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OCCURRENCE AND POTENTIAL SOURCES OF Cd, Cu, AND Pb IN REACH 6 OF THE SANTA ANA RIVER

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OCCURRENCE AND POTENTIAL SOURCES OF Cd, Cu, AND Pb
IN REACH 6 OF THE SANTA ANA RIVER

A Project
Presented to the
Faculty of
California State University,
San Bernardino

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
in
Earth and Environmental Sciences

by
May Mamari
September 2019

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ABSTRACT

The Santa Ana River (SAR) is the largest river in Southern California. The flow of the SAR begins in the San Bernardino Mountains and discharges into the Pacific Ocean at Huntington Beach. The SAR contains one of the most essential and rare biodiversity hotspots on earth. In order to protect the wildlife, and suit population demands, the SAR must meet the Clean Water Act (CWA) regulations. The SAR Reach 6 is the uppermost segment of the river, and is currently listed under the CWA 303(d) List for impaired water due to contamination of cadmium, copper, and lead from an unknown source based on limited data provided in 1997 by the San Bernardino County Flood Control District (SBCFCD). This project focused on confirming the contemporary occurrence and identifying the potential source(s) of Cd, Cu, and Pb by comparing new water sample data with that of previous studies. The analysis of previous data identified an interesting correlation between high water hardness and elevated lead levels. The new results from this study suggest that there continues to be a source of these metals in the upper parts of Reach 6 of the SAR. Moreover, the limited data obtained in this study suggests that the source of the contamination is upstream to the northeast of the primary sampling site, possibly on private lands. Future, more comprehensive studies will be required to determine whether Reach 6 of the SAR should remain on the 303(d) list. Source identification if necessary, will be a further challenge.

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CHAPTER ONE

INTRODUCTION

Purpose and Objective

The purpose of this project is to identify the source of contamination in Santa Ana River Reach 6 (SAR Reach 6). In 2010, SAR Reach 6 was placed on the Clean Water Act Section 303(d) List of water quality limited segments due to contamination with cadmium, copper, and lead from unknown sources. The California State Water Resources Control Board is required to identify impaired waters that do not meet water quality standards. The focus of this research was to compare the concentration of contaminants between multiple groups of samples taken in wet and dry seasons by different agencies to evaluate if there are any environmental influences on the concentration. The comparison will help determine whether the contamination source is either natural or anthropogenic.

Background

The History of the Santa Ana River

The Santa Ana River (SAR) is the largest river system (1) located in Southern California, flowing nearly 100 miles (2). The flow of the SAR begins in the San Bernardino Mountains, formed from the accumulation of snow melt and flood runoff; it discharges into the Pacific Ocean at Huntington Beach (Figure 1). The SAR contributes to the largest watershed in the region, covering nearly 3,000 square miles. This watershed reaches portions of Los Angeles, Riverside,

San Bernardino, and Orange County (3). Historically, the SAR has had a huge effect on the settlement of human population for nearly 9,000 years, originally inhabited by Yuharetum/Serrano and Tongva/Gabrielino tribes. The Serrano Tribe inhabited the San Bernardino Mountains, and the Tongva Inhabited Los Angeles Basin. In 1542, the first European ship sailed past the river by Juan Rodriguez Cabrillo. It wasn't until 1769 when Juan Gaspar de Portola's mission landed in the watershed and named the river and the mountains in honor of Saint Anne's Day. The European mission occupied the watershed up until 1834. Following the Mexican American war in 1848 the watershed area was added to the State of California as part of the United States in 1850 (4).

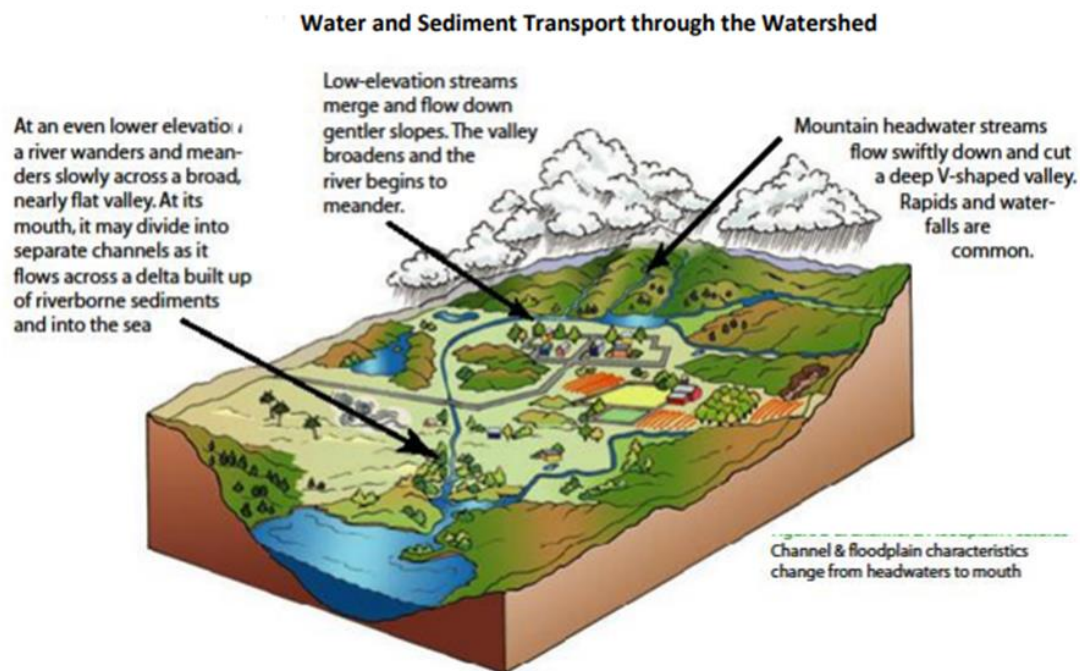


Figure 1. SAR Water Transport Through the Watershed (5).

The population of SAR Watershed kept growing as inhabitants took advantage of its “Life-giving water”, but many were quick to recognize and fear its power when flooding (6). With the rapid increase of human population, the lands that once naturally absorbed flood water from rainfall runoff became occupied, and concern over flood damage spiked (7). The building of Prado Dam was authorized in 1936 with construction starting two years later, reaching completion in 1941 (8). Unfortunately, the construction did not commence until after the most destructive flood in Southern Californian history, sending walls of mud across Orange County (9) and resulting in 19 deaths, 2,000 homeless, and 68,400 acres of flooded area (4). Despite all the improvement projects achieved on the Prado Dam, the 1975 study by The Orange County Flood Control District (OCFCD) showed that Prado Dam can provide only a 70-year level of flood protection (7), meaning statistically, this flood can occur once every 70 years. In 1986, the United States Army Corps of Engineers (USACE) considered the flood threat of the SAR the most dangerous in the U.S. which led to the building of the Seven Oaks Dam in 1999 (1). The Seven Oaks Dam is the tenth largest dam made of compacted natural material like clay, sand, soil, and rocks (8). Even with the fortification brought by the Seven Oaks Dam, a few days of heavy rains in January 2005 caused another drastic flood, evacuating over 800 homes in the City of Corona. Additionally, the Prado Dam, which was under construction for expansion at the time, buckled under the high reservoir brought by the flood and began to crack and leak under the stress (9). A map of the SAR Watershed and its drainage systems is illustrated in Figure 2, below.

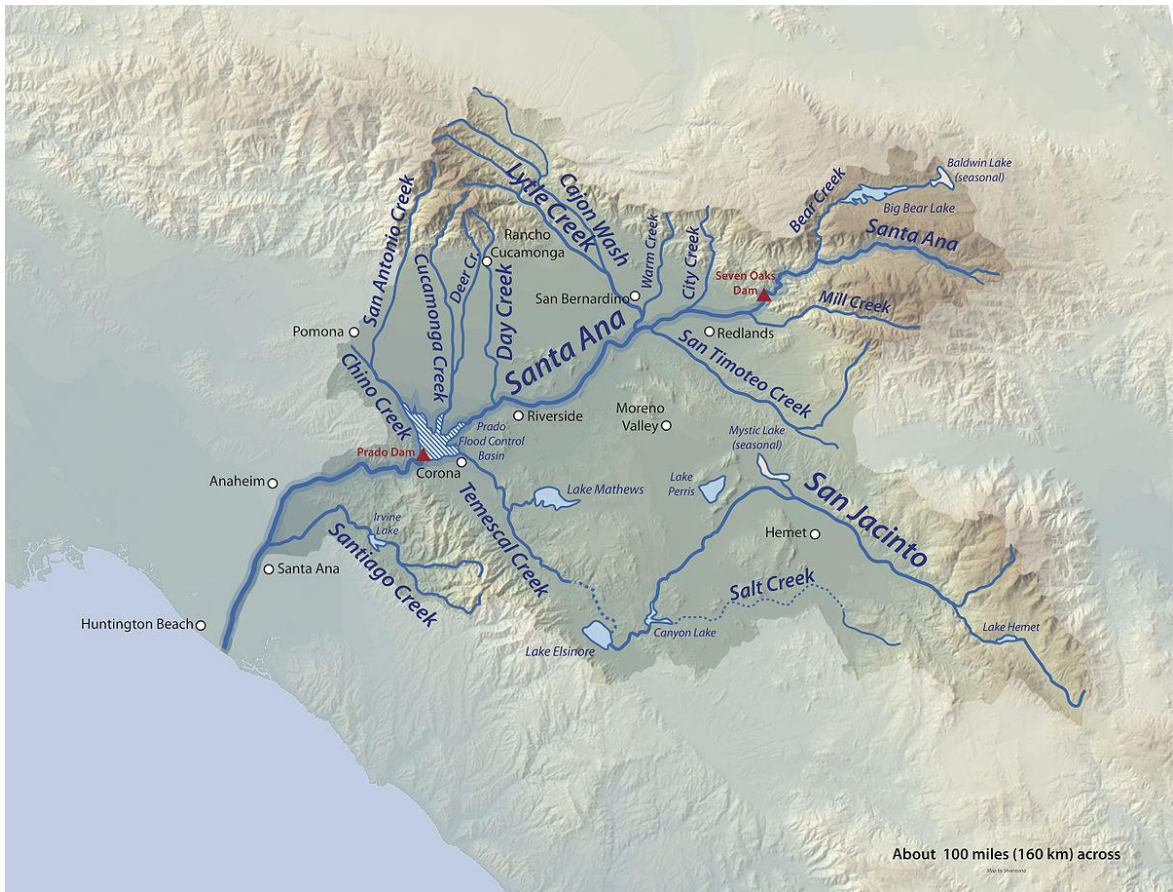


Figure 2. Santa Ana River Watershed and Drainage System (10).

Ecologically speaking, the SAR lies within one of earth's 25 biodiversity hotspots, rich in flora and fauna; yet, is threatened by the human activity that has become dependent upon it (3) where more than 6 million people rely on the SAR Watershed (11). Along the SAR, the Santa Ana River Trail is the longest recreational path, stretching crest to coast some 50 miles allowing for hiking, riding, and biking (1). Tens of millions of people visit the trail and the watershed each year (11). Conservation of the Watershed's resources, including the centric

lifeline of the SAR, is vital to the ecological health of the region, the state, and potentially the world (12). Ensuring the balance between nature and man places pressure on regulatory agencies that must conduct research, maintain water quality, and establish limits for the use of the SAR.

The SAR is divided into six lengths or reaches (Figure 3). Reach 1 is usually a dry flood control facility, and Reach 2 recharges most of the upstream flows into the Orange County groundwater basin (13). Both reaches form the lower watershed of the SAR are located in Orange County. Reaches 3, 4, 5, and 6 form the upper SAR Watershed. Reach 3 is located within Riverside and Los Angeles Counties, and feeds several small tributaries like Sunnyslope Channel and Cucamonga Creek (13). Reach 4 is located in Riverside and San Bernardino Counties, and much of Reach 4 and 5 operate as flood control facilities (13). Reaches 5 and 6 are located in San Bernardino County. Reach 6 flows year- round from snowmelt and storm runoff (13). Many of the SAR reaches “support self-sustaining populations of trout and other indigenous aquatic species. Several rare, threatened, and endangered species inhabit these areas, including the Unarmored Three Spine Stickleback, the San Bernardino Kangaroo Rat, the Mountain Yellow-legged Frog, the Speckled Dace, the Santa Ana Woolly Star, the Least Bell’s Vireo, and the Southwest Willow Flycatcher” (3).

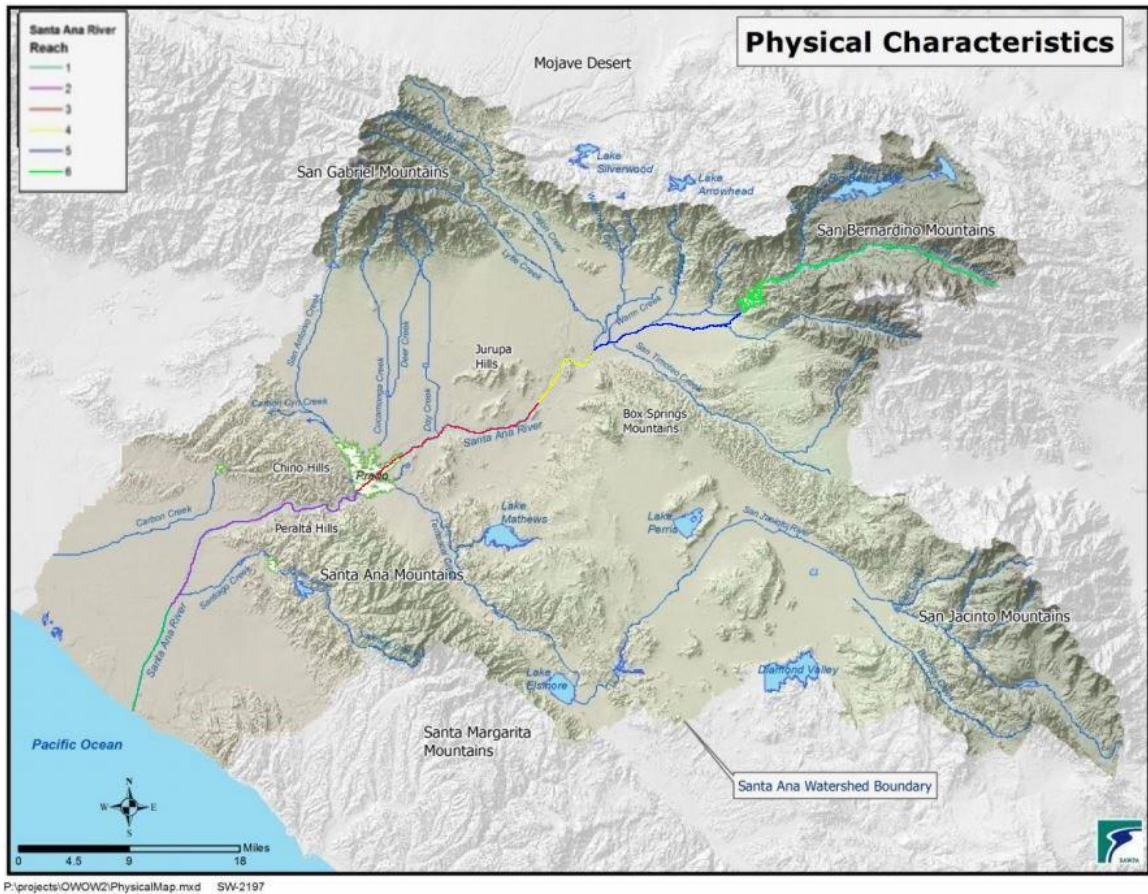


Figure 3. Map Shows Santa Ana River Divided into Six Reaches (14).

Santa Ana River Reach 6

SAR Reach 6 is the uppermost, mountain reach of the SAR (15), located upstream of Seven Oaks Dam. It is located in the Upper Santa Ana Watershed Management Area of the San Bernardino Mountains and consists of several tributaries and streams including Bear Creek, Forsee Creek, Deer Creek, Barton Creek, and Fish Creek (15). The geography of the area is typified by tall peaks, steep slopes, and rugged canyons. Elevations range between approximately

2,000 and 11,000 feet. While currently the area is generally contained in the San Bernardino National Forest under the jurisdiction of the United States Forest Service, there are several areas of private property located in the watershed area such as private residences, churches, schools, vacation cabins, and group camps (15). According to San Bernardino County the estimated year-round residence population as of 2014 was 396 people. The total number of dwelling units was 258 and primarily consisted of one-story, single-family homes. The commercial uses of Reach 6 are concentrated at the northern part of the community (16). The economy of the area is predominantly based on recreational activity like hiking, camping, skiing, and fishing (17).

The 1995 Santa Ana Region Basin Plan states that SAR Reach 6 waterbody's potential and current beneficial uses are "municipal, agriculture, ground water replenishment, Recreational 1, Recreational 2, power, wildlife habitat, and as a spawning area" (18) (17). Additionally, the Clean Water Act, SAR Reach 6 has a beneficial use as a cold freshwater habitat. On December 9, 2016, the Basin Plan proposed the addition of "rare beneficial use" to the list of uses. At the same time, the regulatory water agencies, United States Fish and Wildlife Service (USFWS) and California Department of Fish and Wildlife (CDFW) are developing a habitat conservation plan to reintroduce the Santa Ana Sucker (*Catostomus santaanae*) to SAR Reach 6 in the near future (19).

Statement of Problem

The SAR Reach 6 has a combined use of municipal, agriculture, recreational, power generation, and wildlife habitat. Previous studies have indicated metal contamination of cadmium, copper, and lead, but the known sources are vague. SAR Reach 6 is now listed under 303(d) List of water quality limited segments as impaired water by the State of California. This list helps identify polluted waters and develop plans to restore them. The purpose of this research is to detect pollutant concentrations and propose sources of contamination. Previously collected data by other studies and agencies will be compared to the data from this study to determine if SAR Reach 6 should be unlisted from the 303(d) List due to lack of consistent contamination evidence, or if the 303(d) List process should continue and TDML data should be conveyed to U.S. EPA.

Definition of Terms

This section defines the key concepts and terms mentioned in the project for comprehensive knowledge of the perceptions related to the topic of Clean Water Act and 303(d) List, as well, reference all of the acronyms stated in the text.

- Acute exposure is the short term exposure for the toxic substance.
- Biotic Ligand Model (BLM) is the metals bioavailability modeling in the aquatic environmental and the accumulated toxicity of the metals on gill surfaces organisms.

- California Department of Fish and Wildlife (CDFW) is a state agency established in 1909 dedicated to protect the state's fish, wildlife, plant and native habitats.
- California State Water Resources Control Board (CSWRCB) is a state agency established in 1967 with a mission to protect and enhance water quality in the State of California by implementing the federal law and regulations.
- California Toxics Rule (CTR) it is a rule promulgated by the U. S. EPA to develop numeric criteria to protect the environment and human health.
- Chronic exposure is the repeated exposure for the toxic substance over a long term.
- Clean Water Act (CWA) is a federal law established in 1972 to regulate the discharge of pollutant into water by giving the authority to the U. S. EPA to implement a rule or regulation.
- Clean Water Act Section 303(d) is a program from the U. S. EPA where the states are required to identify and list all polluted waters and develop plans to restore them. Each state is required to submit the list for U. S. EPA approval every two years.
- Dissolved organic carbon (DOC) is the organic matter dissolved in water and can pass through a filter size range between 0.7 and 0.22 μm .
- Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) is a

technique capable of determining a low and ultra-low concentration for wide range of trace elements.

- Microgram per liter ($\mu\text{g/L}$) is a unit used to measure the concentration of a chemical in water in terms of one microgram of chemical per liter of water.
- Milligrams per liter (mg/L) is a unit used to measure the concentration of a chemical in water in terms of one milligram of chemical per liter of water.
- National Pollutant Discharge Elimination System (NPDES) is a permit program created by CWA in 1972 to regulate point sources that discharge a water pollutant in the United States.
- Orange County Flood Control District (OCFCD) established in 1927 by the Orange County Flood Control Act to provide flood and storm water control within the boundaries of Orange County.
- San Bernardino County Flood Control District (SBCFCD) established in 1939 by San Bernardino County Flood Control Act to provide flood and storm water control within the boundaries of the San Bernardino County.
- San Bernardino Forest Services established in 1925 from the Forest Reserve Act that passed in 1891 dedicated to conserve the natural resources of the San Bernardino National Forest.
- Santa Ana Region Basin Plan is the eighth of nine regions in the state of California which establishes the water quality standards for

the surface and ground water in Santa Ana River Basin.

- Santa Ana River (SAR) is the largest river system in the Southern California flowing about 100 miles and divided into six reaches.
- Santa Ana River Reach 6 (SAR Reach 6) is the uppermost reach of the Santa Ana River located within the San Bernardino Mountains upstream of Seven Oaks Dam.
- Santa Ana River Watershed (SAR Watershed) is the 3,000 square miles of land, wetland and waterbody that surrounds the SAR and drain into the Pacific Ocean at Huntington Beach.
- Total Dissolved Solids (TDS) refers to the small amount of organic matter and inorganic salts like calcium, magnesium bicarbonates...etc. that dissolved in water.
- Total Maximum Daily Loads (TMDL) is a term in the Clean Water Act that defines how much of a specific pollutant a body of water can tolerate and still meet water quality standards.
- United States Army Corps of Engineers (USACE) is a federal agency established in March 1802 with a mission to reduce risks from disasters and provide engineering services to public and military.
- United States Environmental Protection Agency (U.S. EPA) is a federal agency established in December 1970 dedicated to protect human and environmental health by setting and enforcing guidelines, policies, and regulations.

- United States Fish and Wildlife Service (USFWS) is a federal agency established in June 1940 with a mission to conserve, enhance, and protect plants, fish, and wildlife and their habitat.
- United States Geological Survey (USGS) is a government agency founded in March 1879 dedicated to study landscape, natural resources, and natural hazards in the United States.

CHAPTER TWO

LITERATURE REVIEW

Contaminant Sources

In 1997, SAR Reach 6 was considered contaminated with the heavy metals of cadmium, copper, and lead from unknown sources due to exceedance of the water quality criteria for the California Toxics Rule (CTR) (20). The samples were taken by San Bernardino County Flood Control District (SBCFCD) during wet and dry seasons. The exceedances were during the wet season. These heavy metal contaminants can be naturally occurring or caused by anthropogenic activities.

Natural Sources

Cadmium is extremely rare and can be found in earth's crust, in lead and copper ores, or in waterways due to natural processes like erosion or volcanic eruption (21). Copper can be found naturally in all waters, and at low levels of intake is essential for most of living organisms involving hemoglobin formation and other metabolism functions (22). Lead is a naturally occurring metal with small amounts in the outer layer of earth's crust; however, it rarely occurs naturally in water (23).

Anthropogenic Sources

Human activity such as legal and illegal waste sites, smelting, mining, leakage from landfill, fertilizer, and burning fossil fuels can increase the concentration of heavy metals particularly zinc, lead, copper, and cadmium (21)

in water. According to the United States Environmental Protection Agency (U.S. EPA) 90 percent of the cadmium found in surface water is due to human activity like mining and urban processes (24). San Bernardino County's common issues within the communities of SAR Reach 6 are illegal junk and trash dumping, excessive outside storage, inoperative vehicles, and construction activities without permits (16). The effect of fertilizers on SAR Reach 6 is minimal because other than personal gardens, there is no large-scale farming in the area. The recreational land use has corresponding effects on the water use of SAR Reach 6. Long term recreational and/or poor waste management activities could lead to leaching heavy metals to the ground, and from there to the water bodies during wet season.

Examining the history of the SAR Reaches and comparing it with similar cases from different water bodies may help identify the sources of contamination. For example, the Blackstone River in South Central Massachusetts has had a history of contamination with copper and lead. The elevated concentration of contamination was due to contribution from urban runoff, wastewater discharges, and contaminated sediment (25). Another case study occurred in the Mississippi River. The heavy metal potential sources were attributed to both natural processes and human activities. Natural processes such as erosion from earth's crust which is naturally high in the heavy metals, releases these heavy metals in small amounts. This process is slow, but overtime can accumulate to reach higher concentrations. Anthropogenic sources of contamination included municipal wastewater-treatment plants, manufacturing industries, mining, and

rural agricultural cultivation and fertilization. The rapid increase in heavy metals trended with the increase of the industrial activity around the river (26).

Contamination history and sources surrounding the SAR is sporadic and vague. SAR Reach 3 is contaminated with copper and lead from unknown sources. SAR Reach 4 is also contaminated with pathogens from unknown sources. These pathogens include an Indicator Bacteria (IB) from an unknown source (27); however, sewage was the suspected source of IB contamination for the lower SAR, but according to a study by Noblet et al. (28), birds and urban runoff were identified as possible sources of contamination. In 1998, some of the mountain communities located within the SAR were listed as containing impaired water bodies for pathogens. Later, it was determined that this contamination was due to faulty subsurface sewage (15).

The information collected from previous studies, such as those listed above, combined with the results of water samples collected for the purpose of this study will aide in further identifying the sources of contamination in the SAR. It is not only important to identify the sources of the contamination, but also to understand the effects that those contaminants may have on the ecological system of the SAR.

Contaminant Health Effects for Aquatic Life Ambient:

Cadmium (Cd)

Cd has no biological function in aquatic life, but the acute exposure causes increased mortality in aquatic organisms. Chronic exposure leads to

adverse effects on growth, reproduction, immune and endocrine systems, development and behavior in aquatic organisms (24). Low water hardness has been known to increase metal toxicity to organisms (29) Total hardness equal to 100mg/L as CaCO₃ (24) used to calculate the criteria for Cd as introduced in Table 1. The classifications of water hardness are as follows: 0 to 60 mg/L as CaCO₃ is classified as soft; 61 to 120 mg/L is classified as moderately hard; 121 to 180 mg/L is classified as hard; and more than 180 mg/L is classified as very hard (30). Although hardness data was not available, the total dissolved solids (TDS) and Conductivity data provided by the San Bernardino Forest Services allows for the rough estimation of hardness (31). The data shows that SAR Reach 6 water hardness likely ranges between soft to moderately hard (31), which suggests that the metals toxicity was not greatly influenced by hardness in SAR Reach 6.

Table 1. 2016 Aquatic Life Ambient Water Quality Criteria for Cadmium (32).

Freshwater	Acute (1- hour, Dissolved Cd)	Chronic (4-days, dissolved Cd)
Cadmium	1.8 µg/L	0.72 µg/L

Copper (Cu)

Cu is essential for growth and metabolism for all living organisms (33). Cu in Invertebrate Hemocyanin has the same function as iron in hemoglobin; both carry oxygen (34). Cu can be lethal at concentrations just above that needed for

life, especially in soft water. In hard water, the cations (e.g., Ca^{2+} and Mg^{2+}) reduce the bioavailability for Cu and thus reduce its toxic effects (33, 29). Acute exposure can be lethal, and the effect of the concentration varies from 1.6 $\mu\text{g/L}$ to 72 $\mu\text{g/L}$ depending on the organisms (34). Chronic exposure results include reduced growth, immune response, reproduction and/or survival (33). Effects of the concentration vary from 3.1 $\mu\text{g/L}$ to 12 $\mu\text{g/L}$ depending on the organisms and the targeted effect (34).

The EPA requires the calculation of site specific water quality criteria based upon bioavailability and toxicity models. In the past EPA has used a hardness based model. But current regulations require the use of the Biotic Ligand Model (BLM) to calculate freshwater ambient water quality criteria (35). The BLM model requires the input of pH, hardness and dissolved organic carbon (DOC) values (35). For this study only pH values were available, Hardness and DOC values were inferred from other data and information.

Hardness at our sampling location was definitely in the soft range i.e., < 60 mg/L as CaCO_3 based upon the TDS values (~100 ppm) and conductivity values (< 170 $\mu\text{S/cm}$) (31). Dissolved organic carbon (DOC) was estimated to be very low given that our site was very high up in the watershed, and the low turbidity values. Table 2 provide the acute criteria based on the hardness and Biotic Ligand Model (BLM). The determination of the water quality criteria for copper using the hardness and BLM models we used the lowest values allowed in their tables, 40 mg/L for hardness and 2 mg/L for DOC. It should be noted that the (BLM) model is particularly sensitive to DOC values. For example, if the DOC

values at our site was actually 4 or 8 ppm, the criterion would increase to 15.8 and 32.4 ppm, respectively.

Table 2. 2007 National Recommended Aquatic Life Criteria for Copper (35).

Freshwater	Acute (Based on Hardness Model)	Acute (Based on BLM Model)
Copper	5.9 µg/L	7.9 µg/L

Lead (Pb)

As stated above, water hardness has a great effect on the toxicity of the heavy metals. Acute exposure can be lethal, yet various marine organisms showed resistance to the acute effect of Pb (36). Wide range in sensitivity for different species was observed for chronic Pb exposure (37). Chronic effects in freshwater fish include spinal deformation and/or a significant increase in red blood cell (RBC) numbers, a decrease in RBC volumes and cellular iron content, and a decrease in RBC δ- amino levulinic acid dehydratase activity (37). Table 3 provide the Acute and chronic criteria for Pb passed on hardness equal to 100mg/L as CaCO₃.

Table 3. 1980 National Recommended Aquatic Life Criteria table for Lead (32).

Freshwater	Acute	Chronic
Lead	65 µg/L	2.5 µg/L

303(d) Listing Process

The term "303(d) List" or "List" refers to a state's list of impaired and threatened waters (e.g. stream/river segments, lakes) (38) as defined by the Clean Water Act. States are required to submit this list for U.S. EPA approval every two years. For each body of water on the list, the state identifies the pollutant (when known) causing the impairment. In addition, the state assigns a priority for development (38) of the Total Maximum Daily Loads (TMDL) based on the severity of the pollution and the potential water uses, among other factors (40 C.F.R. §130.7(b)(4)) (37,38). A TMDL defines how much of a specific pollutant a water body can tolerate and still meet water quality standards (3). TMDL information helps to determine the pollutants reduction targets. The TMDL can be calculated mathematically by using this equation (39):

$$TMDL = \Sigma WLA + \Sigma LA + MOS.$$

Whereas:

- WLA represents the sum of the waste-load allocations from the point sources. *Point sources* are the sources that are regulated under the

National Pollutant Discharge Elimination System (NPDES) program, such as, wastewater treatment facilities.

- LA represents the sum of waste-load allocation from nonpoint sources, which are the remaining sources of pollutants and natural background sources.
- MOS represents the “margin of safety” to include the uncertainty in predicting how well pollutant reductions will result in meeting water quality standards.

TMDL should be determined seasonally and be developed for each pollutant separately. However, because the Clean Water Act (CWA) and U.S. EPA’s regulations don’t define or limit the scale of TMDLs, some states have been developing TMDLs on a watershed-scale basis (39).

On April 1st of every even numbered year, the U.S. EPA requires all states to submit Section 305(b) Water Quality Reports, as well as, the Section 303(d) List of Impaired Waters. The U.S. EPA recommends that states combine them into a single “Integrated Report.” The difference between the two regulations is simply that Section 305(b) reports provide information on the water quality status of all waters in the state, whereas Section 303(d) Lists are only for waters impaired by a pollutant and in need of a TMDL (39). At the recommendation of the State Water Board, the listing decision for each Integrated Report is divided into five categories. The categories 1-5 determine the severity of water pollution in California (40), whereby 1 indicates a water body is not polluted and whereby 5 indicates water standards are not met and a TMDL

is required for the water body. U.S.EPA enforces different requirements for each level. SAR Reach 6 falls under Category 5, and this category includes all impaired waterbodies for which the U.S. EPA has required the development of a TMDL to be completed by a specific date. The TMDL due date for SAR Reach 6 is 2021 (27). Figure 4 shows the 303(d) List water bodies for the SAR Watershed.

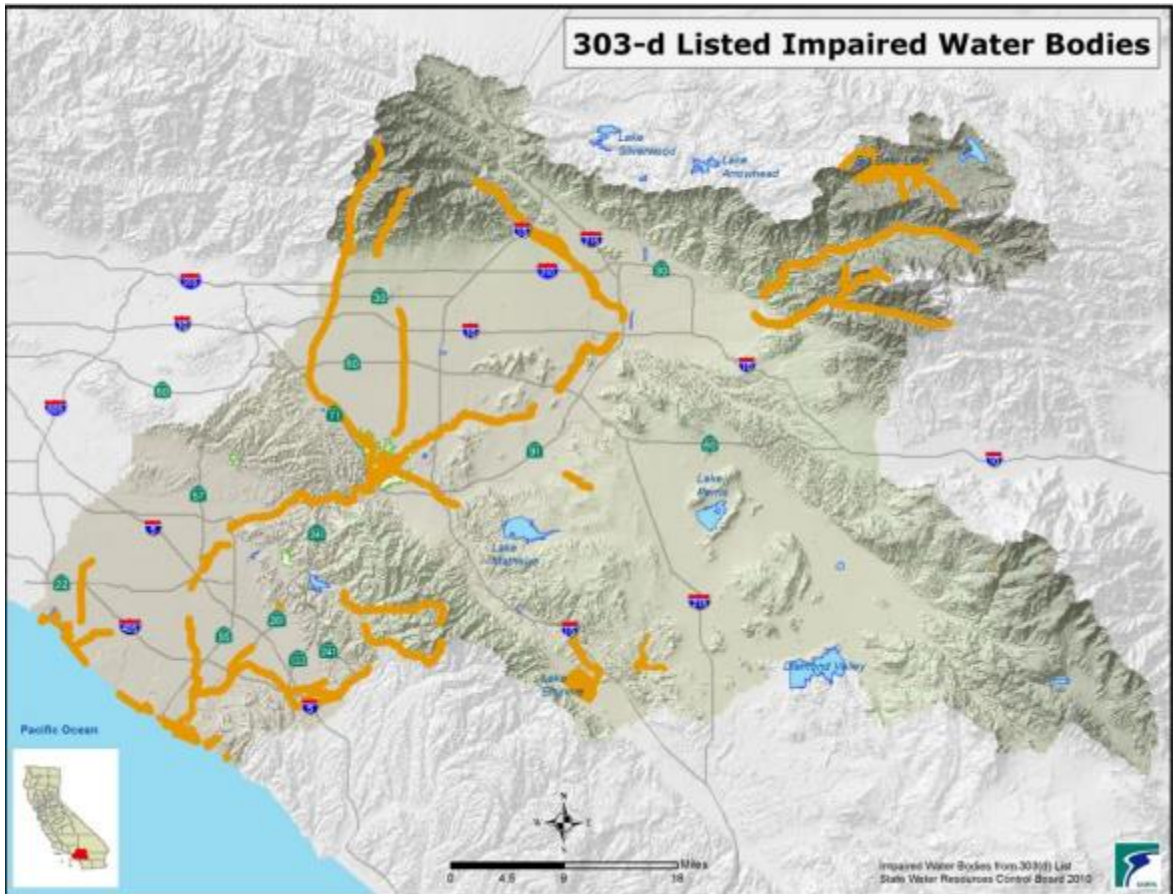


Figure 4. The Water Bodies of the SAR Watershed Defined as Impaired by the CWA, Section 303(d) (5).

CHAPTER THREE

METHODOLOGY

Site Description

The sampling sites were located toward the south end of the SAR Reach 6. Specifically, the section between Forsee Creek and Schneider Creek was selected as a study site because the concentrations of cadmium, lead, and copper exceeded the CTR criteria which could be tied to its beneficial use classification (41). The collection site is located northeast of the town of Angelus Oaks, and south of the City of Big Bear, in San Bernardino County (Figure 5). As of April 1, 2010, the total population of Big Bear was 12,304 (42), while the population of Angelus Oaks was estimated to be about 396 (16). Additionally, the collection site is rich with campgrounds that are open between late spring and early fall (43).

Meteorological aspects of the SAR Reach 6 were also considered in selecting the collection site since weather patterns and topography can potentially affect the deposition of pollutants (13) (Figure 5). The San Bernardino Mountains surrounding the SAR Reach 6 experience heavy snow during the winter seasons. The average annual precipitation is 511 mm, and the average snowfall is 170 cm. The average summer temperature is around 27.3 °C while winter temperatures could reach as low as -6 °C (44).

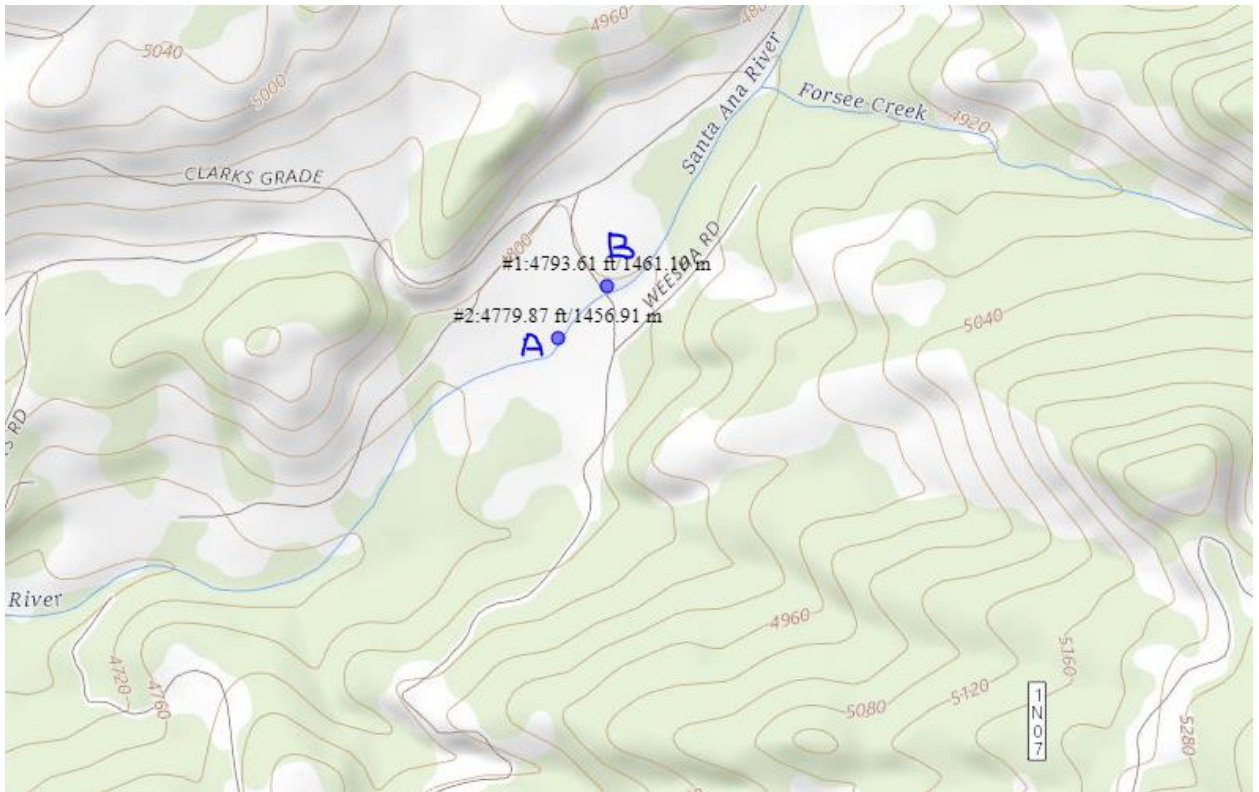


Figure 5. USGS Map of the Collection Sites and Surrounding Topography (45).

As demonstrated by the United States Geological Survey (USGS) topography map shown above (Figure 5) the collection site “A” is 4779.87 feet in elevation and collection site “B” is 4793.61 feet in elevation.

Between June 2015 and June 2016, Robert Taylor and Bill Wells from the San Bernardino Forest Services with the help of CSUSB intern, Maressah Ynfante-Corral, collected multiple samples from SAR Reach 6. The samples collected were analyzed for cadmium, copper and lead at the CSUSB Water Quality Laboratory using graphite furnace atomic absorption spectroscopy (GFAA, EPA Method 200.9 or SM 3113B). All samples but one had non-

detectable levels of the three analytes. The one sample that had very low, but detectable levels of the three metals was collected from a site towards the end of SAR Reach 6, and close to the original collection site that resulted in the SAR being placed on the 303(d) List. The sample concentrations were below the limit of quantitation (< 10 ppb) but above the detection limit of about 1 ppb. Of note, this sample was also collected after a rain event which may support the theory that the contaminants detected may be attributed to runoff from an outside source (41). The site that showed these barely detectable levels was designated site "A", and was selected as the primary sampling site for this study. Collection site "B" was selected as an additional sampling site upstream of collection site "A" in an attempt to further narrow down contamination sources. Collection site "B" is located just inside a private club area to which we were granted very limited and temporary access by the caretaker to collect water samples. Collection site "A" is located within government vacant land. Figure 6 below shows the collections sites in relation to land use.

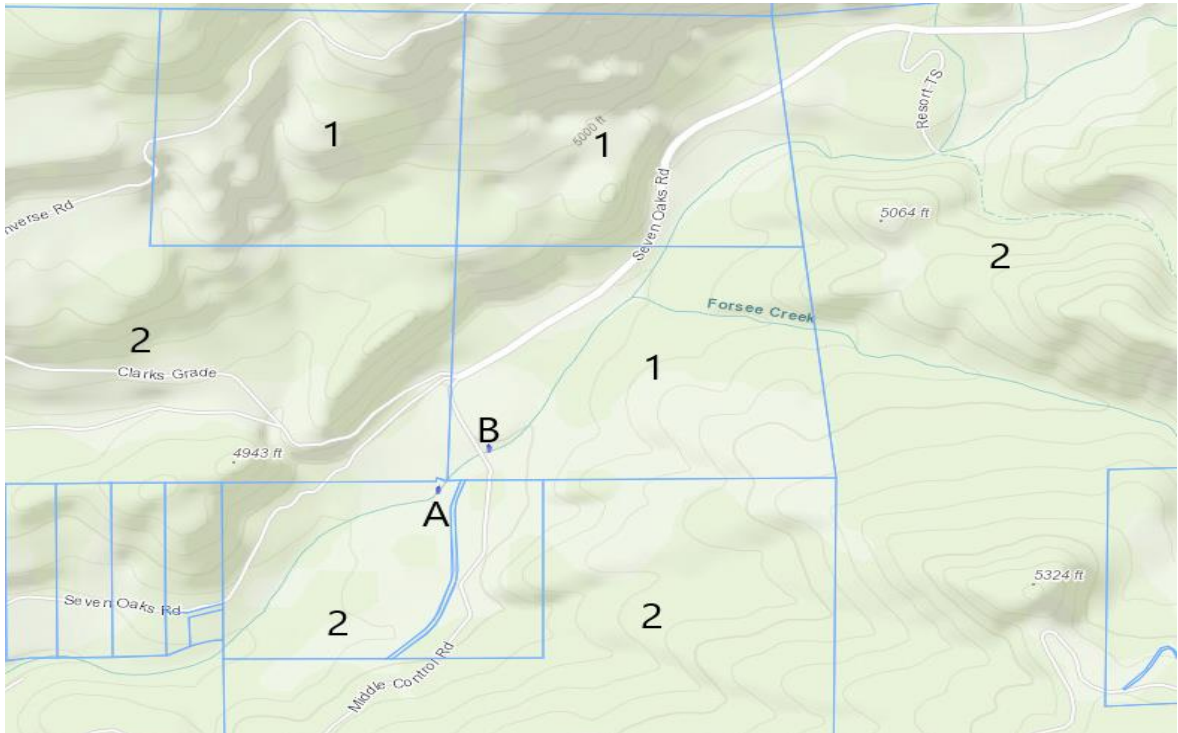


Figure 6. Private (1) vs Government (2) land Use for the Surrounding Area of Collection Sites “A” and “B”(46).

As presented in Figure 6, all zones marked 1 are owned by private owners and used for camping and different activity like fishing or hunting, while the zones marked 2 are vacant lands owned by the government.

Sampling Method

Water Collection

A total of 6 water samples were collected from collection site “A” (34.17121, -116.9502096), which is the same collection site that was indicated by the San Bernardino Forest Services to have detectable levels of cadmium,

copper, and lead resulting in the recommendation of continued sampling and monitoring (41). In addition, a total of two samples were collected from collection site "B" (34.171785, -116.949515). Collection site "B" is upstream of collection site "A", and the distance between them is 300 feet (Figure 5).

Each sample collected was stored in a 500mL, narrow mouth, high density, polyethylene bottle (Figure 7). All sample bottles were pretreated with 10% nitric acid to remove any organic material. Sample bottles were acid washed as per U. S. EPA method protocols for trace metal analysis.



Figure 7. Narrow Mouth High Density Polyethylene Bottle Used for Sample Collection (47).

Samples were collected using the same techniques used by the San Bernardino Forest Service. Gloves were worn to prevent transfer of any contamination from the skin to the water samples. The sample bottles were immersed into the river with the mouth of the bottle facing upstream. The first

volume of water collected was used to rinse the bottle, then the same steps were repeated to collect water. This was done to ensure that no contamination from skin or debris from water flow entered the bottle. After the water filled the bottle to the top, the cap was closed while still submerged in water. Upon collection, samples were then placed in ice during transportation and then promptly refrigerated at 4°C upon arrival at the lab.

Laboratory Analysis

Before the analysis, the first six samples were digested by transferring 50mL from the sample bottle combined with 10 mL of 8M trace metal grade nitric acid in a 250mL beaker. Then each sample was refluxed by heating it on a hot plate at ~90°C until the volume was reduced to < 25mL. The sample was left to cool down for 30 minutes and transferred to a 50mL volumetric flask and diluted to the mark. Then each digested sample was transferred to a 60mL, wide mouth, Polyethylene bottle. Each sample was digested accordingly, and each digested sample bottle was labeled accordingly. This process was performed as per the U.S. EPA method protocol for Total Recoverable Metals. The digested samples were sent to PHŶSIS Environmental Laboratories, Inc. a CA State ELAP certified laboratory in Anaheim, CA. It should be noted that the six original samples taken from sites "A" and "B" were collected between August of 2016 and August of 2017, and the two additional water samples that were taken from sites "A" and "B" were collected in January of 2019. All Samples were analyzed by ICP-MS using the U.S. EPA method 200.8 for total trace metals.

U.S. EPA method 200.8 was used to analyze the digested water samples. This method is a common laboratory method used to determine trace elements in water and wastewater using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). The ICP-MS introduces the samples to radiofrequency plasma by pneumatic nebulization where the energy will cause desolvation, atomization, and ionization. The ions are extracted by a differentially pumped vacuum and separated on the basis of mass-to-charge ratio by a quadrupole mass spectrometer with a minimum resolution capability of 1 amu peak width at 5% peak height. Then the transmitted ions are detected by an electron multiplier, or Faraday detector, and the ion information can be processed by a data handling system. The data will be accessible on the monitor connected to the instrument. Interferences from plasma gas, reagents, instrumental drift or sample matrix must be recognized and corrected (48).

Quality Assurance and Quality Control

For quality assurance, U.S. EPA Method 1669 (49) was followed. All sample containers and laboratory equipment were properly acid washed and rinsed three times with deionized water prior to analysis. Acid-washing is a standard quality assurance protocol in laboratory settings to eliminate impurities (48) that may affect the result of the analysis. To maintain the integrity of the samples, all sample bottles were labeled, and each sample was digested and prepped in a single process to eliminate confusion and cross contamination. The initial water samples collected from the SAR Reach 6 collection sites were

promptly refrigerated to prevent any degradation of molecules that might be present in the water. Samples were stored and refrigerated between 3-4 weeks before they were digested and fully analyzed. During the transferring, storing, and handling of the samples the temperature didn't go below 4°C or above 25°C. A similar study for trace metal in fresh water showed that storing sample for more than three weeks at 25°C or 4°C didn't show much difference for metal speciation or concentration; however, freezing caused permanent changes (50).

CHAPTER FOUR

RESULTS AND DISCUSSION

In order to compare the results of the studies done by the SBCFCD and by the San Bernardino Forest Services (SBFS) with the results from this study, it is important to illustrate how the final comparable values were derived. The U.S. EPA outlines the numeric values of the water quality criteria that are implemented by the California Toxics Rule (CTR). These numeric values help determine if there is a measurable exceedance of concern to place the water segment on the 303(d) List. The CTR is the governing regulation for those bodies of water that are contaminated with priority toxic pollutants (51) and placed on the list. These guidelines require that the criteria for most of the priority toxic pollutants be represented as Dissolved Metal Criterion for better understanding of the biological activity and effect of the metal on the aquatic life (52). The total recoverable metal concentration from each sample are converted to Dissolved Metal Criterion using the following equation:

$$\text{Dissolved Metal Criterion} = \text{Metal}_{TR} \text{ Criterion} \times CF$$

Whereas:

M_{TR} = Total Recoverable Metal Concentration

CF = Conversion Factor

The conversion factor calculates the dissolved fraction of the total recoverable metal. This calculation may take different forms dependent on the biological

activity of each metal in the water column (52). There are different conversion factors depending upon the water body type (i.e. fresh water versus salt water) and for the effects it has on aquatic life and human consumption. The effects are classified as either “acute” short term exposure for the toxic substance over short duration or “chronic” for repeated exposure for the toxic substance over a long time (53). The Conversion Factors for Cd and Pb are hardness dependent. The conversion factors are calculated using a hardness of 100 mg/L as calcium carbonate (CaCO₃) (54). Table 4 displays the acute and chronic freshwater Conversion Factors for the metals in question.

Table 4. Acute and Chronic Freshwater Conversion Factors for the Dissolved Metals of Cadmium, Copper, and Lead (54).

Metal	Conversion Factors	
	Acute	Chronic
Cd	0.944	0.909
Cu	0.960	0.960
Pb	0.791	0.791

The conversion factors for Cd and Pb can be calculated with a given hardness according to the equation provided by the U.S. EPA metal translator guidance (52).

Cadmium conversion factors:

Acute: $CF = 1.136672 - [\ln(\text{hardness}) (0.041838)]$

Chronic: $CF = 1.101672 - [\ln(\text{hardness}) (0.041838)]$

Lead conversion factors:

Acute and Chronic: $CF = 1.46203 - [\ln(\text{hardness}) (0.145712)]$

Table 5 includes the water quality objectives as presented in the 2014-2016 Integrated Report submitted by CSWRCB to the U. S. EPA. The report defines the CTR criteria and analysis data for the contaminants to provide any documentation for exceedances to help on the listing/delisting process. There are allowable limits of exceedances to be able to remove the water body from the 303(d) List (55) as outlined in table 6. The CTR acute/chronic criteria for Cd and Pb are calculated based on the median hardness value (20). The median hardness value for the data provided by the SBCFCD between 2000 and 2006 was 100 mg/L as reported in the table generated for that period.

Table 5. 2016 Water Quality Objectives for SAR Reach 6. (20).

Metals (Total Recoverable)	Water Quality Objectives			
	Units	California Toxics Rule (CTR)		
		Acute Freshwater Aquatic Life ¹	Chronic Freshwater Aquatic Life ¹	Human Health (Water and Organisms)
Cd	µg/L	4.2	2.2	—
Cu	µg/L	13.3	8.9	1300
Pb	µg/L	63.9	2.5	—

¹ CTR acute/chronic criteria and Basin Plan objectives for Cu, Pb and Cd are based on dissolved fraction.

The number of samples and the number of exceedances will help the decision maker to decide either to delist the contaminated water segments from the 303(d) List or continue the listing until further information and documentation to be provided by the State water Board. Table 6 provides an insight into the allowable number of exceedances (dependent upon sample size) to be able to remove from the 303(d) List (55).

Table 6. Maximum Allowable Numbers of Exceedances to Remove from 303(d) List (55).

Sample Size	Delist if the number of exceedances equal or is less than
28 -36	2
37 -47	3
48 -59	4
60 -71	5
72 -82	6
83 -94	7
95 - 106	8
107 - 117	9
118 - 129	10

San Bernardino County Flood Control District
Analysis Data Summary

As stated in the previous chapters SAR Reach 6 was listed under the 303(d) List for impaired water based on the data provided by SBCFCD using the collection site located in SAR Reach 6 about ten miles upstream of Seven Oaks Dam (20). Table 7 provides a summary of the data collected between 1994 and 2006. The data is divided into two categories: 1) the maximum; and, 2) the median total recoverable concentrations of metals for the two, six-year intervals; and, the percent of exceedances from the water quality standards set for in the California Toxic Rule. All data retrieved from SBCFCD was converted to µg/L for

consistency of data interpretation. The 1994-1999 values indicate detectable recoverable concentrations of all three metals (Cd, Cu, and Pb). The 2000-2006 values show no detection for Cd, while Cu and Pb continued to show lower median values and higher maximum values. The results indicate that Cu had the largest percentages of exceedance from the CTR, followed by Pb with less than half, and then Cd with no exceedances.

Table 7. Maximum and Median Values in Water Quality Samples 1994-1999 versus 2000-2006 (20).

Metals (Total Recoverable)	Units	Maximum Value 1994-1999	Median Value 1994-1999 ¹	Maximum Value 2000-2006	Median Value 2000-2006 ¹	% Single Sample Exceedance of Most Stringent Water Quality Objectives
Cd	µg/L	30	30	ND	ND	0
Cu	µg/L	110	6	56000	5	8
Pb	µg/L	51	51	110	5	4

ND: Not Detected in Sample.

¹ Median values were calculated using one half the detection level of the lowest laboratory reporting limit.

Also, the SBCFCD analysis data (provided in the appendix A) shows that every time the hardness reading had a peak, the concentration of Cd, Cu, and Pb had a detectible level. The water hardness is due to calcium or magnesium

carbonate (56), and for the purpose of this study the focus will be on calcium carbonate. Calcium can be dissolved from naturally occurring minerals like limestone, dolomite, and gypsum (56) The fluctuations and high peaks of the water hardness could be a result of dissolved calcium ions that may have reached the water through runoff. Figure 8 shows the correlation between the metal concentration of Pb and the hardness peaks. These trending variables support the hypothesis that the contamination is from nearby runoff source. The correlation between Cd and Cu concentration and the hardness were less supportive of this hypothesis since many of the sample's concentrations were non-detectable; therefore, they were excluded from the graph.

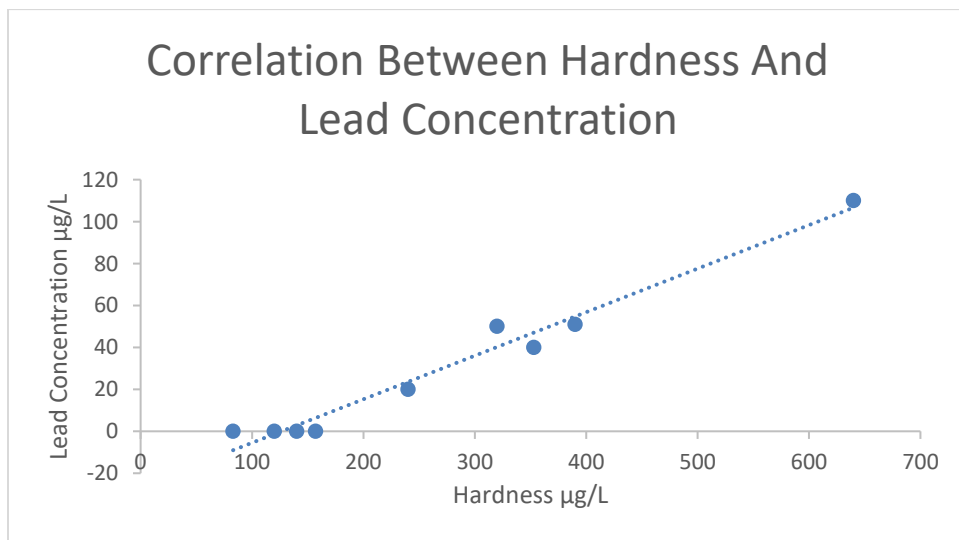


Figure 8. Correlation Between the Hardness and Lead Concentration

San Bernardino Forest Services Analysis Data

The data provided by Sherri Craig and Bill Wells (32) from the study conducted by the San Bernardino Forest Services include samples collected from the same coordinates of the collection site identical to the collection site "A" conducted as part of this project. Table 8 provides the results of this study. The median of the hardness of this study was estimated based on the alkalinity data provided by SBFS to be used for comparison with Tables 4 and 5. The SBFS sample analyses were performed at Clinical Laboratory of San Bernardino, Inc. in a CA ELAP certified laboratory in Grand Terrace, CA. The laboratory followed U.S.EPA method 200.7 using inductively coupled plasma atomic emission spectrometry (ICP-AES) for Cd and Cu and method SM 3113 B using Graphite Furnace-Atomic Absorption Spectrometer (GFAA) for Pb. Although all methods are approved by U.S.EPA CWA as inorganic test procedures (57), method 200.8 (ICP-MS) is the most sensitive method among the three of them (58)(59). Method 200.7 detection limit for Cd is 1 µg/L and for Cu is 3 µg/L (60) and method SM 3113 B detection limits for Pb is 1 µg/L (61); whereas method 200.8 detection limits are for Cd 0.03 µg/L, Cu 0.02 µg/L and Pb 0.05 µg/L (48). This could explain the low detected levels that are presented in Table 9 below. The SBFS samples indicated non-detect values for all three pollutants. This suggesting that the SAR Reach 6 should be considered for removal from the 303(d) List. However, the less sensitive laboratory procedures should be taken into consideration; as well as, the samples sizes need to be more adequate, and collection time needs to represent the wet season as well.

Table 8. San Bernardino Forest Services Analysis Data.

Sampling Date	Sample Site	Total Hardness as mg/L CaCO ₃	Results		
			Cadmium (Cd)	Copper (Cu)	Lead (Pb)
6/10/2017	A	60.10	ND	ND	ND
6/16/2017	A	65.00	ND	ND	ND
6/22/2017	A	70.00	ND	ND	ND
6/26/2017	A	82.00	ND	ND	ND
7/6/2017	A	81.00	ND	ND	ND
7/22/2017	A	80.00	ND	ND	ND
7/28/2017	A	67.00	ND	ND	ND
7/31/2017	A	92.00	ND	ND	ND
8/3/2017	A	84.00	ND	ND	ND
8/3/2017	A		ND	ND	ND
8/11/2017	A	72.00	ND	ND	ND
8/17/2017	A	76.00	ND	ND	ND
8/20/2017	A	68.00	ND	ND	ND

ND: Not Detected in Sample

Project Original Analysis Data

Table 9 contains the results for the total of eight samples collected from Site “A” and “B” for the purpose of this project. The 2016 samples collected from site “A” showed low concentration levels for all metals. The results collected in 2017 and 2019 from both sites indicate higher concentration levels for all metals

and the majority of exceedances were for Pb. While no precipitation occurred at the same day of the sampling, August of 2016 had a total precipitation of 0.14 inches; and September had 0.19 inches, both of which were considered below normal. November 2016 had 1.51 inches total of precipitation and 4.48 inches of snowfall. December 2016 had 6.1 inches of total precipitation and 18.11 inches of snowfall. The total precipitation for August 2017 was 0.69 inches. January 2019 had 5.31 inch of total precipitation and 8.31 inch of snowfall (44).

Table 9. Site “A” and “B” Samples Analysis Data.

Sampling Date	Site	Results			
		Units	Cadmium (Cd)	Copper (Cu)	Lead (Pb)
8/5/2016	A	µg/L	0.106	5.48	3.71
9/30/2016	A	µg/L	0.173	2.99	2.41
11/2/16	A	µg/L	0.0457	1.94	1.02
12/6/16	A	µg/L	0.0652	1.88	0.847
8/6/17	A	µg/L	10.5	7.2	211
1/26/2019	A	µg/L	3.24	4.64	70.2
8/6/17	B	µg/L	53.7	25.7	1040
1/26/2019	B	µg/L	3.6	4.16	77.2

Figure 9 presents the correlation between precipitation and snowfall (left axis) and the Cd, Cu, And Pb concentration (right axis). The samples taken on

8/6/17 for both sites A and B significantly higher levels for all of Cd, Cu, and Pb. On the other hand, the samples by the SBFS taken before and after this date were all non-detect. Further investigation and research needed to be able to define the reason of outliers. It should be noted that all samples collected by CSUSB were subjected to the most vigorous digestion method for Total Recoverable Metals prior to analysis. This was also true for the samples analyzed by the SBCFCD in 1997. Whereas it is not clear if the samples collected by the SBFS in 2017 were digested for Total Recoverable Metals, or just analyzed for dissolved metals. The difference in the digestion methods used could explain the difference in the analytical results obtained. Further sampling and analyses would be required to confirm this hypothesis.

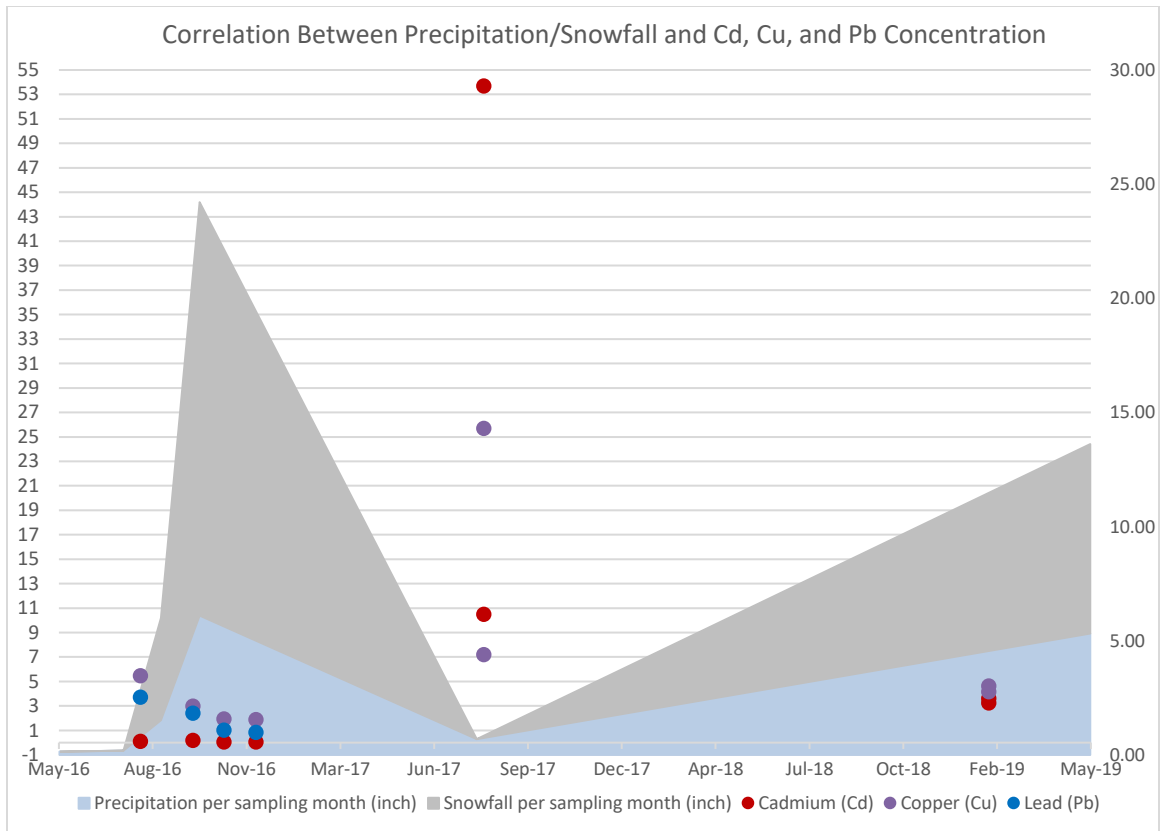


Figure 9 Correlation Between Precipitation/Snowfall (left axis, inches) and Cd, Cu, and Pb Concentration (right axis, µg/L)..

The median hardness value was estimated based on the alkalinity data provided by the Forest Service and was used for generating the Conversion Factors for these samples for comparison to the SBCFCD study. Table 10 provides the corrected Conversion Factors for Cd and Pb using the hardness of <60 mg/L as CaCO₃. The equation from the U.S. EPA metal translator guidance mentioned earlier was used for the calculation of CF.

Table 10. Conversion Factors for the Hardness of <60 mg/L.

Metal	Conversion Factors	
	Acute	Chronic
Cd	0.965	0.930
Cu	0.960	0.960
Pb	0.865	0.865

Table 11 provides the calculated Dissolved Metal Criterion for acute and chronic effects on freshwater aquatic life using a total hardness of <60 mg/L as CaCO₃. The criterion was calculated using the U.S. EPA 2016 Recommended Water Quality Criteria (32) after being corrected for the hardness. The Cd criteria for acute is 1.84 µg/L and for chronic is 0.74 µg/L and the acute criteria for Pb is 71.1 µg/L and the chronic criteria is 2.73 µg/L. Whereas, the acute criteria for Cu based on the hardness is 5.9 µg/L and based on the BLM is 7.9 µg/L. The corrected acute/chronic criteria for the hardness of 60 mg/L as CaCO₃ for lead showed an increase compared to the acute/chronic criteria provided in Table 3, for the hardness of 100 mg/L as CaCO₃. On the other hand, Cd criteria didn't result in a huge change due to the different hardness.

Table 11. Freshwater Criteria Corrected for Total Hardness of <60 mg/L as CaCO₃.

Metal	Freshwater Criteria (Total Hardness =<60 mg/L as CaCO ₃)		
	Units	Acute Criterion (1-hour, dissolved Cd) ¹	Chronic Criterion (4-day, dissolved Cd) ¹
Cd	µg/L	1.842	0.74
Cu	µg/L	5.9 ²	7.9 ²
Pb	µg/L	71.1	2.73

¹ The duration of the 2016 acute criteria was changed to 1-hour to reflect the 1985 Guidelines-based recommended acute duration (32).

² The values for Cu are the hardness based model and BLM model calculated criteria, respectively.

Table 12 provides the summary of the data for the collection sites “A” and “B”; comparing it with the calculated Dissolved Metal Criterion for acute and chronic effects on freshwater aquatic life from Table 10. Four exceedances for the chronic and acute criteria for Cd were identified; Also, three exceedances for the acute criteria; and, five exceedances for the chronic criteria were identified for Pb. The number of exceedances include all samples for collection sites “A” and “B”.

Table 12. Summary Values for Site "A" and "B" Analysis Data.

Metal s	Unit s	Maximum Value Site "A"	Median Value Site "A"	Maximum Value Site "B"	Median Value Site "B"	Single Sample Exceedance Acute Criterion	Single Sample Exceedance Chronic Criterion
Cd	µg/L	10.5	0.14	53.7	28.65	4	4
Cu	µg/L	7.2	3.82	25.7	14.93	-	-
Pb	µg/L	211	3.06	1040	558.6	3	5

Conclusion

The results from this study show that there appears to be a source of copper, cadmium and lead in the upper part of reach 6 of the SAR. The results from samples collected between 2015 and 2019 by CSUSB support the data collected by the SBCFCD in 1997, which caused the original placing of Reach 6 of the SAR on the 303(d) List. The CSUSB results are in contrast to results collected by the USFS in 2017 which showed all non-detect values. However, differences in analytical procedures could explain those results, and further work will be necessary to resolve the discrepancies. In addition to the new data obtained in this study, analyses of older data from the SBCFCD showed an interesting correlation between elevated lead concentrations and high hardness values. The cause of this relationship is not clear and warrants further investigation. It is difficult to compare the new results obtained in this study, as well as the older data from the SBCFCD to ambient water quality criteria because these criteria are based upon dissolved phase concentrations. The Total Recoverable Metals digestion methods used would dissolve metals that were not actually dissolved in the original water samples. The limited number of samples collected, and the new data generated in this study, taken in concert with data from previous studies suggest that there is a real source of these three metals in the upper parts of reach 6 of the SAR. Moreover, the results from sites A and B suggest that the source may be within the privately owned and operated areas to the northeast of Site A. The overall results of this study suggest that a much more comprehensive study is warranted. Further studies should analyze

undigested samples for dissolved metals only, that is the bioavailable and potentially toxic form of the metals. A statistically significant number of samples should be collected, and analyzed for pH, hardness and DOC as well as the metals so that accurate water quality criteria can be determined for each analyte. If the results of the detailed toxicity study show exceedances of the carefully determined criteria, then further work should be done to identify the source of the contamination. Permission to take samples on the private lands should be sought by the USFS as it may be necessary to identify the source of the contamination.

APPENDIX A
SAN BERNARDINO COUNTY FLOOD CONTROL DISTRICT (SBCFCD)
ANALYSIS DATA

Table 13. SBCFCD Analysis Data That Resulted in Listing the SAR Reach 6 Under the 303(d) List.

Sampling Date	Total Hardness as mg/L CaCO ₃	Results			
		Units	Cadmium (Cd)	Copper (Cu)	Lead (Pb)
2/17/1994	133	µg/L	ND	ND	ND
3/19/1994	353	µg/L	30	100	40
11/10/1994	157	µg/L	ND	20	ND
1/23/1995	77	µg/L	NR	ND	ND
3/10/1995	74	µg/L	ND	ND	ND
12/12/1995	81	µg/L	ND	ND	ND
1/31/1996	140	µg/L	ND	20	ND
2/19/1996	320	µg/L	10	100	50
3/4/1996	81	µg/L	ND	ND	ND
3/13/1996	77	µg/L	ND	ND	ND
10/30/1996	89	µg/L	ND	ND	ND
11/21/1996	97	µg/L	ND	ND	ND
12/9/1996	95	µg/L	ND	ND	ND
11/26/1997	390	µg/L	ND	110	51
1/9/1998	110	µg/L	ND	ND	ND
2/3/1998	95	µg/L	ND	ND	ND
3/25/1998	77	µg/L	ND	ND	ND
11/8/1998	83	µg/L	ND	30	ND
1/25/1999	240	µg/L	ND	50	20
2/9/1999	84	µg/L	ND	ND	ND
3/16/1999	94	µg/L	ND	ND	ND
4/7/1999	95	µg/L	ND	ND	ND
1/25/2000	80	µg/L	ND	ND	ND
2/27/2000	87	µg/L	ND	ND	ND

3/4/2000	81	µg/L	ND	ND	ND
4/17/2000	77	µg/L	ND	ND	ND
1/9/2001	100	µg/L	ND	ND	ND
1/24/2001	100	µg/L	ND	ND	ND
2/23/2001	100	µg/L	ND	ND	ND
4/7/2001	100	µg/L	ND	ND	ND
11/13/2001	120	µg/L	ND	ND	ND
11/24/2001	110	µg/L	ND	ND	ND
1/28/2002	98	µg/L	ND	ND	ND
3/17/2002	110	µg/L	ND	ND	ND
11/8/2002	120	µg/L	ND	56000	ND
2/11/2003	110	µg/L	ND	ND	ND
3/15/2003	110	µg/L	ND	ND	ND
12/26/2003	96	µg/L	ND	ND	ND
2/3/2004	89	µg/L	ND	ND	ND
2/19/2004	89	µg/L	ND	ND	ND
10/26/2004	61	µg/L	<2	<10	ND
12/28/2004	110	µg/L	<2	<10	ND
2/17/2005		µg/L			
3/22/2005	67	µg/L	<2	<10	ND
2/28/2006	640	µg/L	ND	170	110
3/11/2006	94	µg/L	ND	ND	ND
3/28/2006	79	µg/L	ND	ND	ND

ND: Not Detected in Sample

The units converted to µg/L by multiplying the mg/L analysis results by 1000.

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