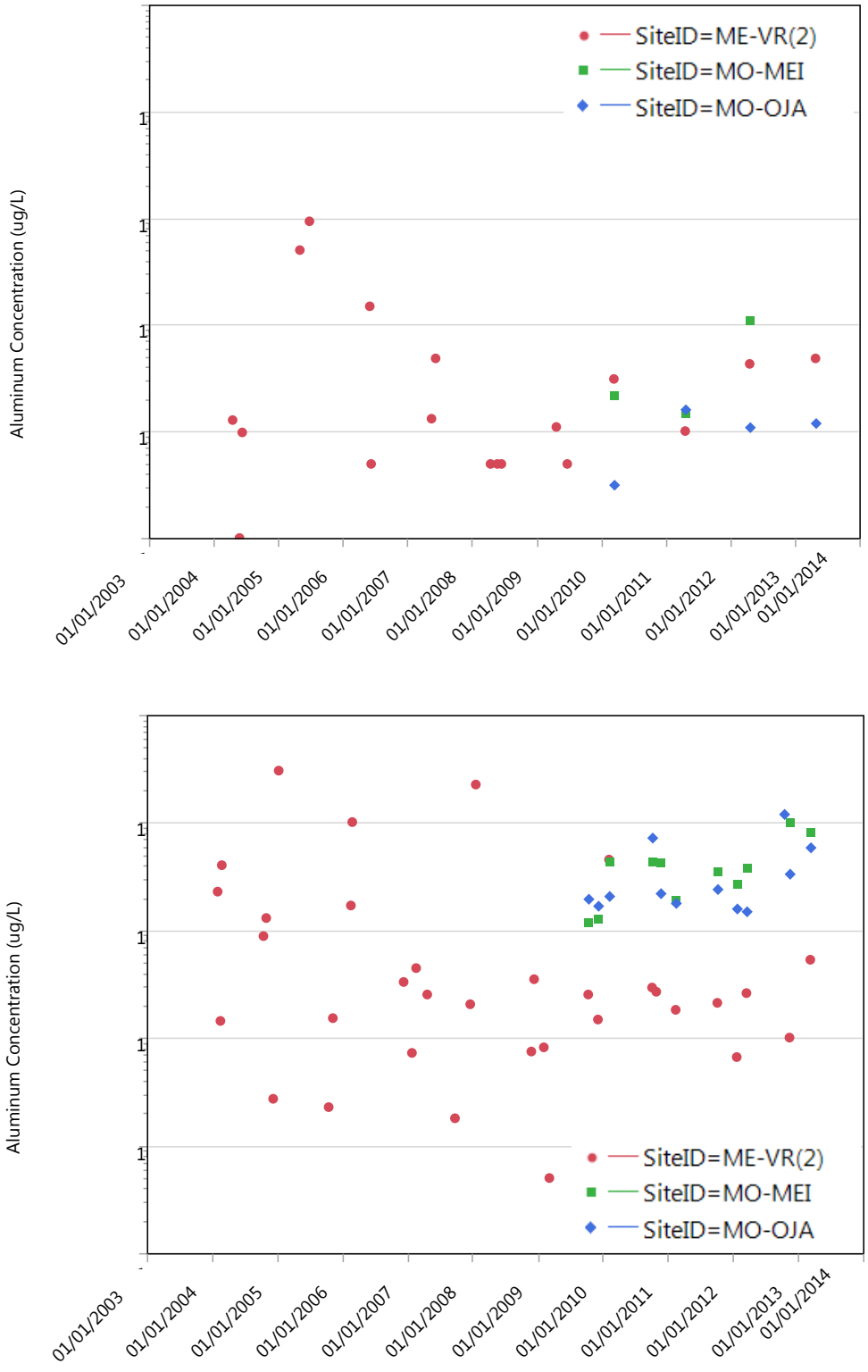

Figure 4: Ventura River Watershed Total Aluminum Concentrations Measured by VCSQMP [Dry Weather (top) and Wet Weather (bottom)].

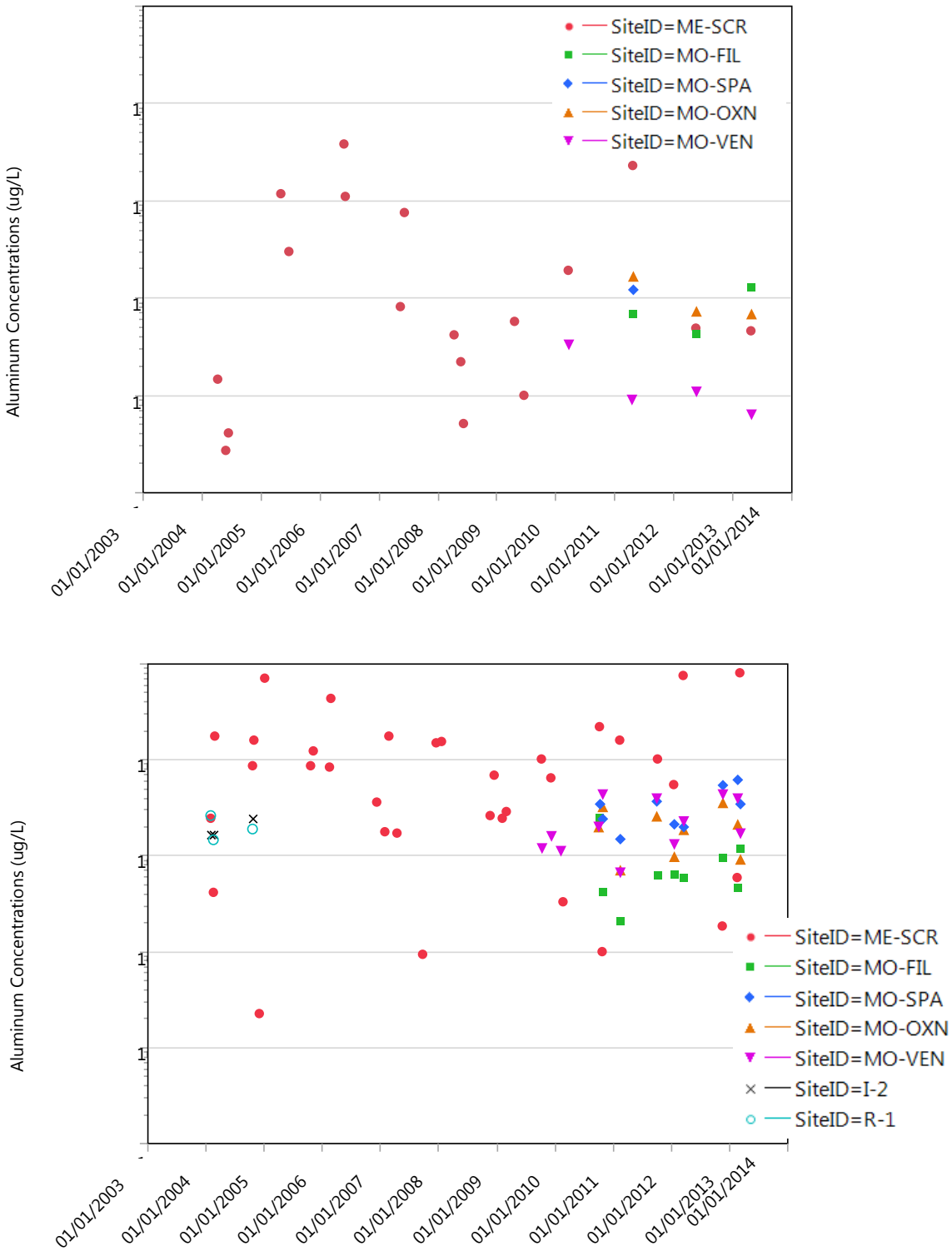

Figure 5: Santa Clara River Watershed Total Aluminum Concentrations Measured by VCSQMP [Dry Weather (top) and Wet Weather (bottom)].

Calleguas Creek

As shown in the top graph of **Figure 6**, only a single dry weather total aluminum sample collected in Calleguas Creek exceeded the Title 22 Primary MCL of 1000 µg/L during the period 2004 – 2013. This exceedance was from a sample collected at the mass emission site ME-CC in June 2006. All dry weather total aluminum concentrations measured at major outfalls in the Calleguas Creek Watershed were below the Title 22 Primary MCL for the metal. Conversely, wet weather total aluminum concentrations measured in the Calleguas Creek Watershed rarely fell below the Title 22 Primary MCL. Total aluminum concentrations in excess of the water quality objective were measured at all sites monitored in the watershed during multiple wet weather monitoring events. Wet weather total aluminum concentrations measured at historical (i.e., no longer monitored) land use (A-1; agriculture) and receiving water (W-3 and W-4) monitoring sites are similar to concentrations observed at the mass emission site ME-CC. The major outfall representing urban discharges from the City of Simi Valley, MO-SIM, reported the lowest total aluminum results during dry weather monitoring that occurred between 2011 and 2013.

Localized Elevated Aluminum Levels

Similar to the percent exceedance information shown in **Table 5** for each watershed, percent exceedance of the Title 22 Primary MCL for total aluminum was calculated for environmental data collected at each VCSQMP monitoring site under both dry and wet weather conditions as a means to identify any "hotspots" within a watershed. For the purpose of this analysis, the term hotspot is used to describe a monitoring location that shows frequent exceedances of the water quality objective, without consideration of the specific total aluminum concentrations that produced an exceedance of the objective. As shown in **Table 6** and described above, dry weather exceedances of the Title 22 Primary MCL for total aluminum were limited to water quality samples collected at the mass emission stations in the Santa Clara River Watershed (ME-SCR) and the Calleguas Creek Watershed (ME-CC). In contrast, wet weather exceedances of the water quality objective are ubiquitous in all watersheds. All monitoring sites showed exceedance levels greater than 50% except for the current mass emission station in the Ventura River Watershed (ME-VR2; 15.4% exceedance), the City of Fillmore's major outfall (MO-FIL; 22.2% exceedance), and the Port Hueneme major outfall (MO-HUE; 11.1% exceedance).

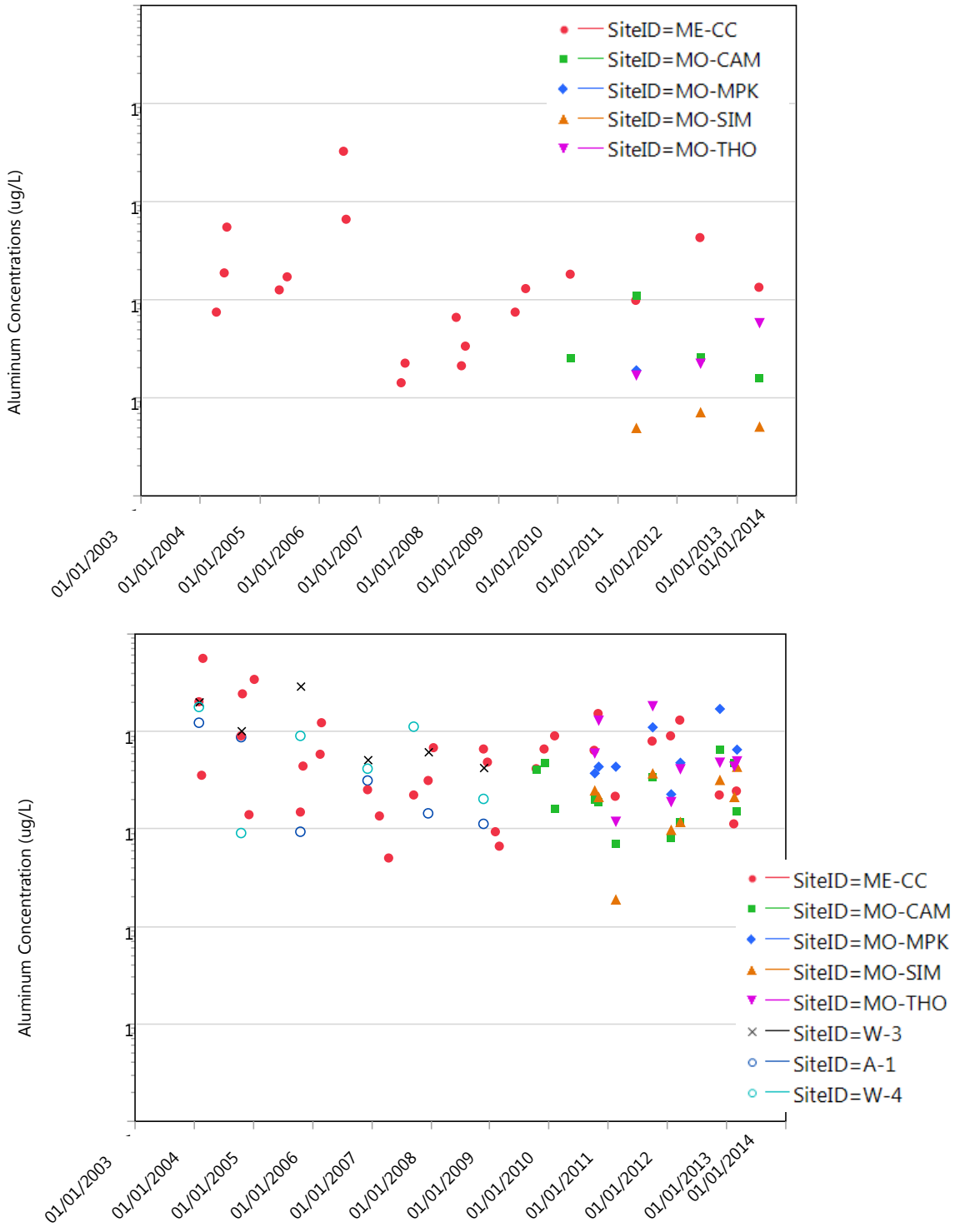

Figure 6: Calleguas Creek Watershed Total Aluminum Concentrations Measured by VCSQMP [Dry Weather (top) and Wet Weather (bottom)].

Table 6: Calculated Percent Exceedances of the Title 22 Primary MCL for Total Aluminum by Event Type and VCSQMP Monitoring Location.

		Dry Weather		Wet Weather	
Watershed	Site ID[1]	Total Samples (n)	% Exceedance	Total Samples (n)	% Exceedance
Ventura River	**MO-MEI**	3	0	11	100
	MO-OJA	4	0	12	100
	ME-VR	3	0	7	57.1
	ME-VR2	15	0	26	15.4
Santa Clara River	**MO-FIL**	3	0	9	22.2
	MO-SPA	1	0	9	100
	ME-SCR	18	22.2	34	79.4
	R-1	---	---	3	100
	I-2	---	---	3	100
	MO-VEN	4	0	12	91.7
	MO-OXN	3	0	9	66.7
Calleguas Creek	**MO-MPK**	1	0	8	100
	MO-SIM	3	0	9	77.8
	W-3	---	---	6	100
	MO-CAM	4	0	12	83.3
	MO-THO	3	0	9	100
	ME-CC	18	5.6	33	90.9
	A-1	---	---	6	83.3
	W-4	---	---	6	83.3
Pacific Ocean	**MO-HUE**	3	0	9	11.1

1. Site IDs within watersheds are listed in upstream to downstream order.

Stations currently monitored by the VCSQMP are shown in bold type.

COMPARISON OF CCWTMP DATA TO VCSQMP DATA COLLECTED IN THE CALLEGUAS CREEK WATERSHED

TMDL compliance monitoring performed in the Calleguas Creek Watershed by the CCWTMP from 2008 to 2013 included sampling at many more locations than monitored by VCSQMP in the watershed. CCWTMP monitored 19 sites that represent pollutant loadings from four different land use characterization types (agricultural runoff, POTW discharge, urban runoff, and receiving water). Receiving water monitoring is meant to capture pollutant loadings from all types of land uses and discharges upstream of a given monitoring point in the receiving water. As shown in the top graph of **Figure 7**, the highest total aluminum concentrations measured during dry weather monitoring occurred at sites representing agricultural runoff and receiving water, and the lowest total aluminum concentrations were measured in POTW discharge. Total aluminum concentrations in urban runoff are less than those measured in agricultural runoff and receiving waters, but appreciably higher than those observed in POTW discharges. These differences in dry weather total aluminum concentrations among the four different land use characterization types are easily visualized in the box-and-whisker plots provided in **Figure 8**.

Similar to the VCSQMP dry weather monitoring results in the Calleguas Creek Watershed, dry weather total aluminum concentrations measured by the CCWTMP rarely (4.0%) exceed the Title 22 Primary MCL.

As shown in the bottom graph of **Figure 7**, wet weather total aluminum concentrations measured in the Calleguas Creek Watershed by the CCWTMP are much higher than dry weather concentrations, often exceeding the Title 22 Primary MCL of 1000 µg/L. Similar to dry weather monitoring, wet weather monitoring shows the highest total aluminum concentrations in agricultural runoff and receiving waters, followed by urban discharges. POTW discharges are not monitored during wet weather events because wastewater effluent quality during storm events can be highly influenced by inflow and infiltration (I & I) in the POTW's collection system. Monitoring from the most recent storm event (January 25, 2013) resulted in lower concentrations than any of the previous storm events, with all but one total aluminum concentration existing below the Title 22 Primary MCL. The box-and-whisker plots in **Figure 8** are useful in visualizing the differences in total aluminum concentrations measured by the CCWTMP for the three land use characterization types monitored during wet weather. Median total aluminum concentrations measured in agricultural runoff and receiving waters are similar. Although there is more variability in total aluminum concentrations measured in agriculture runoff as compared to receiving waters. Dry and wet weather total aluminum results show a wide range of concentrations within each sampling event due to the varying pollutant loadings contributed by the variety of land use characterization sites monitored within the watershed. No trends in total aluminum concentrations are apparent for dry weather samples. The highest wet weather total aluminum concentrations measured by CCWTMP occurred in winter 2011, with lower concentrations observed before and after that period.

In comparing the total aluminum data collected in the Calleguas Creek Watershed by CCWTMP and the VCSQMP, the highest median wet weather concentration of 4233 µg/L (highest among all watershed monitored) was calculated using data collected by VCSQMP (see **Table 4**). That value is significantly higher than the 2525 µg/L median value calculated from wet weather total aluminum samples collected by CCWTMP. The highest average wet weather total aluminum concentration (8,204 µg/L) was calculated using data collected by CCWMP. However, the average was certainly elevated by a single total aluminum concentration of 134,049 µg/L measured during a mid-2011 storm (see **Table 4**). Overall, wet weather total aluminum concentrations measured by VCSQMP in the Calleguas Creek Watershed appear to be slightly higher than those measured by CCWTMP when comparing the VCSQMP Calleguas Creek data distribution shown in **Figure 3** with the CCWTMP receiving water data distribution shown in **Figure 8**.

Percent exceedance of the Title 22 Primary MCL for total aluminum was calculated for environmental data collected at each CCWTMP monitoring site under both dry and wet weather conditions as a means to identify any "hotspots" among the TMDL monitoring sites located within the Calleguas Creek Watershed. As described above with regard to VCSQMP total aluminum data, the term hotspot is used to describe a monitoring location that shows frequent exceedances of the water quality objective, without consideration of the specific total aluminum concentrations that produced an exceedance of the objective. Similar to what was observed for total aluminum samples collected by the VCSQMP, dry weather samples collected by the CCWTMP showed approximately 20% or less exceedance rates of the Title 22 Primary MCL, as shown in **Table 7**.

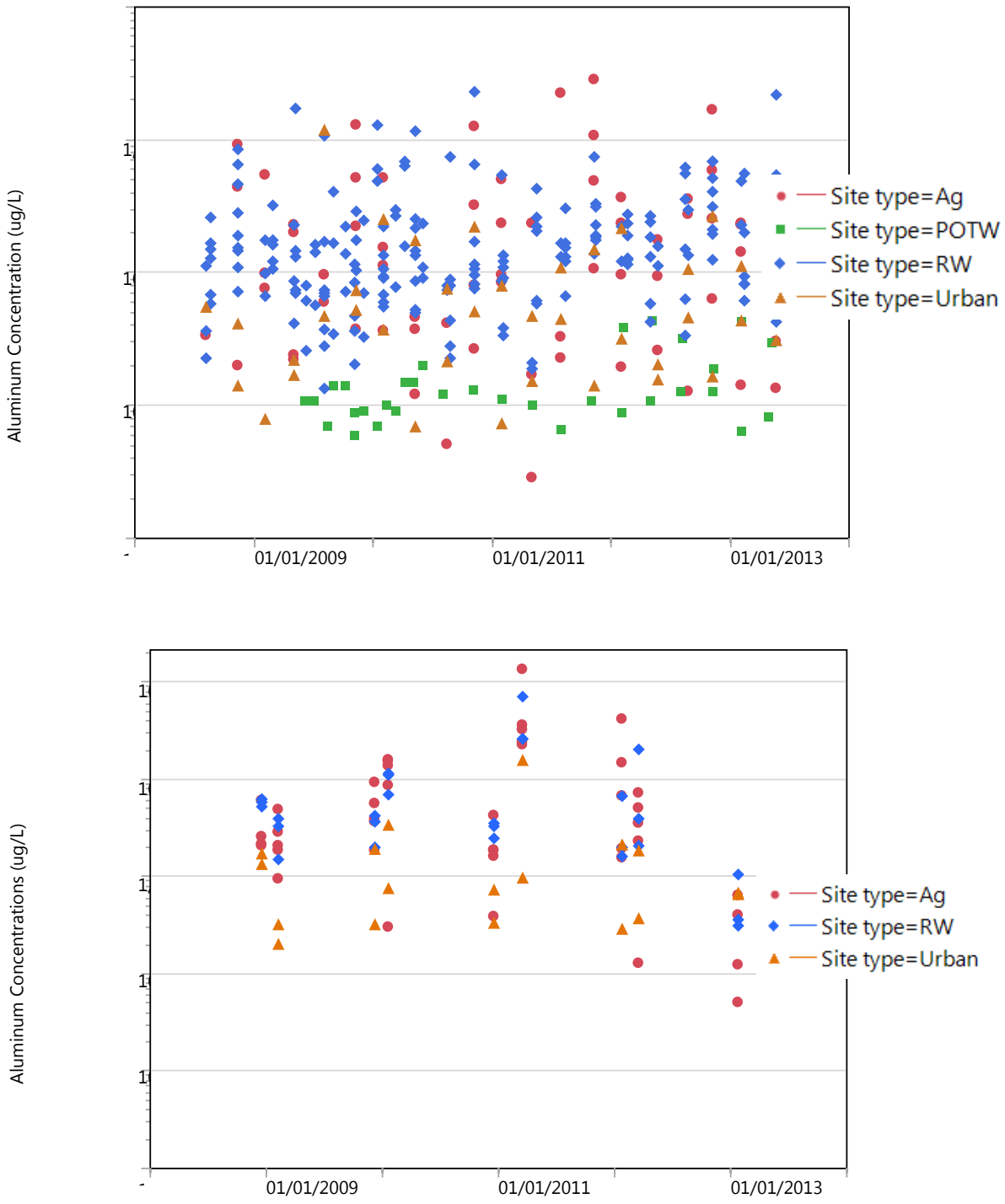

Figure 7: Calleguas Creek Total Aluminum Concentrations Measured by CCWTMP [Dry Weather (top) and Wet Weather (bottom)].

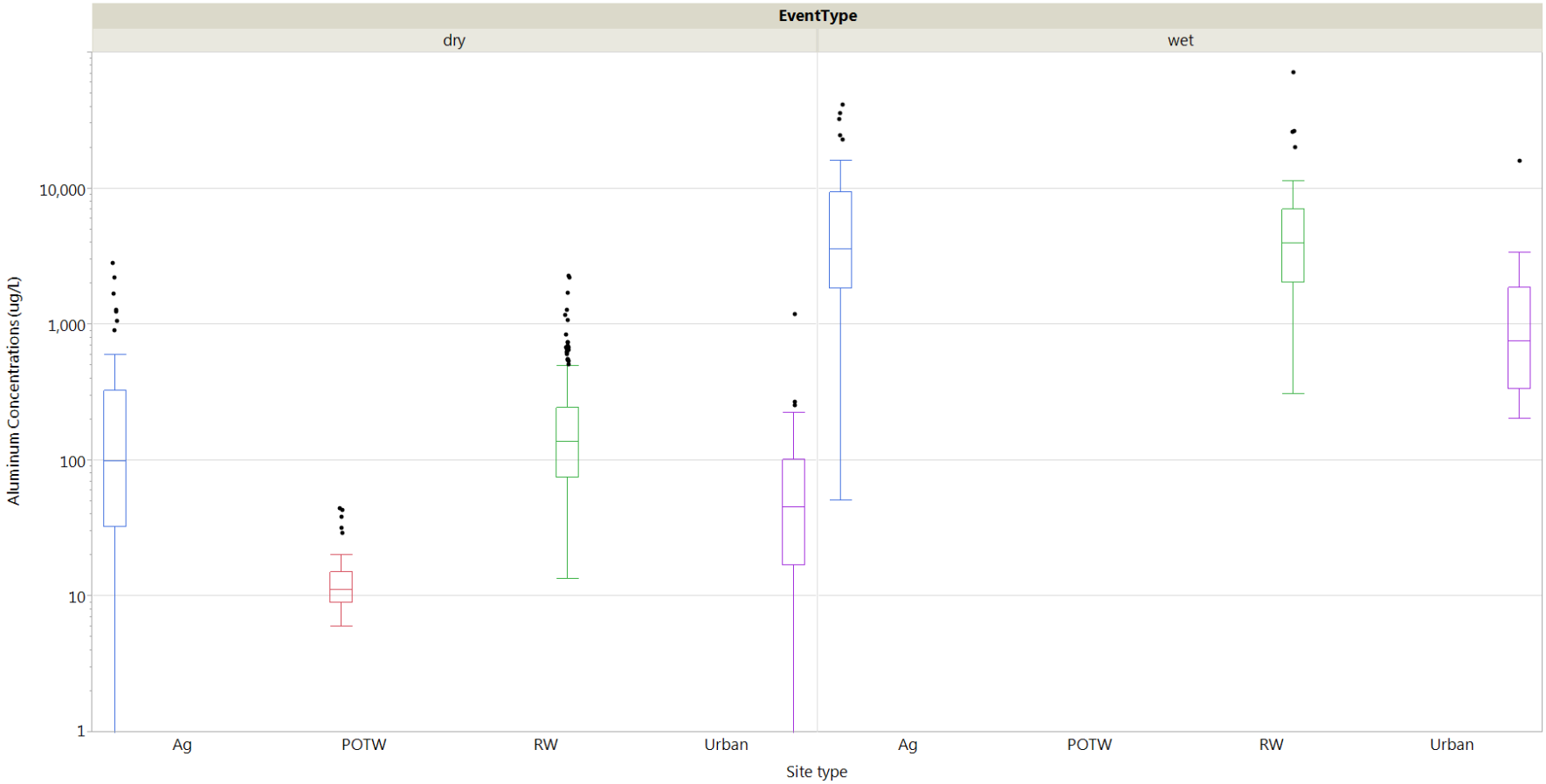

Figure 8: Comparison by Land Use Characterization Type of Total Aluminum Concentrations Measured during Dry and Wet Weather Monitoring Events in the Calleguas Creek Watershed by CCWTMP.

Also similar are the wet weather exceedance rates observed for both monitoring programs. The CCWTMP collected total aluminum data showed exceedances of the water quality objective at each site monitored during wet weather events. All monitoring locations except for D_ADOLF, located in the Conejo subwatershed, posted water quality objective exceedances greater than 50 percent. Generally speaking, there appears to be no upstream-downstream trend to the total aluminum concentrations causing exceedances of the water quality objective. There is much variability in the average concentrations of water quality samples that exceed the Title 22 Primary MCL for total aluminum at those sites where exceedances are observed. Within the Calleguas Creek Watershed, it appears that upstream agricultural land use discharges appreciably influence surface water total aluminum concentrations measured downstream of such discharges within a subwatershed.

Table 7: Calculated Percent Exceedances of the Title 22 Primary MCL for Total Aluminum by Event Type and CCWTMP Monitoring Location in the Calleguas Creek Watershed.

		Dry Weather		Wet Weather	
Subwatershed[1]	Site ID	Total Samples (n)	% Exceedance	Total Samples (n)	% Exceedance
Arroyo Simi	D_SIMI	6	0	---	---
Conejo	D_GERRY	2	0	8	87.5
	D_ADOLF	20	0	9	11.1
	D_HILL	1	0	---	---
Calleguas Creek	D_CAMA	25	0	---	---
	UNIV	29	0	9	88.9
	D_BROOM	14	21.4	8	50.0
	PCH	2	0	---	---
Revolon Slough	D_SANTV	19	15.8	9	88.9
	VENTRA	20	5.0	9	66.7
	D_WOOD	12	0	9	88.9
	WOOD	29	3.4	9	88.9
Magu Lagoon	ODDS	20	0	9	88.9
	SG_74	29	20.0	---	---
	RR_BR	20	3.4	9	100
	BPT_15	20	0	---	---
	BPT_14	20	0	---	---
	BPT_6	20	0	---	---
	BPT_3	20	0	---	---

1. Subwatersheds and Site IDs are listed in upstream to downstream order.

RELATIONSHIP OF ALUMINUM TO TSS AND FLOW

A key observation made clear by the above water quality objective exceedance evaluations is that total aluminum concentrations in surface waters are infrequently observed to exceed the Title 22 Primary MCL for the metal during dry season, low flow conditions when surface waters are low in total suspended solids (TSS). Conversely, exceedances of the water quality objective

are consistently observed during wet season, high flow conditions when surface waters contain elevated levels of TSS. As shown in **Table 8**, dry weather average TSS concentrations are significantly lower than wet weather average TSS concentrations. Furthermore, mass emission and receiving water sites exhibited higher average TSS concentrations under both dry and wet conditions than did major outfalls or other land use sites. To provide a sense of the clarity of the water collected and analyzed for dry weather events, a wastewater treatment plant providing secondary treatment is typically required to produce effluent having a TSS concentration of 30 mg/L or less.

Table 8: Average Dry and Wet Weather TSS Concentrations Measured at VCSQMP NPDES Stormwater Monitoring Sites: 2004 – 2013.

			Dry Weather	Wet Weather
Watershed	**Site ID[1]**	**Site Description**	**Avg TSS (mg/L)**	**Avg TSS (mg/L)**
Ventura River	**MO-MEI**	Major outfall	7	342
	MO-OJA	Major outfall	6	234
	ME-VR	Mass emission	2	1092
	ME-VR2	Mass emission	7	548
Santa Clara River	**MO-FIL**	Major outfall	9	34
	MO-SPA	Major outfall	7	202
	ME-SCR	Mass emission	67	3326
	R-1	Residential land use	---	28
	I-2	Industrial land use	---	99
	MO-VEN	Major outfall	10	227
	MO-OXN	Major outfall	44	192
Calleguas Creek	**MO-MPK**	Major outfall	10	411
	MO-SIM	Major outfall	6	431
	W-3	Receiving water	---	4200
	MO-CAM	Major outfall	7	272
	MO-THO	Major outfall	---	294
	ME-CC	Mass emission	23	743
	A-1	Agricultural land use	---	273
	W-4	Receiving water	---	2106
Pacific Ocean	**MO-HUE**	Major outfall	14	59

1. Site IDs within watersheds are listed in upstream to downstream order.

Stations currently monitored by the VCSQMP are shown in bold type.

As a means to determine the strength of the suspected relationship between total aluminum concentrations measured in the water column and (1) TSS measured in the water column (at a given site during a given event) or (2) flow (event mean flow calculated for a given site during a given event), District staff performed a Kendall correlation analysis to measure the degree of correspondence or association between sets of ranked, non-parametric data. A non-parametric test was used because the aluminum, TSS, and flow data are not normally distributed; they more closely fit a log-normal distribution. A Kendall tau (τ) rank correlation coefficient was

calculated to determine the strength of the correlation between either total aluminum and (1) TSS or (2) flow. District staff performed correlation analyses for data collected at the mass emissions sites (ME-CC, ME-SCR, ME-VR(2)) in each watershed using data combined from wet and dry events and from wet events only. As a check on the Kendall correlation, a simple linear regression of the various data pairs was performed on log-transformed data to calculate a correlation coefficient (r) and coefficient of determination (R^2 or R-squared). Correlation analyses for total aluminum and flow could not be performed for the mass emission site in the Santa Clara River Watershed due to the longstanding inability to accurately measure flow at the ME-SCR site. The statistics for all pairwise analyses are provided in **Table 9**.

Table 9: Kendall Correlation and Simple Linear Regression Analyses Statistics Calculated for Aluminum, TSS, and Event Mean Flow Data Collected at Mass Emission Sites.

		Dry + Wet Weather Data		Wet Weather Data Only	
Site ID	**Statistic**	**TSS**	**Flow**	**TSS**	**Flow**
ME-VR(2)	Tau	0.63	0.16	0.63	0.30
	p-value	<0.0001	0.123	<0.0001	0.019
	r	0.794	0.397	0.830	0.592
	R-squared	0.631	0.158	0.689	0.351
	p-value	<0.001	0.006	<0.001	0.001
ME-SCR	Tau	0.69	---	0.43	---
	p-value	<0.0001	---	0.0008	---
	r	0.870	---	0.725	---
	R-squared	0.757	---	0.526	---
	p-value	<0.001	---	<0.001	---
ME-CC	Tau	0.75	0.63	0.53	0.40
	p-value	<0.0001	<0.0001	<0.0001	0.002
	r	0.924	0.823	0.674	0.620
	R-squared	0.853	0.678	0.454	0.384
	p-value	<0.001	<0.001	<0.001	<0.001
All Mass Emission Sites Combined	Tau	0.74	---	---	---
	p-value	<0.0001	---	---	---
	r	0.876	---	0.841	---
	R-squared	0.768	---	0.707	---
	p-value	<0.001	---	<0.001	---

The statistics provided in **Table 9** from the Kendall correlation and simple linear regression analyses performed on aluminum, TSS, and event mean flow data collected at the VCSQMP's mass emission sites show that measured total aluminum and TSS concentrations are strongly correlated for both wet weather and combined dry and wet weather data at significance levels less than 0.001 or better. Total aluminum and TSS concentrations are more highly correlated at the ME-CC monitoring site, followed by the ME-SCR site and then the ME-VR(2) site. Total aluminum and event mean flow are strongly correlated at the ME-CC monitoring site, but the Kendall correlation analysis shows no significant correlation between the two variables at the

ME-VR(2) site. The simple linear regression analysis of the ME-VR(2) data shows significant correlation of total aluminum and event mean flow, but the association between the two parameters is not as strong as it is for total aluminum and TSS at the monitoring site. The information provided in **Table 9** suggests that total aluminum concentrations at the mass emission sites evaluated are more strongly correlated with TSS than with flow, indicating that measured water column aluminum concentrations are more dependent on the amount of solids suspended in the water column than the flow transporting the aluminum and TSS.

Scatter plots of the paired data collected at the Calleguas Creek mass emission site, ME-CC, are provided in **Figure 9** and **Figure 10**. Additional scatter plots for the ME-VR(2), ME-SCR, and all mass emission sites are included in Appendix A.

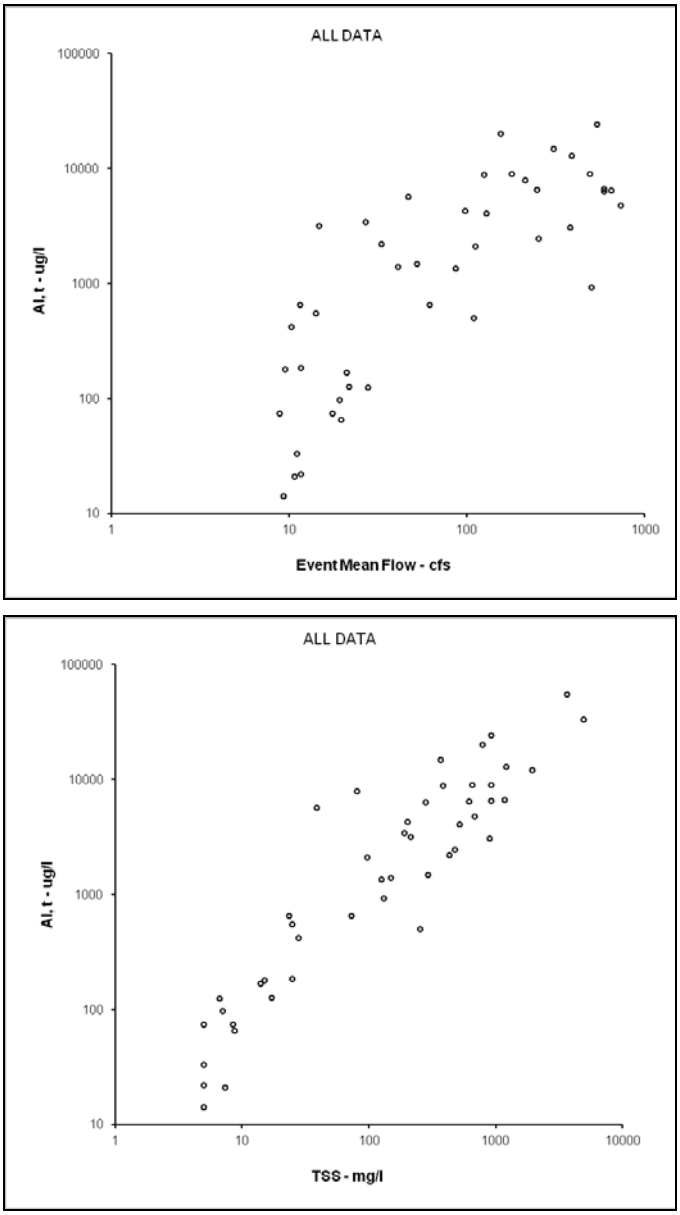

Figure 9: Scatter Plots of Aluminum Vs Event Mean Flow and Aluminum Vs TSS for Combined Dry and Wet Weather Data Collected at the Calleguas Creek Mass Emission Site, ME-CC.

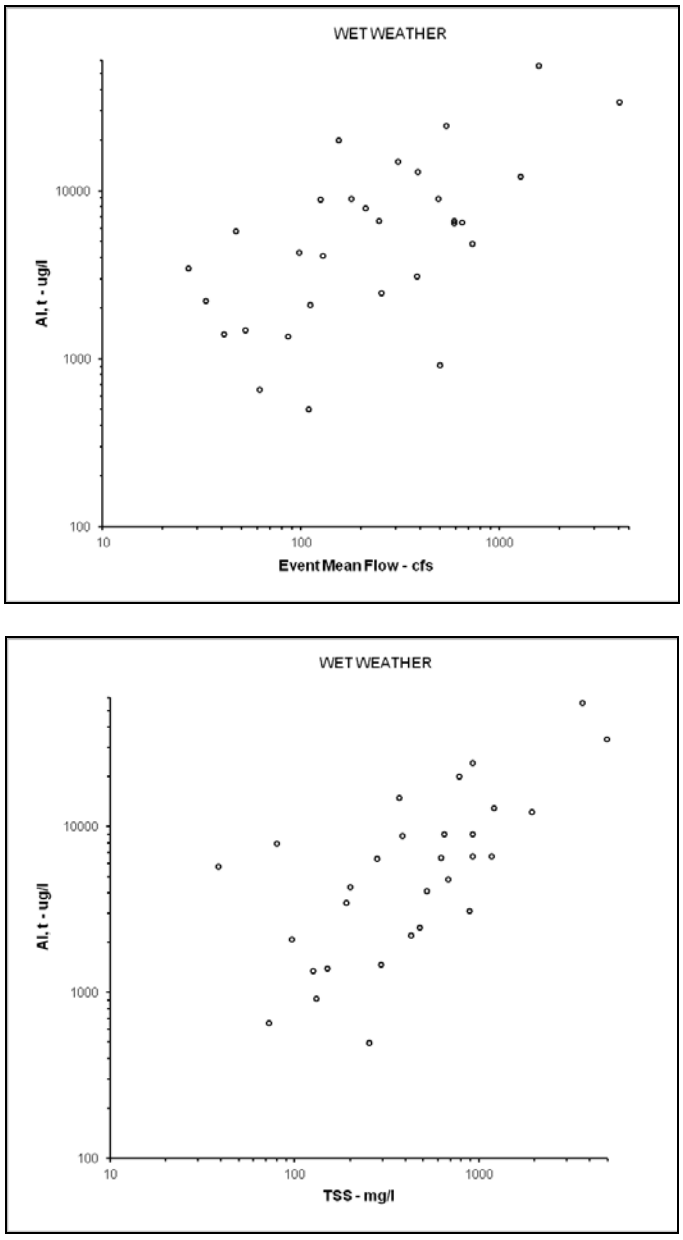

Figure 10: Scatter Plots of Aluminum Vs Event Mean Flow and Aluminum Vs TSS for Wet Weather Data Collected at the Calleguas Creek Mass Emission Site, ME-CC.

Aluminum in Ventura County Soils

Based on the elevated levels of total aluminum measured in Ventura County surface waters, it is useful to have an understanding of total aluminum concentrations measured in the County's soils since the earlier evaluations of average TSS concentrations and the correlation analyses showed that suspended solids, certainly containing soil particles and fine sediments, were observed to increase substantially in combination with total aluminum and flows during wet weather events. An online search for Ventura County soils data containing total aluminum concentrations resulted in the acquisition of data from only three monitoring programs: the Southern California Bight Monitoring Program (lead by SCCWRP), the Southern California Stormwater Monitoring Coalition (SCSWMC), and the State's Surface Ambient Monitoring Program (SWAMP). All soils data were queried from the California Environmental Data Exchange Network (CEDEN) online database. Soils data were available for all three watersheds monitored by the VCSQMP, with most data obtained from the Santa Clara River Watershed. Total aluminum soils data were reported as single or multiple concentration measurements at each monitoring site. An average concentration was calculated for those monitoring sites where multiple measurements were provided in CEDEN. Soil samples were collected adjacent to water bodies in each watershed. **Table 10** shows soil total aluminum concentrations at 14 monitoring sites in Ventura County. The total aluminum concentrations provided in **Table 10** are graphically displayed within discrete concentration ranges in **Figure 11**. The total aluminum concentrations shown in **Table 10** range from 6,820,000 µg/kg (Santa Paula Creek, Santa Clara River Watershed) to 105,692,500 µg/kg (average value at Calleguas Creek Main Stem, Calleguas Creek Watershed).

Table 10: Total Aluminum Soil Concentrations at Monitoring Locations in Ventura County.

Watershed	Monitoring Site	Total Al (µg/kg)	Monitoring Program
Ventura River	Ventura River Bio 0	75,894,500 avg (4)	SWAMP
	Ventura River Estuary	34,764,000	SWAMP
Santa Clara River	Sespe (Upper) 02363	36,080,000	SCSWMC
	Piru Creek 02764	20,646,000	SCSWMC
	Newhall Ranch Blue Cut	38,200,000 avg (2)	SWAMP
	Piru Creek	47,200,000	SWAMP
	Sespe Creek 04868	46,519,000	SCSWMC
	Sepse Creek	75,238,600 avg (5)	SWAMP
	Santa Paula Creek	6,820,000	SCSWMC
	Santa Clara River Estuary	63,869,400 avg (5)	SWAMP
	Ventura Marina 4	64,180,000	SWAMP
Calleguas Creek	Calleguas Ck below Camrosa WWTP	50,195,750 avg (4)	SWAMP
	Calleguas Creek Main Stem	105,692,500 avg (2)	SWAMP
	B08-6543	15,300,000 avg (6)	SoCal Bight

Numbers shown parenthetically for average total aluminum concentrations represent the number of data points used in calculating an average concentration.

As a means to compare total aluminum water column concentrations measured in the surface waters of the three watersheds to total aluminum soil concentrations measured in the watersheds, it is first necessary to determine the mass of total aluminum per mass of TSS measured in a water quality sample. Paired total aluminum and TSS results from wet weather events were used to calculate µg of total aluminum per kg of TSS. These µg/kg results calculated for all paired data were then averaged across each watershed. It was assumed that all aluminum measured in a water quality sample existed in the total fraction, which is close to the average 98.4 percent of measured aluminum that was calculated to exist in the total fraction across all wet weather samples collected across all VCSQMP monitoring sites. The information presented in **Table 11** allows for a comparison of the mass of total aluminum per mass of total solids measured in water column and soil samples collected in the three watersheds.

Table 11: Mass of Total Aluminum per Mass of Total Solids Measured in Water Column and Soil Samples Collected in Ventura County.

Watershed	Average Total Al per TSS (µg/kg) Measured in Water	Range of Total Al Concentrations (µg/kg) Measured in Soil
Ventura River	24,129,972	34,764,000 – 75,894,500
Santa Clara River	29,731,875	6,820,000 – 75,238,600
Calleguas Creek	24,314,428	15,300,000 – 105,692,500

The range of total aluminum soil concentrations shown in **Table 11** is in line with concentrations identified in two separate surveys of California soils. The first is a 1996 California Benchmark Soils Study that reported a mean total aluminum concentration across California soils of 73,000,000 µg/kg, along with a minimum of 30,000,000 µg/kg and a maximum of 106,000,000 µg/kg (Kearney, 1996). The second study[2] is a survey of 14 Air Force installations in 10 California counties that reported a mean, depth-integrated total aluminum concentration of 7,560,000 µg/kg and a 95th percentile concentration of 23,000,000 µg/kg (Hunter and Davis, 2001; Hunter et al., 2005). Hunter et al. reported that total aluminum soil concentrations vary with depth in the soil profile, and measured total aluminum concentrations were greatest in soil samples collected from 3 feet to 15 feet below ground level. Mean total aluminum concentrations were moderately lower in soil samples collected from the surface to a depth of 3 feet, and appreciably lower in soil samples collected deeper than 15 feet from the surface as compared to samples collected in the middle strata (3 – 15 feet). Total aluminum soil concentrations reported between the two studies bookend the range of concentrations measured in Ventura County. Furthermore, the average mass of total aluminum per mass of TSS in the water column that was calculated for the three watersheds appears to be consistent with the range of total aluminum soil concentrations measured in the three watersheds. Stated differently, there do not appear to be total aluminum water column concentrations measured in the various watersheds that are in excess of the concentration of total aluminum that could be contributed from the erosion of area soils. These observations in combination with the earlier evaluation that showed a high correlation between total aluminum and TSS concentrations measured in

[2] The study focused on uncontaminated sample locations to gain an understanding of background (naturally occurring) concentrations of inorganic chemicals to use for comparison against known contaminated sites in risk assessment and risk management work carried out by the Air Force.

VCSQMP water quality samples suggests that the total aluminum measured in water quality samples is derived from the erosion of soil.

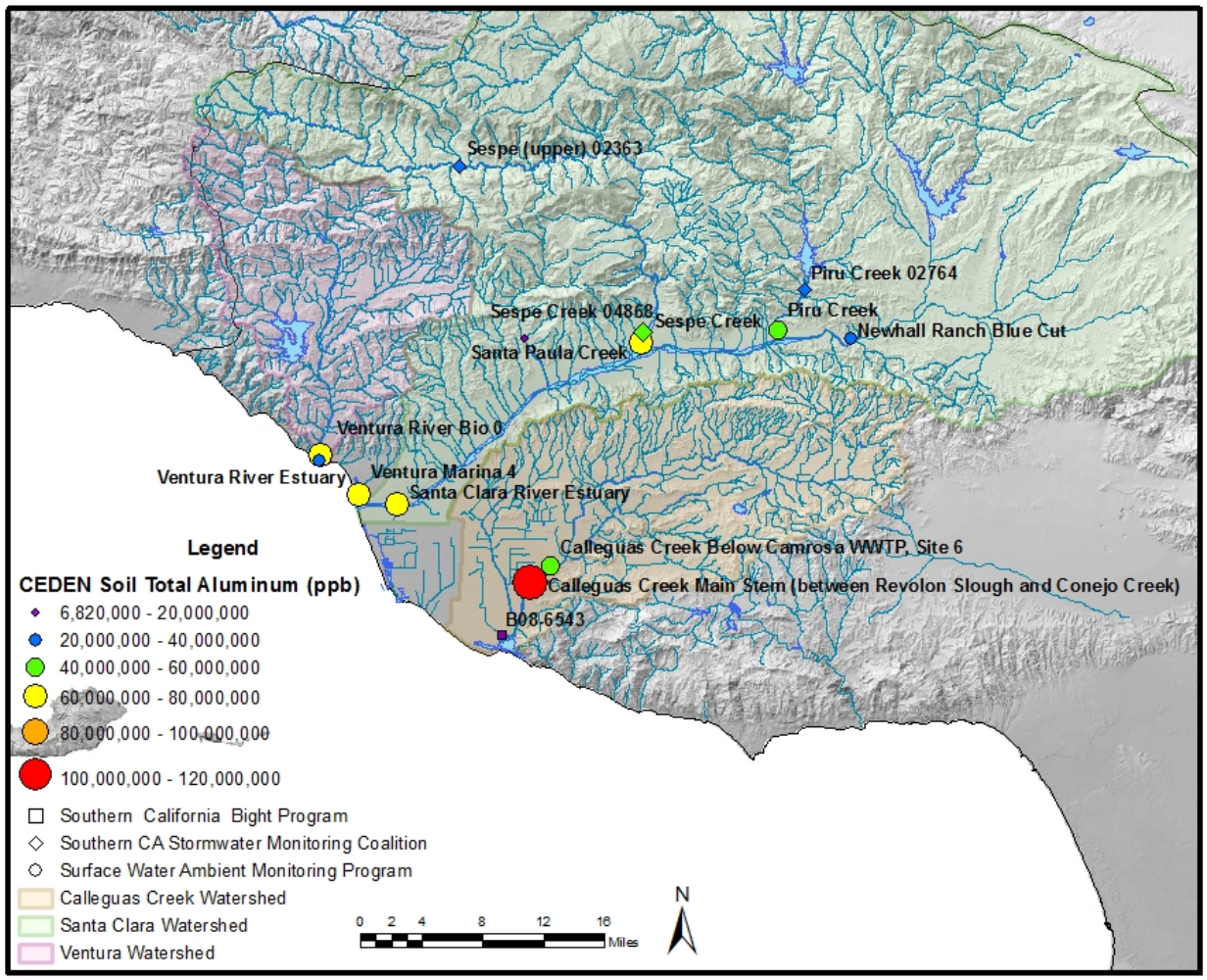

Figure 11: Total Aluminum Soil Concentration Range at Select Monitoring Locations in Ventura County.

Data Gaps and Additional Monitoring

The above analyses suggest that total aluminum measured in dry and wet weather water quality samples collected by the VCSQMP and others is derived from the erosion of area soils. It is currently unknown if anthropogenic activities occurring in the three watersheds hasten the transport of sediments to surface waters at a rate greater than natural erosion processes in the watersheds contribute sediments to local water bodies. In viewing the monitoring sites visited by both the VCSQMP and the CCWTMP, none of them are upstream of areas influenced by anthropogenic activities. This creates a data gap in the VCSQMP's database that would be helpful to close. It has been suggested that additional aluminum data be collected from new monitoring locations that represent land uses little affected by human activities. SCCWRP has recently identified several potential "reference stream" monitoring locations in Ventura County that it may monitor in support of an ongoing project it has in San Diego County. SCCWRP would be looking to monitor sites in Ventura County that meet specific criteria for being undisturbed by human activities. District staff has recently evaluated locations within each of the three watersheds it monitors that lie upstream of existing monitoring sites for the purpose of collecting water quality samples for aluminum and TSS analyses that would be little influenced by anthropogenic activities upstream of the site of collection. The monitoring locations for the collection of additional aluminum data are listed in **Table 12** and shown in **Figure 12**.

Table 12: Monitoring Locations Upstream of Anthropogenic Activities Chosen for Collection of Additional Aluminum Data.

Site Name/Location	Watershed	Monitoring Agency
North Fork Matilija Canyon at Hwy 33 above Wheeler Gorge Campground	Ventura River	VCSQMP, SCCWRP(1)
Matilija Canyon at the Forest Service Gate		
Canada Larga Canyon off of Canada Larga Road		VCSQMP
Sespe Creek near the Piedra Blanca Trailhead (near Rose Valley)	Santa Clara River	VCSQMP
Sisar Creek off of Sisar Road in Upper Ojai		
Sespe Creek at the end of Grand Avenue		
Santa Clara River upstream of Torrey Road		
Upstream of Las Llajas Dam	Calleguas Creek	VCSQMP
Happy Camp Canyon		

1. Matilija Canyon locations potentially to be monitored by SCCWRP in the future.

2013/14 ADDITIONAL ALUMINUM MONITORING

Upstream Sites

With regard to VCSQMP monitoring activities, water and sediment grab samples were collected twice (December 2013 and February 2014) during the 2013/14 monitoring season at the sites shown in **Table 12**. The December 2013 monitoring effort occurred during dry weather and was focused on collecting sediment samples within the streambed and water samples where sites contained water. Results from the December 2013 event are presented in **Table 13**. The

February 2014 monitoring effort occurred during wet weather and was focused on comparing total aluminum and TSS concentrations between mass emission stations and their upstream counterpart locations. Results from the February 2014 event are provided in **Table 14**.

Table 13: Total Aluminum and Total Suspended Solids Concentrations Measured During Dry Weather at Upstream Locations Having Limited Exposure to Anthropogenic Influences – December 18-19, 2013.

Watershed	Site	Matrix	Parameter	Result	Unit
Ventura River	North Fork Matilija Canyon above Wheeler Gorge	sediment	Aluminum, Total	13,000,000	µg/kg
		water	Aluminum, Total	7.4	µg/L
		water	TSS	1 DNQ	mg/L
	Matilija Canyon @ USFS Gate	sediment	Aluminum, Total	14,000,000	µg/kg
	Canada Larga Canyon	sediment	Aluminum, Total	5,100,000	µg/kg
Santa Clara River	Sespe Crk near Piedra Blanca	sediment	Aluminum, Total	8,800,000	µg/kg
	Sisar Creek off Sisar Rd.	sediment	Aluminum, Total	16,000,000	µg/kg
		water	Aluminum, Total	5.9	µg/L
		water	TSS	2 DNQ	mg/L
	Sespe Creek near the end of Grand Ave.	sediment	Aluminum, Total	7,100,000	µg/kg
		water	Aluminum, Total	6	µg/L
		water	TSS	1 DNQ	mg/L
	Santa Clara R. U/S Torrey Rd.	sediment	Aluminum, Total	2,300,000	µg/kg
Calleguas Creek	Upstream of Las Llajas Dam	sediment	Aluminum, Total	7,000,000	µg/kg
	Happy Camp Canyon	sediment	Aluminum, Total	2,000,000	µg/kg

Table 14: Total Aluminum and Total Suspended Solids Concentrations Measured During Wet Weather at Mass Emission Stations and Their Upstream Counterpart Locations – February 28, 2014.

Watershed	Site	Matrix	Parameter	Result	Unit
Ventura River	North Fork Matilija Canyon above Wheeler Gorge	water	Aluminum, Total	19,000	µg/L
		water	TSS	2,600	mg/L
	ME-VR2	water	Aluminum, Total	5,300	µg/L
		water	TSS	100	mg/L
Santa Clara River	Sespe Creek near the end of Grand Ave.	water	Aluminum, Total	30,000	µg/L
		water	TSS	11,000	mg/L
	ME-SCR	water	Aluminum, Total	37,000	µg/L
		water	TSS	3,000	mg/L
Calleguas Creek	Upstream of Las Llajas Dam	water	Aluminum, Total	250,000	µg/L
		water	TSS	17,000	mg/L
	ME-CC	water	Aluminum, Total	24,000	µg/L
		water	TSS	2,300	mg/L

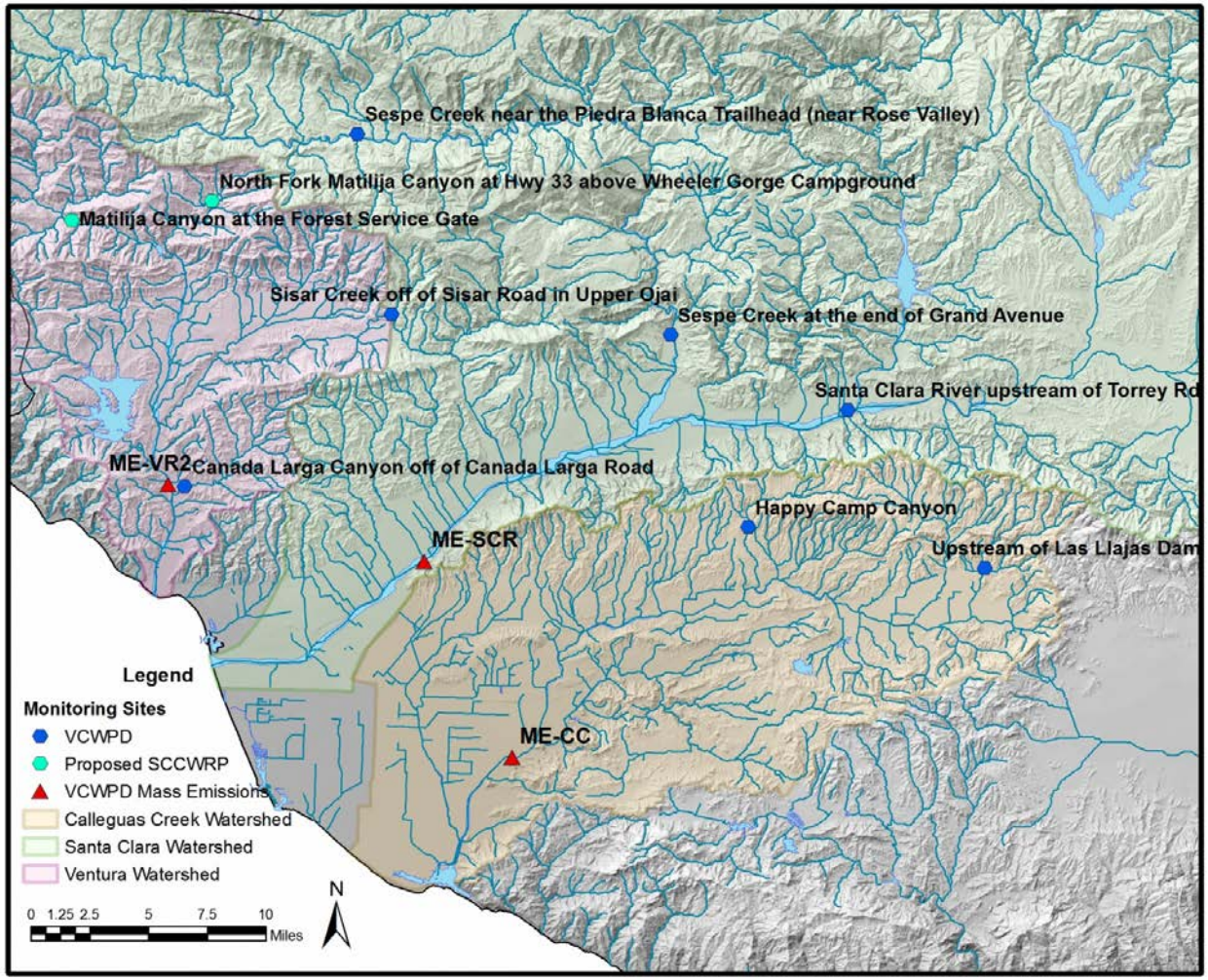

Figure 12: Potential Future Aluminum Monitoring Sites within the Three Subject Watersheds Chosen for Their Limited Exposure to Upstream Anthropogenic Influences.

Results from the December 2013 dry weather monitoring event (see **Table 13**), although limited, show that total aluminum concentrations in streambed sediments are elevated. The total aluminum sediment concentrations measured at the new upstream locations in the Ventura River and Calleguas Creek watersheds were lower than those observed at other sites in each watersheds as measured by other monitoring programs (see **Table 11**). Total aluminum sediment concentrations at the new upstream monitoring sites in the Santa Clara River Watershed are in line with those measured by other programs, with the exception of the Santa Clara River upstream of Torrey Road site. Total aluminum sediment concentrations at this site were lower than those previously measured in this watershed (see **Table 11**). Total aluminum and TSS water column concentrations measured at three of the new upstream sites where water was present during the dry weather monitoring event showed ultra low concentrations of each constituent. The low total aluminum concentrations observed were very much in line with the nearly non-detected TSS concentrations measured, thus supporting the relationship of total aluminum to TSS and flow evaluated earlier. The ultra low base flows observed at the three sites contained ultra low concentrations of total aluminum and TSS.

The February 2014 wet weather monitoring event (see **Table 14**) produced total aluminum and TSS water column concentrations in each of the three watersheds that for the most part were in line with concentrations historically observed in each watershed (see **Table 4**). Precipitation and runoff from the February storm event produced high flows in each watershed that in turn produced mid to upper range concentrations of the two parameters in the water column when compared to historical data. Exceptions to this were the total aluminum and TSS concentrations measured at the new site upstream of the Las Llajas Dam in the Calleguas Creek Watershed that were the highest ever recorded by the VCSQMP for the watershed. Furthermore, the 250,000 µg/L total aluminum concentration observed at the site was the highest aluminum concentration ever measured by the Program across all of its monitoring sites. With the exception of the Santa Clara River Watershed, total aluminum and TSS concentrations measured at the upstream locations were greater than concentrations measured at the downstream mass emission stations within a given watershed. In regard to the Ventura River and Calleguas Creek watersheds, the new upstream monitoring sites with limited exposure to anthropogenic influences were observed to possess higher total aluminum and TSS concentrations than their downstream counterpart locations (i.e., mass emission stations). All total aluminum concentrations measured in samples collected in February 2014 exceeded Title 22 Primary MCL of 1000 µg/L for the parameter. Again, higher flows – having greater erosive and sediment transport capacity – appear to be well-correlated with higher total aluminum and TSS concentrations measured in stormwater runoff.

If SCCWRP eventually monitors the two sites in the Ventura River Watershed that it has classified as meeting its criteria for a reference stream, then the VCSQMP would use these additional data in its continued background characterization of aluminum in the Ventura River Watershed.

Parking Lot Runoff Characterization

As a means to characterize stormwater quality for aluminum and TSS produced by a common urban runoff contributor, the VCSQMP chose to collect wet weather water quality samples from two Ventura County Government Center parking lots during February and March 2014. District staff collected precipitation-based composite samples and grab samples from a large

(14.26 acres) and small (3.63 acres) parking lot, respectively. Composite sample collection of runoff from the large parking lot was possible due to the permanent installation of an auto-sampler adjacent to this area. Both the large and small parking lots were sampled during the February 2014 monitoring event, whereas only the large parking lot was monitored during the March 2014 event. Aluminum and TSS data collected at the two parking lots during the two wet weather monitoring events are provided in **Table 15**.

Table 15: Wet Weather Stormwater Runoff Quality Measured at Ventura County Government Center Parking Lots.

Site	Date	Sample Representation	Parameter	Result	Unit
Large Parking Lot	2/7/2014	0.010 – 0.10 inches (composite)	Aluminum - Total	2100	µg/L
			Aluminum - Dissolved	43	µg/L
			TSS	210	mg/L
		0.10 – 0.20 inches (composite)	Aluminum - Total	780	µg/L
			Aluminum - Dissolved	49	µg/L
			TSS	61	mg/L
Small Parking Lot	2/7/2014	0.10 – 0.20 inches (grab)	Aluminum - Total	260	µg/L
			Aluminum - Dissolved	61	µg/L
			TSS	20	mg/L
		0.20 – 0.30 inches (grab)	Aluminum - Total	240	µg/L
			Aluminum - Dissolved	63	µg/L
			TSS	17	mg/L
Large Parking Lot	3/8/2014	0.010 – 0.10 inches (composite)	Aluminum - Total	1100	µg/L
			Aluminum - Dissolved	48	µg/L
			TSS	180	mg/L
		0.10 – 0.20 inches (composite)	Aluminum - Total	1700	µg/L
			Aluminum - Dissolved	15	µg/L
			TSS	290	mg/L
		0.20 – 0.30 inches (composite)	Aluminum - Total	1200	µg/L
			Aluminum - Dissolved	12	µg/L
			TSS	150	mg/L
		0.30 – 0.85 inches (composite)	Aluminum - Total	760	µg/L
			Aluminum - Dissolved	15	µg/L
			TSS	89	mg/L

The aluminum and TSS data presented in **Table 15** offer a preliminary characterization of the concentrations of these two constituents measured in stormwater runoff from a typical, well-used urban parking lot. Samples were collected at discrete points throughout a storm event to be representative of a specific pollutant concentration present after a certain volume of precipitation had fallen. The February data show that concentrations of total aluminum and TSS measured at the large parking lot were greater that those measured at the small parking lot. Based only on the

two sample representations for each site, it appears that there was a 'first flush' phenomenon with higher total aluminum and TSS concentrations that occurred at the large parking lot during the first 0.10 inches of precipitation that fell, whereas concentrations of all three parameters were quite similar across the two samples collected at the small parking lot. The March monitoring event shows a peak in concentrations for total aluminum and TSS taken at the second discrete sampling (0.10 – 0.20 inches), and overall concentrations for both parameters that are not dissimilar from those measured in the large parking lot during the February event. Across two sites and both sampling events, dissolved aluminum concentrations were always significantly lower than total concentrations.

Average wet weather total aluminum concentrations at VCSQMP monitoring sites measured from 2004 to 2013 are presented in **Table 16**. Only two monitoring locations – the major outfalls MO-FIL and MO-HUE – possess average total aluminum concentrations less than the 1000 µg/L Title 22 Primary MCL for the metal. The average wet weather concentrations at all other monitoring locations exceed the Primary MCL. The limited parking lot runoff data for total aluminum (see **Table 15**) showed four exceedances of the Title 22 Primary MCL for the metal out of the eight samples analyzed. While the parking lot samples are limited in their number, their measured total aluminum concentrations are generally lower than the average total aluminum concentrations calculated for the major outfall, mass emission, and other land use characterization monitoring sites listed in **Table 16**. In comparing the wet weather concentrations of TSS measured in runoff collected from the Government Center parking lots to wet weather concentrations measured at VCSQMP monitoring locations, particularly major outfalls, the parking lot TSS concentrations shown in **Table 15** are generally lower than the average wet weather TSS concentrations shown in **Table 8**. Furthermore, parking lot TSS concentrations are appreciably lower than the average wet weather TSS concentrations calculated for mass emission and receiving water monitoring sites, also presented in **Table 8**. Because the concentrations of total aluminum and TSS measured in Government Center parking lot runoff represent only single, discrete sources of these pollutants to the overall contributions of these constituents made by urban runoff, additional monitoring and analysis of other parking lot runoff and other urban runoff pollutant sources would be necessary in order to ascertain the overall contribution of total aluminum and TSS from parking lot and urban runoff to area receiving waters.

Table 16: Average Wet Weather Total Aluminum Concentrations Measured at VCSQMP NPDES Stormwater Monitoring Sites: 2004 – 2013.

Watershed	Site ID[(1)]	Site Description	Avg Total Aluminum (µg/L)
Ventura River	**MO-MEI**	Major outfall	4,155
	MO-OJA	Major outfall	3,667
	ME-VR	Mass emission	5,560
	ME-VR2	Mass emission	1,653
Santa Clara River	**MO-FIL**	Major outfall	844
	MO-SPA	Major outfall	3,367
	ME-SCR	Mass emission	14,162
	R-1	Residential land use	1,973
	I-2	Industrial land use	1,913
	MO-VEN	Major outfall	2,373
	MO-OXN	Major outfall	2,001
Calleguas Creek	**MO-MPK**	Major outfall	6,738
	MO-SIM	Major outfall	2,251
	W-3	Receiving water	12,350
	MO-CAM	Major outfall	7,468
	MO-THO	Major outfall	6,478
	ME-CC	Mass emission	8,446
	A-1	Agricultural land use	4,518
	W-4	Receiving water	7,468
Pacific Ocean	**MO-HUE**	Major outfall	562

1. Site IDs within watersheds are listed in upstream to downstream order.

Stations currently monitored by the VCSQMP are shown in bold type.

Conclusions

The VCSQMP regularly observes exceedances of the Title 22 Primary MCL for total aluminum of 1000 µg/L in the wet weather water quality samples it collects at various monitoring locations as required by its NPDES MS4 Permit. Exceedances of the Title 22 Primary MCL also are observed for dry weather water quality samples, but on a much less frequent basis. The MS4 Program is responsible for reducing pollutants concentrations in municipal runoff, and the measurement of concentrations that exceed relevant water quality objectives, in particular, places the District and its fellow Copermittees in a position to investigate the cause(s) of such exceedances and implement actions to limit such exceedances where possible. To better understand the sources of aluminum measured in the various watersheds, monitoring was performed on river sediments, as well as wet weather flows from pristine upstream areas and below urbanized areas. The ubiquitous occurrence of aluminum in the earth's crust makes the metal difficult to prevent from entering surface waters as soil, even from pristine areas, is eroded and washed into water bodies, especially during stormwater runoff events.

The various analyses performed in support of the current background evaluation of aluminum in the Ventura River, Santa Clara River, and Calleguas Creek watersheds found that total aluminum is present in concentrations that exceed the Title 22 Primary MCL for the metal as measured at all VCSQMP monitoring locations during wet weather sampling. On average, 74.2 percent of wet weather samples collected from February 2004 to May 2013 exceeded the water quality objective for aluminum. In contrast, dry weather samples collected during the same period show just under a 6 percent exceedance rate. Because the VCSQMP analyzes for both total and dissolved fractions of aluminum, it is known that over 98 percent of the aluminum contained in wet weather samples is present in the total fraction. On average, over 87 percent of the aluminum measured in dry weather samples is present in the total fraction. A comparison of individual VCSQMP monitoring sites showed wet weather exceedance rates greater than 50% except for the current mass emission station in the Ventura River Watershed (ME-VR2; 15.4% exceedance), the City of Fillmore's major outfall (MO-FIL; 22.2% exceedance), and the Port Hueneme major outfall (MO-HUE; 11.1% exceedance). Only water quality samples collected at two mass emissions sites (ME-SCR and ME-CC) were observed to exceed the water quality objective for total aluminum during dry weather monitoring.

A comparison of total aluminum data collected in the Calleguas Creek Watershed by the VCSQMP with data collected by the CCWTMP in the same watershed showed that both data sets are comparable. The CCWTMP data set includes monitoring of agricultural inputs, POTWs, urban inputs, and receiving waters which are used to characterize all inputs to the subwatershed upstream of the point of collection. The ability to distinguish between different land uses with the CCWTMP data set showed that agricultural discharges contribute higher levels of total aluminum to receiving waters than urban discharges. With respect only to dry weather monitoring, the CCWTMP data show that POTWs contribute very little total aluminum to surface waters. Within the Calleguas Creek Watershed, it appears that upstream agricultural land use discharges appreciably influence surface water total aluminum concentrations measured downstream of such discharges within a subwatershed. A future analysis of TSS concentrations in samples collected by the CCWTMP could provide insight into whether agricultural discharges contribute higher concentrations of TSS to receiving waters than do urban discharges.

Correlation analyses of total aluminum and TSS and total aluminum and flow were performed by District staff using a Kendall correlation test and confirmed independently as part of this evaluation using simple linear regression. Results of the correlation analyses showed that measured total aluminum and TSS concentrations are strongly correlated for both wet weather and combined dry and wet weather data at significance levels less than 0.001 or better. Total aluminum and TSS concentrations are more highly correlated at the ME-CC monitoring site, followed by the ME-SCR site and then the ME-VR(2) site. Total aluminum and event mean flow are strongly correlated at the ME-CC monitoring site, but the Kendall correlation analysis shows no significant correlation between the two variables at the ME-VR(2) site. The simple linear regression analysis of the ME-VR(2) data shows significant correlation of total aluminum and event mean flow, but the association between the two parameters is not as strong as it is for total aluminum and TSS at the monitoring site. The correlation analyses also suggest that total aluminum concentrations at the mass emission sites evaluated are more strongly correlated with TSS than with flow, indicating that measured water column aluminum concentrations are more dependent on the amount of solids suspended in the water column than the flow transporting the aluminum and TSS.

A review of available Ventura County soils data in each of the three watersheds revealed that total aluminum concentrations in the County are in line with those of other published studies conducted in California. The average mass of total aluminum per mass of TSS in the water column that was calculated for the three watersheds appears to be consistent with the range of total aluminum soil concentrations measured in the three watersheds. These observations in combination with the earlier evaluation that showed a high correlation between total aluminum and TSS concentrations measured in VCSQMP water quality samples suggests that the total aluminum measured in water quality samples is derived from the erosion of soil.

Through the evaluation of historical total aluminum monitoring data collected by the VCSQMP and CCWTMP, it was determined that both programs lacked data collected in upstream portions of a watershed where measured total aluminum concentrations would be little influenced by anthropogenic activities. This data gap prompted the Program to initiate the monitoring of locations far upstream in the three watersheds in December 2013 and February 2014. The new monitoring sites were chosen because their locations are believed to have limited exposure to upstream anthropogenic impacts, and thus act as reference sites with regard to “natural” total aluminum inputs to surface waters. Results from the two monitoring events where water and sediment grab samples were collected at these new monitoring sites showed that upstream locations in each of the three watersheds also possess elevated concentrations of the metal.

Dry weather monitoring performed in December 2013 revealed that total aluminum sediment concentrations at upstream sites in the Ventura River and Calleguas Creek watersheds were lower than those observed elsewhere in each watershed as measured by other monitoring programs. Total aluminum sediment concentrations at the new upstream monitoring sites in the Santa Clara River Watershed are in line with those measured by other programs, with the exception of the Santa Clara River upstream of Torrey Road site. Total aluminum sediment concentrations at this site were lower than those previously measured in this watershed. Total aluminum and TSS water column concentrations measured at three of the new upstream sites where water was present during the dry weather monitoring event showed ultra low concentrations of each constituent. The low total aluminum concentrations observed were very much in line with the nearly non-detected TSS concentrations measured, thus supporting the

relationship of total aluminum to TSS and flow revealed through analysis of the Program's historical data.

Wet weather monitoring of upstream natural areas performed in February 2014 showed total aluminum and TSS water column concentrations in each of the three watersheds that were for the most part in line with concentrations historically observed in each watershed. Although the high flows observed for the late February storm event resulted in a total aluminum concentration of 250,000 µg/L measured at the Las Llajas Dam location in the Calleguas Creek Watershed that is not only the highest concentration ever measured in the watershed, but also among all sites monitored by the Program since it began evaluating aluminum in 2004. With the exception of the Santa Clara River Watershed, total aluminum and TSS concentrations measured at the upstream locations were greater than concentrations measured at the downstream mass emission stations within a given watershed. All total aluminum concentrations measured in samples collected in February 2014 exceeded Title 22 Primary MCL of 1000 µg/L for the parameter. The higher flows observed during this wet weather event, with their greater erosive and sediment transport capacity, appear to be well-correlated with the higher total aluminum and TSS concentrations measured in the water quality samples collected at both the new upstream monitoring sites and the existing mass emission stations. A limited evaluation of total aluminum and TSS concentrations measured in wet weather stormwater runoff collected from Ventura County Government Center parking lots showed these two parameters to generally be present in lower concentrations in parking lot runoff as compared to concentrations observed at the Program's major outfalls, mass emission stations, and other land use characterization sites.

The VCSQMP will need to continue to review and analyze historical and new aluminum data collected in the three watersheds, along with initiating discussions with Regional Board staff, in order to support the use of an appropriate regulatory mechanism or "off ramp" that would limit the Copermittees' liability for controlling high background concentrations of aluminum. A sound scientific and regulatory approach to managing the elevated concentrations of aluminum observed in Ventura County surface waters will be needed to sufficiently protect beneficial uses potentially impacted by this naturally occurring metal.

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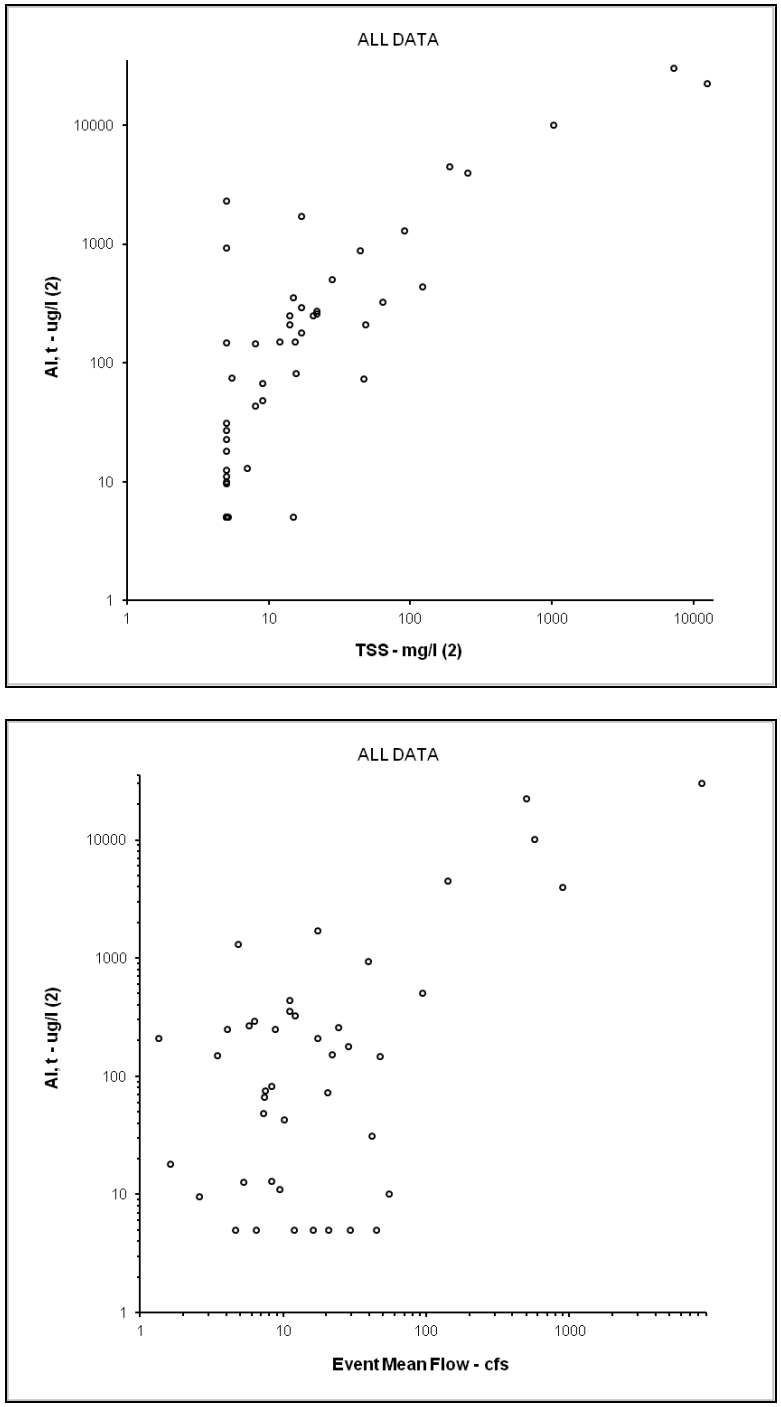

Figure 13: Scatter Plots of Aluminum Vs Event Mean Flow and Aluminum Vs TSS for Combined Dry and Wet Weather Data Collected at the Ventura River Mass Emission Site, ME-VR(2).

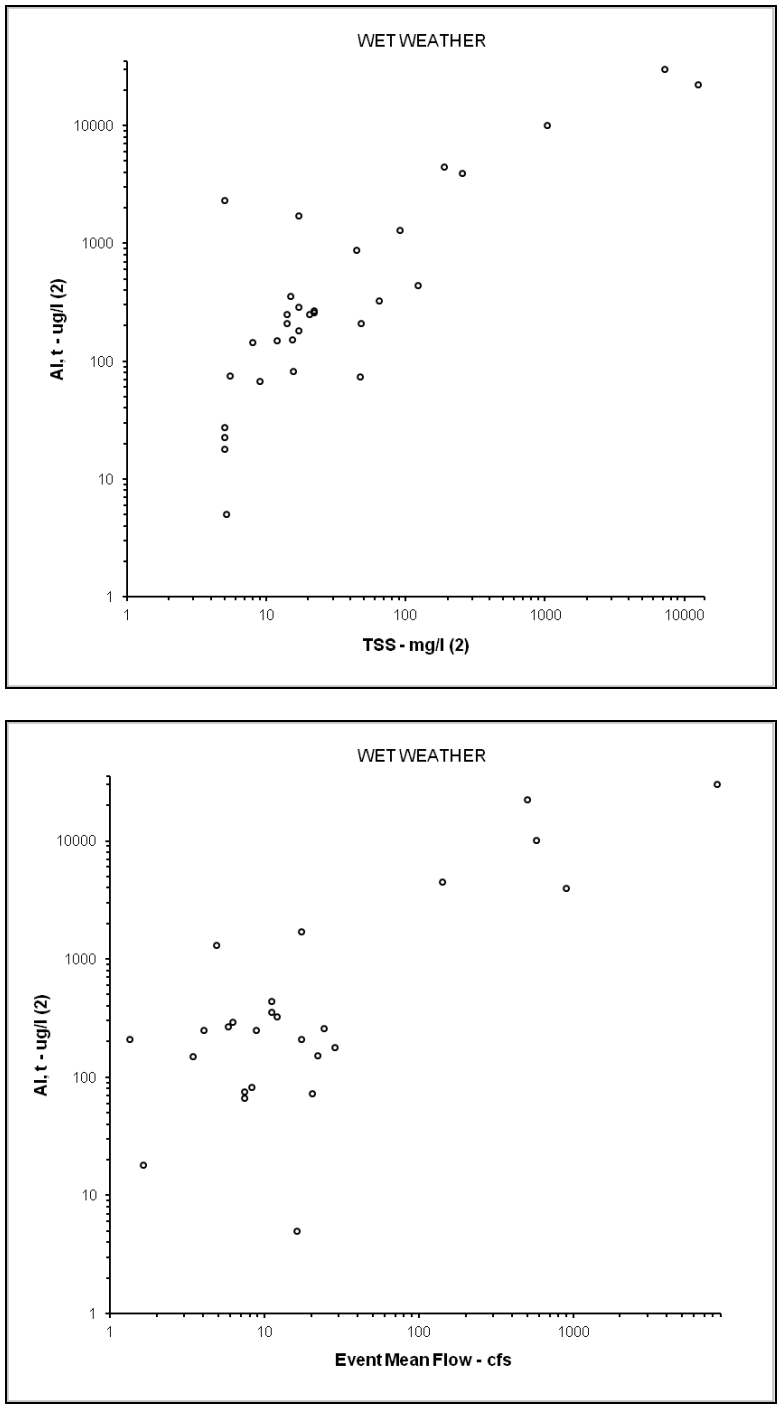

Figure 14: Scatter Plots of Aluminum Vs Event Mean Flow and Aluminum Vs TSS for Wet Weather Data Collected at the Ventura River Mass Emission Site, ME-VR(2).

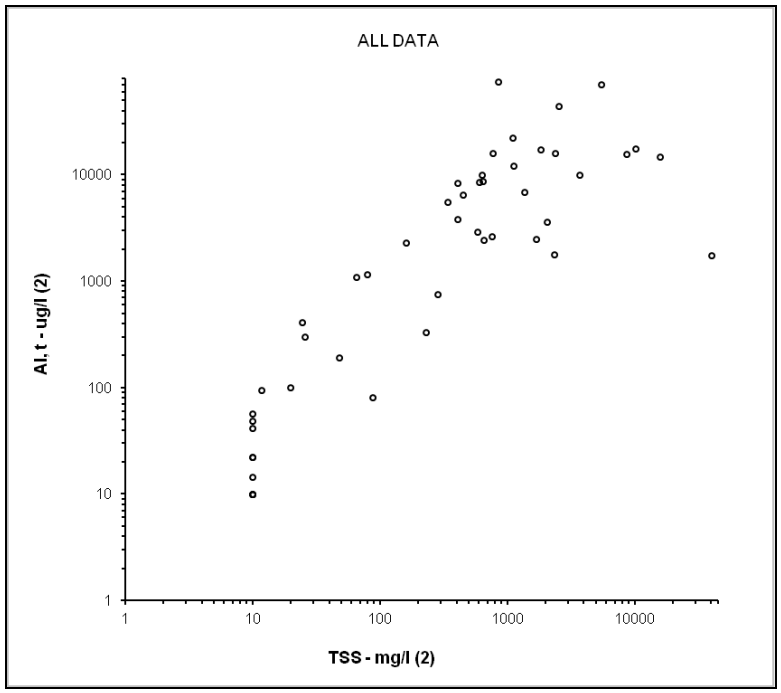

Figure 15: Scatter Plot of Aluminum Vs TSS for Combined Dry and Wet Weather Data Collected at the Santa Clara River Mass Emission Site, ME-SCR.

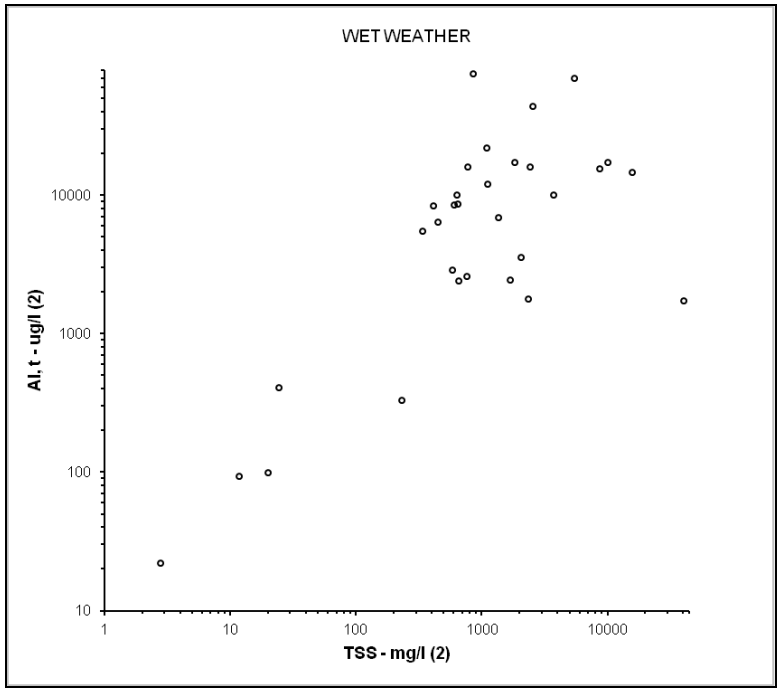

Figure 16: Scatter Plot of Aluminum Vs TSS for Wet Weather Data Collected at the Santa Clara River Mass Emission Site, ME-SCR.

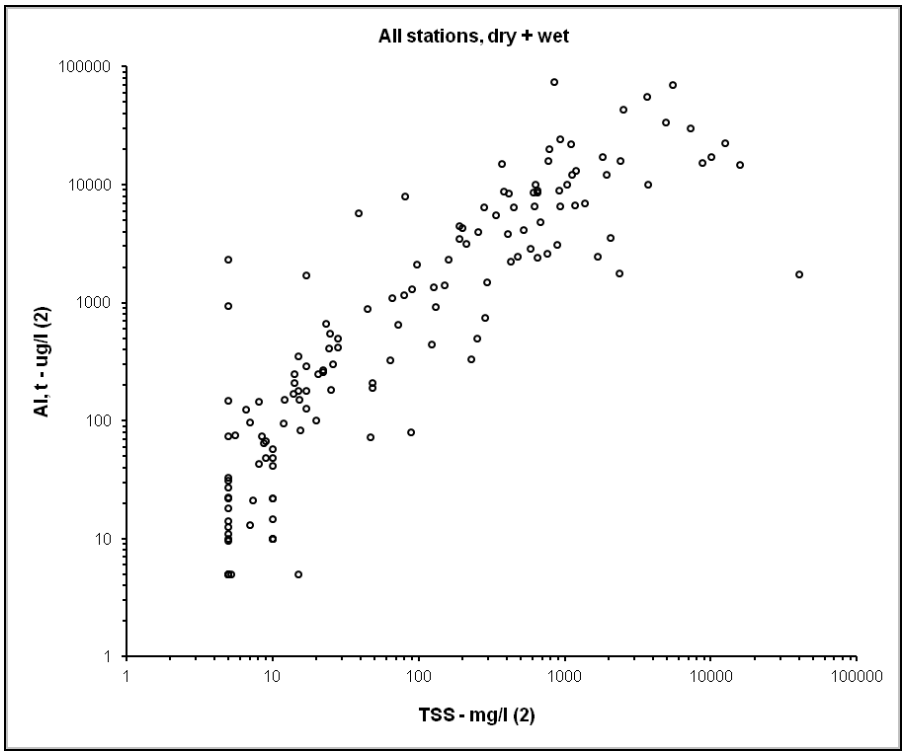

Figure 17: Scatter Plot of Aluminum Vs TSS for Combined Dry and Wet Weather Data Collected Across All Mass Emission Sites.