Selenium, Nitrate, and Other Constituents in San Diego Creek and Newport Bay Watersheds

2004 - 2008

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1 May 2008

Prepared for
Santa Ana Regional Water Quality Control Board

by

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PREFACE

This project evaluates several subregions in the San Diego Creek and Newport Bay Watersheds for sources and sinks of selenium and nitrate. The work was supported by the State of California Water Resources Control Board through a proposition 13 contract, and administered through the Santa Ana Regional Water Quality Control Board (Terri Reeder, Contract Manager). The research was carried out by the Department of Geological Sciences, California State University-Los Angeles (Barry Hibbs, Principal Investigator).

Field investigations were performed at several sites to assess existing in-channel and near-channel systems for possible removal or attenuation of selenium and nitrate Sites included (1) in-channel sedimentation basins in the foothills of the watershed, (2) sedimentation basins in the mixing zone between San Diego Creek and Upper Newport Bay, (3) the treatment wetland at San Joaquin Marsh, and (4) the estuarine system at Upper Newport Bay. In a concurrent part of this investigation, studies were conducted to examine the regional and local sources and concentrations of selenium, nitrate, and arsenic in the shallow groundwater of the San Diego Creek Watershed. The results of our work are presented in 7 chapters, entitled:

- **Chapter 1** - Introduction and Methodology: Selenium, Nitrate, and Other Constituents in San Diego Creek and Newport Bay Watersheds, 2004 - 2008

- **Chapter 2** - Sources and Distribution of Selenium and Arsenic in Shallow Groundwater: San Diego Creek Watershed

- **Chapter 3** - Time Series Analysis of Groundwater Chemistry in San Diego Creek Watershed (*with a section on newly installed urban storm drains)*

- **Chapter 4** - Selenium Dynamics in San Joaquin Marsh: San Diego Creek Watershed

- **Chapter 5** - Time Series Analysis of Nitrate and Selenium in Downstream Sedimentation Basins: San Diego Creek

- **Chapter 6** - Time Series Analysis of Nitrate and Selenium in Upper Newport Bay

- **Chapter 7** - Nitrate and Selenium in Ephemeral Flows in Upstream Sediment Basins: San Diego Creek Watershed

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Chapter 3
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Chapter 4
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Chapter 7
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Table of Contents

PREFACE

1. Purpose of Study
2. Setting of Study Area
3. Organization of Report (stand alone chapters)

CHAPTER 1 – REVISION OF REGIONAL CONCEPTUAL MODEL

CHAPTER 2 – SUPPORTING DRAIN STUDIES

1. El Modena Channel
2. Edinger Circular Drain
3. Valencia Drain
4. Atela Circular Drain
5. San Joaquin Channel
6. Barranca Circular Drain
7. Lane Channel, Lower
8. Lane Channel, Upper
9. Santa Ana Delhi Channel
10. Santa Ana Gardens Channel

CHAPTER 3 – GROUNDWATER TIME SERIES & NEW DRAINS

CHAPTER 4 – SAN JOAQUIN MARSH

CHAPTER 5 – DOWNSTREAM SEDIMENT BASINS

CHAPTER 6 – UPPER NEWPORT BAY

CHAPTER 7 – UPSTREAM SEDIMENT BASINS

APPENDIX A – FIELD METHODS

APPENDIX B – LABORATORY AND ANALYTICAL METHODS

APPENDIX C – WATER COLUMN DATA TABLES, DOWNSTREAM BASINS

APPENDIX D – WATER COLUMN DATA TABLES, UPPER NEWPORT BAY

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CHAPTER 2 – SUPPORTING DRAIN STUDIES
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1. El Modena Channel
2. Edinger Circular Drain
3. Valencia Drain
4. Atela Circular Drain
5. San Joaquin Channel
6. Barranca Circular Drain
7. Lane Channel, Lower
8. Lane Channel, Upper
9. Santa Ana Delhi Channel
10. Santa Ana Gardens Channel

CHAPTER 3 – GROUNDWATER TIME SERIES & NEW DRAINS
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CHAPTER 5 – DOWNSTREAM SEDIMENT BASINS
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CHAPTER 7 – UPSTREAM SEDIMENT BASINS AND PERENNIAL STATIONS
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Chapter 1

Introduction and Methodology: Selenium, Nitrate, and Other Constituents in San Diego Creek and Newport Bay Watersheds

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1 May 2008

Prepared for
Santa Ana Regional Water Quality Control Board

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INTRODUCTION

Study Area

The San Diego Creek/Newport Bay Watershed (*hereafter called the San Diego Creek Watershed for simplicity*) forms the southern end of the Coastal Plain that covers much of Los Angeles County and Orange County, California (Figure 1.1). The watershed area has fairly flat topography that rises gradually to the alluvial fans that are juxtaposed against the Santa Ana Mountains to the northeast. Surface elevation of the watershed ranges from sea level at Upper Newport Bay, to 400 ft just above the El Toro Military Air Station, to elevations exceeding 1000 ft in the foothills.

The San Diego Creek Watershed is drained by Peters Canyon Wash and San Diego Creek, and by a series of surface channels and drains that are tributary to Peters Canyon Wash and San Diego Creek. Principal surface tributaries include Hicks Canyon Wash, Central Irvine Channel, El Modena Channel, Como Channel, Santa Fe Channel, Barranca Channel, Lane Channel, San Joaquin Channel, Sand Canyon Wash, and Bonita Creek. Flows in these channels eventually move into Upper Newport Bay. Santa Ana Delhi Channel flows directly into Upper Newport Bay.

Land use in the study area was originally used for livestock grazing. Livestock grazing was gradually replaced by irrigated agriculture. Since 1970, rapid commercial and residential developments have replaced most of the tracts of farmland, and very limited agriculture remains in the northeastern part of the study area. The central part of the watershed was a marshland as recently as the late 1800s, and the edges of the marsh

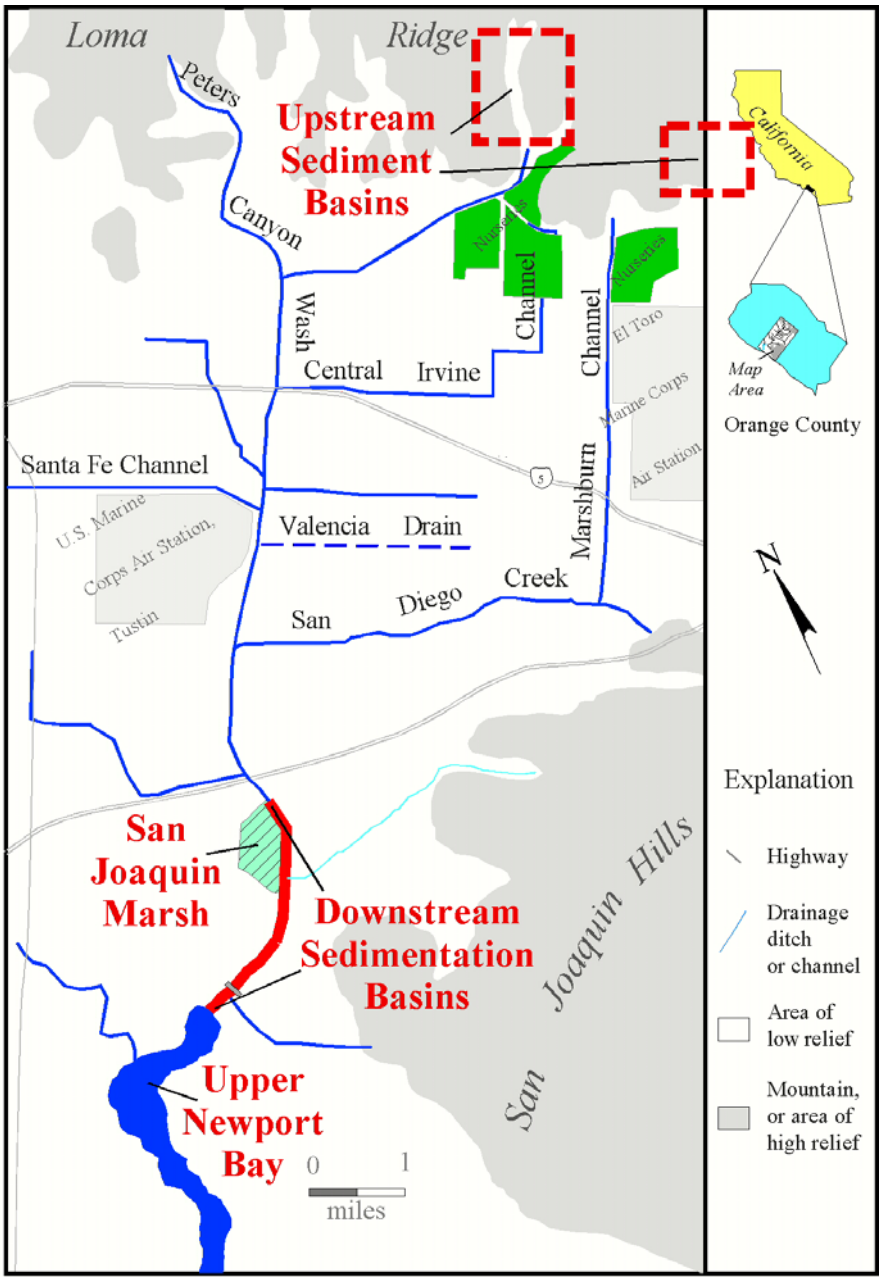

Figure 1.1. Study area location map showing San Diego Creek/Newport Bay Watershed, and subregions (in red text) where intensive water quality studies were conducted during this investigation.

were used for grazing sheep and cattle. The historic marsh, known to the locals of the time as "La Cienaga de las Ranas," or "Swamp of the Frogs" marsh was a large peat bog (Liebeck, 1990). Drainage ditches and channels (some of which still exist) were constructed to drain the marsh for agriculture (Figure 1.1). San Diego Creek Watershed is a rapidly urbanizing area today.

Problem Statement

Heavy selenium and nitrate loads have been identified in surface flows in San Diego Creek Watershed (Hibbs and Lee, 2000; CRWQCB, 2001; Meixner and others, 2004). These flows may threaten migratory waterfowl and other species. Selenium can be a harmful element in aquatic habitats; therefore the USEPA adopted an interim 96-hour, 5 ug/L chronic water quality criterion for selenium in surface water. The existing water quality data indicate that surface flows in San Diego Creek Watershed often exceed 15 to 20 ug/L, potentially placing habitats at risk (Meixner and others, 2004). This is a special concern because the San Diego Creek Watershed hosts a very active migratory and non-migratory bird population that can be sensitive to selenium bioaccumulation. Upper Newport Bay, the coastal receiving water body for these watersheds is a protected ecological reserve that is home to five threatened and endangered bird species.

A principal source of selenium and nitrate loading is from shallow groundwater discharge to surface channels (Hibbs and Lee, 2000). Other probable sources of selenium include particulates that are eroded and transported from the highlands in the Santa Ana

Mountains, Loma Ridge, and San Joaquin Hills (Figure 1.1). This project assesses the dynamics of selenium and nitrate across the watershed.

Selenium occurs in several oxidation states that are highly sensitive to reduction/oxidation conditions in surface water and groundwater systems. The most oxidized form of selenium, selenate (+6) is the dominant species in many shallow groundwaters and most surface water in San Diego Creek Watershed (Meixner and others, 2004). Selenate is highly soluble and mobile and tends to remain in solution. As conditions become more reducing, selenium is converted readily to lower oxidation states, such as selenite (+4), elemental selenium (0), and selenide (-2). These reduced forms tend to be removed from solution by sorption to solid particles and by precipitation. Plants in relatively quiet water bodies can also convert dissolved selenium into dimethyl selenite gas. Methylated forms of selenium accumulate in living plant and animal tissue. Organic detritus from dead plants and animals containing selenium accumulates on bottom sediments in watersheds.

Several temporary receiving water bodies in San Diego Creek Watershed may contain micro-and-macro reducing environments in bottom soils and water column. These include sediment basins in the upper and middle portion of the watershed, the treatment wetland at San Joaquin Marsh, the in-channel sedimentation basins near San Joaquin Marsh, and the estuary at Upper Newport Bay. If selenium and nitrate are removed from the water column in these relatively quiet water bodies, or sequestered in soils of streambeds or wetlands, it will be technically useful to identify these uptake or

removal processes. If selenium is precipitated and sorbed in reduced forms in sediments, then the sediments can be removed periodically from these retention facilities, thus eliminating a source of potentially toxic selenium from the watershed.

STUDY APPROACH AND OBJECTIVES

This project evaluates several subregions in the San Diego Creek Watershed for sources and sinks of selenium and nitrate. The project complements the work done by Hibbs and Lee (2000) and Meixner and others (2004) by looking at the spatial distribution and sources of selenium, nitrate, and arsenic in shallow groundwater in the watershed.

Field investigations were performed at several sites to assess existing in-channel and near-channel systems for possible removal or attenuation of selenium and nitrate (Figure 1.1). Sites included (1) in-channel sedimentation basins in the foothills of the watershed, (2) sedimentation basins in the mixing zone between San Diego Creek and Upper Newport Bay, (3) the treatment wetland at San Joaquin Marsh, and (4) the estuarine system at Upper Newport Bay. Our studies in these systems looked at hydrochemical processes and flow dynamics over time.

In a second concurrent part of this investigation, studies were conducted to examine the regional and local sources and concentrations of selenium, nitrate, and arsenic in the shallow groundwater of the San Diego Creek Watershed. The local studies were done in the vicinity of open and underground channels and drains. Time series

analysis of the hydrochemistry of the shallow aquifer in the watershed was performed during a record drought year, and compared to earlier time-series analysis when conditions were wetter (Meixner and others, 2004). The results of our work are presented in 7 chapters.

BACKGROUND INFORMATION AND ACTIVITIES BY CHAPTER

Chapter 1

Title: Introduction and Methodology: Selenium, Nitrate, and Other Constituents in San Diego Creek and Newport Bay Watersheds, 2004 to 2008

Chapter 1 (this chapter) provides a brief description of the field activities and goals of Chapters 2 through Chapter 7. Specific field activities that are pertinent to each chapter are described. Field methods and laboratory methods that are germane to all chapters are described at the end of this chapter.

Chapter 2

Title: Sources and Distribution of Selenium and Arsenic in Shallow Groundwater: San Diego Creek Watershed

The purpose of this research is two-fold: (1) to examine the regional sources and concentrations of selenium and nitrate in the shallow groundwater of the San Diego Creek Watershed; and (2) to focus extensively on the sources, spatial distribution, and concentrations of selenium, arsenic, and associated hydrochemical and isotopic

parameters in shallow groundwater near selected drains and channels. This is done in several sections, entitled:

2.1. Analysis of Selenium and Nitrate – A Regional Conceptual Model
2.2. El Modena Channel Studies
2.3. Santa Ana Delhi Channel Studies
2.4. Alton Drain Studies
2.5. Santa Fe Underground Circular Drain Studies
2.6. Edinger Underground Circular Drain Studies
2.7. Valencia Underground Drain Studies
2.8. Lane Channel Studies
2.9. Barranca Underground Circular Drain Studies
2.10. San Joaquin Channel Studies

Some sections cover areas studied previously by Hibbs and Lee (2000) and by Meixner and other (2004), while other sections cover new areas that haven't been studied. Section 2.1 is a regionally focused study. Sections 2.2 to 2.5 cover the region of "perennially wetted" soils in predevelopment times (Meixner and others, 2004) and discuss data supporting a selenium-nitrate oxidation model in groundwater. Sections 2.6 and 2.7 cover the "ephemerally wetted" area of very elevated selenium and arsenic concentrations in groundwater (Meixner and others, 2004). Sections 2.8 and 2.9 cover flowpath transects that extend from a transitional "Swamp Fringe" zone into an elevated salinity zone deep within the interior of the historic Swamp of the Frogs Marsh. Finally, Section 2.10 provides hypotheses on a low salinity, low selenium area located within the historic marsh boundary.

Chapter 3

Title: Time Series Analysis of Groundwater Chemistry in San Diego Creek Watershed (with a section on newly installed urban storm drains)

Time series monitoring of select groundwater discharge points located both within and outside of the historic marsh boundary was undertaken in order to track seasonal variability in hydrochemical parameters (salinity, sulfate, chloride, nitrate and dissolved selenium). Monitoring over 2006 - 2007 occurred over one of the driest years on record. However, the availability of a complementary data set collected over a moderately wet year (2002 - 2003) gives the unique opportunity to compare changes in these hydrochemical parameters over a wet year and a drought year. This permits a better understanding of meteorological processes governing the release of nitrate and selenium from soil matrix into groundwater. Changes in nitrate and selenium loads in the watershed occur over seasonal cycles. Understanding the changes that affect these constituents in the groundwater environment will aid our understanding of how these changes manifest in surface waters.

Groundwater quality was monitored monthly during a moderately wet year (2002 - 2003) and a drought year (2006 - 2007) at five groundwater discharge points. Concomitantly, groundwater levels in the shallow aquifer were monitored at six monitoring wells located throughout the basin. Depth to the water table was measured in order to observe changes in groundwater elevation.

In early 2006 the construction of new residential storm drains was noted adjacent to Peters Canyon Wash. Initially, four drains were investigated internally to determine what are the source flows emanating from the drains and to collect samples for water quality analysis. It was discovered that groundwater in these storm drains leaks through joints in the concrete lining. These drains act as a point source discharge of groundwater into Peters Canyon Wash. Construction of these drains intercepts natural groundwater flowpaths, which inhibits the natural removal of nitrate and selenium during natural seepage of groundwater through organic rich streambed sediments, where nitrate and selenium are partially removed by plant uptake, denitrification, and redox processes (Meixner and others, 2004).

Monitoring of water emanating from drains began March 2006 and terminated January 2007, comprising three sampling events in which water from each drain outlet was sampled to obtain an integrated value of all source flows contributing to flow in the drains. An expanded sampling campaign was also conducted in September 2006.

Chapter 4

Title: Selenium Dynamics in San Joaquin Marsh: San Diego Creek Watershed

The Irvine Ranch Water District established freshwater ponds at San Joaquin Marsh for the specific purpose of naturally cleansing flows from the San Diego Creek Watershed before returning flows back into Upper Newport Bay. Approximately 3.2 to

6.5 million gallons of water from San Diego Creek are diverted into the San Joaquin Marsh daily. The water circulates through a series of large freshwater ponds for 10 to 14 days, where microbes in the soil release nitrogen from the water in a natural purifying process before flows are routed back into San Diego Creek (IRWD 2002).

In our study, San Joaquin Marsh was analyzed for selenium and nitrate to assess removal, uptake, and possible remobilization/immobilization that may be occurring in the marsh. During the 1.5 years we monitored the marsh, there were periodic shutdowns of the marsh for channel and marsh maintenance. Total and dissolved selenium, index parameters, anions (sulfate, chloride) and select nutrients (nitrate, orthophosphate) were measured twice monthly when the marsh was circulating flows to and from San Diego Creek. Total and dissolved selenium were also measured every day for a two week period, and every hour during one twenty-four (24) hour period at the marsh inlet and outlet. Sediments were collected from the marsh and analyzed for selenium species.

At specific times, water column samples were collected from strategic stations in the marsh for selenium speciation analysis. These stations included inlet basins, mid-basins, and outlet basins in the marsh.

Chapter 5

Title: Time Series Analysis of Nitrate and Selenium in Downstream Sedimentation Basins: San Diego Creek

The main purpose of this study is to observe the water quality characteristics of the San Diego Creek estuarine interface (prebasin) and in-channel sedimentation basins above the Upper Newport Bay Ecological Reserve. As a transitional zone for terrestrial (dilute) freshwater and marine (saline) water, conditions in the sedimentation basins and prebasin alter water quality and sediment dynamics. Tracing hydrologic fluxes through depth-dependent conductivity/salinity, temperature, and dissolved oxygen measurements indicates mixing or stratification schemes that occur in the in-channel sedimentation basins and the mixing prebasin above Upper Newport Bay. An analysis of the water column interface provides a look at potential processes that contribute to mixing and chemical transformations in the basins.

To characterize the sedimentation basins and the mixing prebasin, a suite of chemical parameters were tested in the basins. Samples were collected and analyzed for dissolved selenium, selenium species, nitrate, orthophosphate, ammonium, sulfate, and chloride. Multiple stations were established in each of the in-channel sedimentation basins and the prebasin. Monitoring stations were sampled primarily from a boat. Water-column data were collected from November 2005 to February 2007.

Depth dependent water column measurements (one-half or one-foot intervals depending on total depth) for specific conductance/salinity, temperature, pH, and

dissolved oxygen were also taken with water quality meters. At each site, water-column samples for selenium parameters, nutrients, and anions were collected through grab sampling to observe any vertical water-quality gradients. Water column samples were collected from the top portion of the water column (approximately 6 inches from the surface) and from the deep section located 7.5 inches above the riverbed. Sampling runs rotated between the three upstream in-channel sedimentation basins and the mixing prebasin above Upper Newport Bay; each basin being sampled about once per month.

Chapter 6

Title: Time Series Analysis of Nitrate and Selenium in Upper Newport Bay

The existing aquatic and wildlife habitat of Upper Newport Bay comprises approximately 210 acres of marine aquatic habitat, 214 acres of mudflat habitat, 277 acres of salt marsh, and 31 acres of riparian habitat located within, and adjacent to, the 752-acre Upper Newport Bay Ecological Reserve (Santa Ana Regional Water Quality Control Board, 2000). Upper Newport Bay is home to over 200 species of birds as well as fish and other wildlife. San Diego Creek, which discharges directly into the bay just downstream of the bridge at Jamboree Road, is the primary source of freshwater flows to Upper Newport Bay.

Levels of selenium and nitrate in the surface waters of the creek are of potential concern to water quality and the ecological health of Upper Newport Bay. Selenium concentrations in surface flows downstream of the San Joaquin Marsh have been found to

occasionally exceed the USEPA freshwater quality criterion of 5 μg/L for selenium. Nitrate leads to algal blooms in Upper Newport Bay. The Santa Ana Regional Water Quality Control Board is currently implementing TMDL standards for total nitrogen and total phosphorous in the watershed.

Our work in Upper Newport Bay provides information on the amount of nitrate and selenium reaching the bay. Four water-quality monitoring stations were established within the bay. Depth profiles including specific electrical conductance, pH, and dissolved oxygen were recorded on a monthly basis at each of these sites over a six-month period beginning October 2007 and ending March 2008. Additionally, water samples were collected from the top and bottom of the water column at each station to monitor water quality parameters such as the concentrations of nitrate and selenium. An expanded set of parameters was collected in January 2008, including total nitrate, ammonia, total kjeldahl nitrogen, total phosphorous, and selenium species. Sediments were also collected from four sites very near to water quality sites and analyzed for total selenium and selenium species.

Chapter 7

Title: Nitrate and Selenium in Ephemeral Flows in Upstream Sediment Basins: San Diego Creek Watershed

In order to characterize upstream sources of selenium and nitrate, surface waters were collected during wet weather flows in two upland canyons: Hicks Canyon Wash and

Round Canyon. These ephemeral streams are dry throughout most of the year. Their physiographic position limits flow, which occurs exclusively in response to precipitation. It is thought that selenium is derived through the weathering and erosion of upland marine shales, especially those of Miocene age such as the Monterrey and Puente formations (Tracy, 1990). These formations consist of interbedded sandstones, siltstones and shales. Soil samples, assumed to have weathered from these geologic formations, were collected from the streambed in the canyons in order to quantify the amount of selenium contained therein.

The two upstream tributaries selected for monitoring; Hicks Canyon Wash (which drains the northern part of the watershed and empties ultimately into Peters Canyon Wash) and Round Canyon (which drains the eastern part of the watershed and empties ultimately into San Diego Creek) were monitored during ephemeral flows. Field parameters were measured on site with portable pH/temperature/conductivity and dissolved oxygen meters. Surface runoff was collected every two hours at a downstream point along Hicks Canyon Wash on January 5, 2008, following intensive precipitation. Flow in Round Canyon was not observed on this date.

We were able to sample surface waters from both tributaries during a storm that occurred January 6 - 7, 2008 as well as collect a rainwater sample from the vicinity of Hicks Canyon. During this event, surface flows were collected every two hours from the downstream station at each tributary. These water samples were analyzed for anions and dissolved selenium. Additionally, surface flows were collected from upstream, middle,

and downstream stations along each tributary. These synoptic samples were analyzed for an expanded set of parameters, including selenium species.

Additionally soil samples were collected from each streambed in December 2007 prior to wet-weather flows, but after fires had exfoliated the surrounding terrain. These soils were analyzed for total selenium and selenium species as well as subjected to leaching tests in order to quantify the amount of leachable nitrate and selenium contained therein. Soils were subjected to leaching by two types of water: artificial rainwater, which was made to mimic the concentration of standard inorganic parameters found in rainwater native to southern California; and a nitrate-rich water, which was mixed to approximate the average nitrate concentration found in the shallow aquifer.

FIELD SAMPLING METHODS

A variety of methods were used to collect the samples from the diverse number of sites we investigated (Appendix 1.0). These included surface water and groundwater samples and streambed and land surface sediment samples. Most field water samples were collected via grab sampling in LDPE bottles. Sample bottles were soaked and triple rinsed in deionized water and inspected prior to field usage. Additionally all bottles were triple rinsed with the water being sampled in the field prior to filling. Aquatic and groundwater sampling sites included field-filtered and unfiltered samples. Filtered samples were obtained using 0.45 micrometer filters. Samples were stored on ice until returned to the lab. Sample preservation with acid was done in the field for those

samples requiring it. All sites had conductivity, temperature, dissolved oxygen, and pH measured in the field using portable meters (YSI meters). Meters were calibrated according to manufacturer's guidelines.

Homogenization of samples was done with 1 gallon containers when water was collected from streams or from other surface flows such as drains. A one gallon container was filled, mixed, and used to breakout aliquots for the various sample matrices (different containers to different labs, or different containers for different preservation methods). Homogenization of groundwater was done when duplicates were taken but not during most other times. Samples were collected at the wellhead or at the springs/weepholes as quickly as containers could be reliably filled with groundwater. Filtering was done when necessary to satisfy matrix requirements.

Surface water samples were taken several inches below the surface of the stream or pond when depth of water was less than 1 foot. This was the normal case for many conditions in the study area. A bottle was inverted and then re-inverted to allow the container to fill up. When depth of water was greater than 1 foot, we collected depth-integrated samples or discrete-depth (multiple vertical) samples depending on task requirements. Equal volumes were collected at the various stream depths (e.g., top, bottom; or top, middle, bottom) and either combined and homogenized for depth-integrated samples or placed into separate containers for discrete-depth samples. We used water sampling devices that allowed containers to be filled at prescribed stream

depths in streams by releasing a check valve when the water sampler was at the prescribed depth.

Width-integrated sampling was done along streams when specific field conditions dictated that this should be done (e.g., when a tributary flows into a stream above the sample location). This means that several samples were taken along the width of the stream at regular intervals and equal quantities were mixed and homogenized to collect a width-integrated sample. When upstream tributaries or other field conditions did not require a width-integrated sample, we collected grab samples at the middle of the stream.

Monitoring well sampling was done with battery operated "whaler pumps." The pumps and pump tubing were rinsed first with a deionized water/phosphate-free laboratory detergent mixture and afterwards with a pure deionized water solution before they were used. This was done in the field between sampling events, and after returning from the field. Carboys filled with these solutions were used in the field to perform rinses.

Before sampling groundwater from monitoring wells, the wells were purged and stabilized. Well purging means the removal of a sufficient volume of groundwater in the well casing so that a representative water sample from the aquifer can be collected. When the well was pumped, it was necessary to set up a purge pump to extract stagnant water from the well bore. This was accomplished by setting up portable equipment and taking temperature, specific conductance, and pH readings at two minute intervals. When the measurements stabilized, the wells were sampled. Checks for stabilization of

index parameters was done after wells had been pumped long enough to purge at least three casing volumes of water from the well bore. After wells were pumped, samples were collected and preserved in accordance with methods described above for groundwater.

Surface water discharge measurements were made using Marsh-McBirney Model 2000 portable flowmeters and top-setting wading rods. When highly accurate measurements were needed, a straight stream reach with a relatively symmetrical channel cross section and shallow depth of flow was chosen. A cloth measuring tape strung across the stream perpendicular to the direction of flow was used to divide the stream into uniform increments. At the midpoint of each increment, the depth of water was measured and the sensor on the flow meter placed at 0.6 times the depth of flow. The velocity was averaged by the flow meter at 40 second intervals. The velocity was then multiplied by the width and depth of the increment to arrive at a value of stream discharge for that increment. The sum of the incremental discharges (10 to 15 when stream width was less than 4 feet and 20 when stream width was greater than 4 feet) gave the total stream discharge for the stream reach. When rapid flow measurements were needed, the width and average depth of the stream was recorded and the velocity was measured at 3 or more segments of the channel to provide a "rough" estimate of discharge.

Sediment samples were collected using stainless steel hand augers, stainless steel shovels, and stainless steel spades. Auger samples were collected in properly identified (depth and location information) and wrapped plastic bags. After the soil sample was

bagged and preserved for chemical analysis and grain size analysis, a portion of the soil sample that had been separated from the bagged sample was examined at the recovery site for color, field grain size characteristics (qualitative such as silty-sand; clayey-sand; silt), organic matter, odor (organic matter, hydrogen sulfide), and cohesiveness.

The sediment sampling devices were cleaned first with a deionized water/phosphate-free laboratory detergent mixture and afterwards with a pure deionized water solution before the samplers were reused. This was done in the field between sampling events, and after returning from the field. Based on sample matrices, there were no byproducts of cleaning of sediment sampling apparatus that require special disposal procedures.

LABORATORY METHODS

Anion analysis was conducted by ion chromatography in the Hydrogeology Laboratory at California State University-Los Angeles. Analysis of total dissolved selenium and selenium speciation was conducted by hydride generation atomic absorption (HG-AA) following the method described by Zhang and others (1999) at the University of California-Riverside (Appendix 1.0). Cation analysis was conducted by hydride gas generation-atomic absorption (HGG-AA) at the Water Quality Center Laboratory, University of Arizona. Other metals analyses (iron, manganese, molybdenum and vanadium) were conducted by inductively coupled argon plasma mass spectrometry (ICAP-MS) by MWH Laboratories (Monrovia, CA). Arsenic speciation

was performed by ion chromatography inductively coupled plasma dynamic reaction cell mass spectrometry (IC-ICP-DRC-MS) by Applied Speciation (Tukwila, WA). Iron speciation analysis was performed by ICP-DRC-MS by Applied Speciation.

Isotope ratios for common elements (H, O, and S) were analyzed by gas source ion ratio mass spectrometry (IRMS) at the Isotope Geochemistry Laboratory at the University of Arizona. Stable isotopes of oxygen and nitrogen in nitrate were analyzed by ion chromatography elemental analyzer isotope ratio mass spectrometry (IC-EA-IRMS) by Isotech Laboratories (Champaign, IL). Stable isotopes are reported in "delta" notation as a per mille deviation from the accepted reference standard. Table 1.1 shows the standards and delta notation used in this study.

Table 1.1 Standards and Delta Notation Used for Stable Isotopes.

Element	**Notation**	**Standard**
Hydrogen	δD or δ^2H	VSMOW (Vienna Standard Mean Ocean Water)
Oxygen	$\delta\,^{18}O$	VSMOW
Nitrogen	$\delta\,^{15}N$	AIR (Atmospheric Nitrogen)
Sulfur	$\delta\,^{34}S$	CDT (Canyon Diablo Troilite)

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Appendix 1.0

Water Sampling Protocols

23

Analysis	Sampling Protocol	Preservative	Refrigerated (<4˚C)	Headspace filled	Method of Analysis	Laboratory
anions (Fl, Cl, Br, NO3, PO4, SO4)	field filtered	none	Yes	No	Ion chromatography	CSLA
cations (Mg, Ca, Na, K)	field filtered	HNO3	Yes	No	HG-AA	U. of Arizona
Trace elements (Fe, Mn, Mo, V)	field filtered	HNO3	Yes	No	ICP-MS	MWH
Se speciation	field filtered	none	Yes	Yes	ICP-OES	UC-Riverside
dissolved Se and As	field filtered	none	Yes	Yes	ICP-OES	UC-Riverside
As speciation	field filtered	2 mL buffered EDTA	Yes	Yes	IC-ICP-DRC-MS	Applied Speciation
Fe speciation	field filtered	purged HCl	Yes	Yes	Ferrozine spectrophotometry	Applied Speciation
isotopes of nitrate (δ15N, δ18O)	field filtered	H2SO4	Yes	Yes	IRMS	Isotech Laboratories
isotopes of water (δ18O, δD)	unfiltered	none	No	Yes	IRMS	U. of Arizona
sulfur isotopes (δ34S)	unfiltered	none	No	Yes	IRMS	U. of Arizona
ammonia	unfiltered	H2SO4	Yes	Yes	Ion selective electrode	CSLA

24

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Chapter 2

Sources and Distribution of Selenium and Arsenic in Shallow Groundwater: San Diego Creek Watershed

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1 May 2008

Prepared for
Santa Ana Regional Water Quality Control Board

by

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INTRODUCTION

The research undertaken and presented in this chapter expands on work previously completed by others (Hibbs and Lee, 2000; Lee, 2001; Meixner and others 2004; Sjolin, 2004; and Walker, 2006). Its purpose is two-fold: (1) to examine regionally the sources and concentrations of selenium and nitrate in the shallow groundwater of the San Diego Creek Watershed; and (2) to focus extensively on the sources, spatial distribution, and concentrations of selenium, arsenic, and associated hydrochemical and isotopic parameters in shallow groundwater in local areas. Local areas were studied in the vicinity of open and underground channels and drains.

This work provides supplemental and newer information on selenium, arsenic, and associated contaminants and assesses the controls affecting their mobility. This information is expected to help policy-makers to mitigate the effects of these trace elements in the surface waters and groundwater of the watershed.

Geomorphic and Land Use History of the Study Area

The San Diego Creek Watershed covers approximately 112 square miles in Orange County, California and occupies a major portion of the historic San Joaquin Ranch. Regional streams drain headwaters from the Santa Ana Mountains in the north and northeast and the San Joaquin Hills in the southeast. These waters drain ultimately into Upper Newport Bay, one of the last remaining coastal estuaries of southern California (Hibbs and Lee, 2000). Before 1890, waters draining from the highlands collected in the central low-lying part of the watershed creating a wetland

environment known as the "Swamp of the Frogs" Marsh (Figure 2.0.1) (Trimble, 2003). Wetlands existed where the water table was at ground surface, creating an area where water-logged soils prevented land development. In the late part of the nineteenth century, part of this swamp was drained to make way for the expansion of ranching and agriculture (Mendenhall, 1905; Trimble, 2003). By dredging channels to drain the marsh, the water table was effectively lowered by several feet so that today a shallow groundwater system exists above deeper regional aquifers.

Land use history and agriculture play important roles in controlling groundwater quality in the shallow aquifer. During the late 1860s, the San Joaquin Ranch supported at least 40,000 sheep (Conard, 1990). By the early 1880s, the primary emphasis had shifted to cattle. Crop farming took on primary importance in the 1890s, and approximately 31,000 acres were planted with barley, with other lands planted with beans, wheat, corn, and potatoes (Conard, 1990). By 1911, lima beans had replaced barley as the principal crop grown on San Joaquin Ranch (Conard, 1990).

The early 1900s saw some experimentation with orchard crops on San Joaquin Ranch, especially walnuts, apricots, lemons, and oranges. The success of the orchards led to their expansion; citrus in particular remained an important cash crop through the 1970s. Lima beans continued to be one of the principal crops with as many as 17,000 acres planted in lima beans in the 1930s and 1940s (Conard, 1990).

Three factors placed constraints on specific types of historic agricultural development of the land that was previously occupied by the Swamp of the Frogs

Marsh: 1) poor drainage of heavy, fine textured soils; 2) high salinity and high alkali content of soils; and, 3) shallow depth to the water table (Figures 2.0.2, 2.03, and 2.0.4). The soils of the watershed formed due to historic drainage features of the catchment, where coarser grained materials formed along the flood plains of the ancestral San Diego Creek and other washes, and finer-grained material formed in the central, low-lying part of the watershed (Figures 2.0.4 and 2.0.5). The boundary of the historic swamp, as inferred from soil alkalinity contours, coincides with a soil type first known as the "San Joaquin black adobe soil" (Figure 2.0.4). The distribution of different soils in the watershed and the factors that led to their development plays an important role in controlling the distribution of selenium in the groundwaters of the catchment (Hibbs and Lee, 2000; Meixner and others, 2004).

Some of the best information on types of agriculture in the area once occupied by the Swamp of the Frogs Marsh is found in early USDA Soil Survey Reports (Holmes, 1901; Eckmann and others 1919). In the first USDA report on the area, Holmes (1901) described the relationship between the San Joaquin black adobe soil, the alkali soils, and the ability to raise crops in areas once occupied by the marsh:

> *"A reference to the alkali map will show that the alkali east of the Santa Ana River, of this region, occurs as a large and continuous area of varying intensity, in all 13,150 acres [i.e., Swamp of the Frogs Marsh]……..These alkali lands have never been irrigated, but are always moist through subirrigation. The alkali is all found accumulated in the first two or three feet of the soils, with the greater part as a crust on the surface.*

> *"The large areas of alkali south and southeast of Santa Ana [city] occurs mainly in the San Joaquin black adobe silts, being the largest continuous area of alkali in this region. All land which carries more than 0.60 percentage of alkali is used for pasture land, no attempt being made to grow crops other than the native saline vegetation….. Nothing but saline vegetation grows upon soil having more than 0.60 percent [alkali], although much of the vegetation is good pasture for stock."*

Holmes (1901) elaborates further on the potential for growing crops on the San Joaquin black adobe soil, if the soils can be conditioned and reclaimed:

> *"The alkali east of Santa Ana River occurs in a heavy soil, mainly the black adobe, so its reclamation will be more difficult that that of sandier soils, because the alkali is not so easily washed out, as water travels slowly through a heavy soil. With plenty of irrigation water and with proper tile drainage this soil might in time be made valuable for alfalfa and other alkali-resisting plants."*

By 1919, the USDA had renamed the San Joaquin black adobe the "Chino silty clay" (Eckmann and others, 1919). The historic Swamp of the Frogs Marsh region was occupied primarily by the "heavy phase" of this soil type (Eckmann and others, 1919) (Figure 2.0.4). Up to that time, the areas occupied by the Chino silty clay, heavy phase had seen limited agricultural development. This is specifically mentioned by Eckmann and others (1919) who describe the limited crop development in the soil:

> *"The principal areas of the Chino silty clay, heavy phase, lie south of Santa Ana [i.e., Swamp of the Frogs Marsh]….The surface is nearly flat or gently sloping. Frequently the areas occupy the broad depressions that carry the drainage of higher lying types. Some areas are swampy during most of the year, and drainage is poor over all the phases. Seepage springs and flowing wells are common and the water table is high. Strong concentration of alkali occur in*

most of the areas. The Chino silty clay, heavy phase, is relatively unimportant, only a small part being used for crop production."

The preceding passage indicates that parts of the Swamp of the Frogs Marsh had not been completely drained by 1919, especially the lower lying areas of the marsh (Figures 2.0.1 and 2.0.5). Some limited improvements of the lands once occupied by the marsh had been effected by this time for the purposes of growing alkali resistant crops (Eckmann and others (1919). Eckmann and others (1919) saw little potential for planting orchard crops in the area once occupied by Swamp of the Frogs Marsh, noting that *"the deep-rooted orchard crops are not grown under average alkali conditions, as much because of adverse drainage conditions as the presence of alkali."* Historic topographic maps produced by the USGS in 1948 show numerous orchards that encompass the boundaries of the former marsh, but there was almost no historical orchard development within the historic marsh boundary.

Considerable effort was subsequently made to improve the poorly drained, alkali lands and increase their productiveness. Additional lowering of the water table did much toward reducing salt concentration, while irrigation water, natural rainfall, and in some instances overflow waters assisted in leaching away the alkali (Eckmann, 1919). As a result, lima beans were eventually put into production in some parts of the area once occupied by the historic marsh (Figures 2.0.2, 2.03, and 2.04). Lima bean production in that part of the San Joaquin Ranch was short-lived however (<15 years). In 1942, the lima bean fields within the historic marsh boundary were displaced by the Tustin Marine Corps Air Station (Figure 2.0.6).

The Tustin Air Station was centered within the boundaries of the historic Swamp of the Frogs Marsh (Figure 2.0.7). Synthetic nitrogen fertilizers had not yet been developed when the air station was established on the historic marsh site. This provided important controls on the amounts and types of fertilizer applied to areas once occupied by Swamp of the Frogs Marsh. Lima beans are nitrogen-fixing legumes, requiring little to no fertilizer. Application of nitrogen based fertilizers in the area of the historic orchards, at topographic elevations above the historic swamp, has had a much greater impact on groundwater quality in the shallow aquifer beneath San Diego Creek Watershed (French and others, 2006).

Relationship Between the Historic Marshland and Selenium

Geologic history plays an important role in controlling groundwater quality in the shallow aquifer. Previous research found high levels of selenium in the shallow groundwaters that flow within the boundary of the historic Swamp of the Frogs Marsh (Hibbs and Lee, 2000). Hibbs and Lee (2000) proposed that the historic marsh acted as a sink for selenium derived from weathering and erosion of upland marine shales. Draining the marsh changed prevailing hydrologic and geochemical structure of the land, essentially converting this selenium sink to a selenium source whereby infiltrating precipitation and shallow groundwaters leach selenium from the historic marsh deposits. These selenium-rich groundwaters contribute substantial flow to surface streams via groundwater baseflow, groundwater seepage, and springs (Hibbs and Lee, 2000; Meixner and others, 2004).

Selenium may originate from upland marine shales of Miocene age (Tracy, 1990). Major rock types of the Santa Ana Mountains and the San Joaquin Hills are sandstones, siltstones and shales of the Vaqueros, Sespe, Puente and Monterey Formations (Figure 2.0.1). The soils of the lowlands reflect the historic drainage features of the catchment where coarser grained materials are found along the flood plains of the ancestral San Diego Creek and finer-grained material is found in the low-lying parts of the watershed (Figure 2.0.4). The boundary of the historic swamp, as inferred from soil alkali contours, coincides with the San Joaquin black adobe soil (Figure 2.0.4). The distribution of these geologic materials within the basin may play a role in controlling the distribution of selenium in the groundwaters of the catchment.

High levels of selenium in surface water have been linked to birth defects and increased mortality of fish and waterfowl (Lemly and others, 1987; Frankenberger, 1998). Aquatic life forms depend on regional streams and on the principle drainage feature of the catchment, Upper Newport Bay. Habitats in San Diego Creek Watershed and in Upper Newport Bay could potentially suffer adverse impacts from this naturally occurring source of selenium.

OBJECTIVES AND STRUCTURE OF CHAPTER

The chapter's first objective is to examine the regional sources and concentrations of selenium and nitrate in the shallow groundwater in the San Diego Creek Watershed. This is done in the section entitled, ***2.1. Analysis of Selenium and Nitrate – A Regional Conceptual Model.*** The second objective is to focus

extensively on the sources, spatial distribution, and concentrations of selenium, arsenic, nitrate, and associated hydrochemical and isotopic parameters in shallow groundwater in local areas of the watershed. This is done in sections 2.2 to 2.10 of the chapter, entitled respectively:

2.2. El Modena Channel Studies

2.3. Santa Ana Delhi Channel Studies

2.4. Alton Drain Studies

2.5. Santa Fe Underground Circular Drain Studies

2.6. Edinger Underground Circular Drain Studies

2.7. Valencia Underground Drain Studies

2.8. Lane Channel Studies

2.9. Barranca Underground Circular Drain Studies

2.10. San Joaquin Channel Studies

Some sections cover areas studied previously by Hibbs and Lee (2000) and by Meixner and other (2004), while other sections cover new areas that haven't been studied. Sections 2.2 to 2.5 cover the region of "perennially wetted" soils in predevelopment times (Meixner and others, 2004) and discuss data supporting a selenium-nitrate oxidation model in groundwater. Sections 2.6 and 2.7 cover the "ephemerally wetted" area of very elevated selenium and arsenic concentrations in groundwater (Meixner and others, 2004). Sections 2.8 and 2.9 cover flowpath transects that extend from a transitional "Swamp Fringe" zone into an elevated salinity zone deep within the interior of the historic Swamp of the Frogs Marsh.

Finally, Section 2.10 provides hypotheses on a low salinity, low selenium area located within the historic marsh.

METHODS

Summary details of field and laboratory methods employed in this chapter are provided below. More extensive details encompassing methods undertaken in all of the chapters of this report are provided in Chapter 1.

Field parameters were measured by two field instruments: a Yellow Springs Instrument-63 (YSI-63) gave readings for pH, temperature, temperature-compensated electrical conductivity (EC), and salinity while a YSI-550A gave readings for dissolved oxygen (DO) in percent saturation and concentration (mg/L). In addition to field parameters, a number of water samples were collected at each site depending on the types of chemical analyses required. All groundwater samples were collected in triple-rinsed HDPE or LDPE bottles. Aliquots were separated and preserved within twenty-four hours of collection for various chemical analyses. Filtration was performed using 0.45 µm polycarbonate filter paper.

Samples collected for anion analysis were filtered and kept refrigerated below a temperature of 4˚C. Samples to be analyzed for dissolved selenium, dissolved arsenic, and selenium speciation were also preserved in this way. Samples to be analyzed for cations and other metals (iron, manganese, molybdenum and vanadium) were filtered and acidified to less than pH 2 with nitric acid (HNO_3) then kept refrigerated (< 4˚C). Samples collected for arsenic speciation were preserved with 2-mL buffered EDTA ascetic acid/acetate solution. Samples

collected for iron speciation analysis were acidified to less than pH 2 with degassed hydrochloric acid (HCl). Samples for silica analysis were not filtered or acidified, but kept cool below a temperature of 4˚C.

For stable isotopes of water and sulfur in sulfate, unpreserved sample was collected in a 250-mL HDPE bottle filled to the rim to ensure no headspace remained in the bottle. Samples collected for isotopic analysis of nitrate were filtered and preserved to less than pH 2 with sulfuric acid (H_2SO_4). For stable isotopes of carbon in dissolved inorganic carbon (DIC), sample was not filtered or acidified but kept cool below a temperature of 4˚C.

Anion analysis was conducted by ion chromatography in the Hydrogeology Laboratory at California State University-Los Angeles. Analysis of total dissolved selenium and selenium speciation was conducted by hydride generation atomic absorption (HG-AA) following the method described by Zhang and others (1999) at the University of California-Riverside. Cation analysis was conducted by hydride gas generation-atomic absorption (HGG-AA) at the Water Quality Center Lab, University of Arizona. Other metals analysis (iron, manganese, molybdenum and vanadium) were conducted by inductively coupled argon plasma mass spectrometry (ICAP-MS) by MWH Laboratories (Monrovia, CA). Arsenic speciation was performed by ion chromatography inductively coupled plasma dynamic reaction cell mass spectrometry (IC-ICP-DRC-MS) and iron speciation analyses was performed via ICP-DRC-MS by Applied Speciation (Tukwila, WA).

Isotope ratios for common elements (H, O, and S) were analyzed by gas source ion ratio mass spectrometry (IRMS) Isotope Geochemistry Lab at the

University of Arizona. Stable isotopes of oxygen and nitrogen in nitrate were analyzed by ion chromatography elemental analyzer isotope ratio mass spectrometry (IC-EA-IRMS) by Isotech Laboratories (Champaign, IL).

GEOCHEMISTRY OF SELENIUM AND ARSENIC

To assist the reader, a brief summary of the redox geochemistry of selenium and arsenic is provided. Details on the more simplistic hydrochemistry of nitrate is not included here, but may be found in standard texts such as Freeze and Cherry, 1979; Horne and Goldman, 1994; and Kadlec and Knight, 1996.

Selenium is an essential micro-nutrient without which livestock can develop muscular dystrophy and humans can suffer from heart disease (Thornton, 1983; Frankenberger, 1998). It can also be a toxic trace element. Above a certain threshold, it can induce birth defects in fish and waterfowl. Extensive deformities documented in wildlife at the selenium-impacted Kesterson Reservoir led the US EPA to adopt an interim chronic water quality criterion of 5 µg/L selenium for surface water bodies.

Selenium can exist in one of four oxidation states. Under oxidizing conditions selenium exists dominantly in the +VI oxidation state as the highly soluble anion selenate (SeO_4^{2-}). Under intermediate redox conditions selenate (Se^{6+}) can be reduced to selenite (SeO_3^{2-}) in the +4 oxidation state, which tends to exist as a sorbed ion. Under more reducing conditions, selenium can be further reduced to elemental selenium (Se^0) or selenide (Se^{2-}). Reduced selenide can bind with hydrogen to produce a volatile gas. Alternatively, it can also react with ferrous

iron and other metals and precipitate as a mineral phase (Elrashidi, et. al., 1987). Redox transformations of selenium tend to be biologically-mediated in natural systems (Dowdle and Oremland, 1998; Losi and Frankenberger, 1998; Zawislanski and Zavarin, 1996). The redox behavior of selenium is analogous to that of sulfur, thus it is not uncommon to find selenium in association with the iron-sulfide mineral pyrite (Johnson and others, 1999). The redox characteristics of sulfur and selenium are summarized in Table 2.0.1.

Table 2.0.1. Redox Characteristics of Sulfur and Selenium.

Redox Condition	Selenium Species	Oxidation State	Sulfur Species	Oxidation State	Aqueous Mobility
OXIDIZING	SeO_4^{2-} (aq)	VI	SO_4^{2-} (aq)	VI	High
↓	SeO_3^{2-} (aq)	IV	SO_3^{2-} (aq)	IV	Moderate
↓	Se (s)	0	S (s)	0	Low
REDUCINIG	Se^{2-} (g)	-II	S^{2-} (g)	-II	Low

Abundant organic matter found in marshlands tends to create anoxic reducing conditions. Such conditions would have acted as a sink for sulfur and selenium. Hibbs and Lee (2000) proposed a scenario by which selenium eroded from upland marine shales was oxidized to soluble forms allowing it to advect with surface and groundwater flows until reaching the reducing waters of the Swamp of the Frogs Marsh. There, aqueous selenate would have been reduced and immobilized as solids like iron selenide ($FeSe_2$) and perhaps elemental selenium and selenite. Drainage of the marsh permitted the infiltration of oxygen-rich waters that act to oxidize and re-mobilize the selenium sequestered in the marsh. Thus groundwaters act as a non-point source of selenium contamination to the watershed.

Research has shown that nitrate can also act to oxidize reduced selenium to selenate (Wright, 1999; Masscheleyn and others, 1990) which has important ramifications for the San Diego Creek Watershed, where groundwaters have elevated nitrate concentrations associated with historic agricultural practices (French, 2006).

Arsenic can exist in numerous organic and inorganic forms in the environment. It is a known toxin that can induce various types of cancer as well as adverse neurological and cardiovascular effects in humans (Le, 2002). For this reason the EPA reduced the Maximum Contaminant Level for drinking water from 50 μg/L to 10 μg/L. Presently, there is no criterion for arsenic concentrations in surface waters.

In the mineral phase, arsenic is found to be most abundant as arsenopyrite (FeAsS). Arsenic is often found in association with pyrite deposits, which are common secondary minerals in wetland and watershed sediments (Francesconi and Kuehnelt *in Frankenberger*, 2001). The predominant forms of arsenic found in natural waters tend to be in one of two oxidation states: in oxic waters arsenate (As^{5+}) dominates, whereas in suboxic or more reducing waters arsenite (As^{3+}) becomes more abundant. Under normal environmental oxygen levels, arsenate is thermodynamically more stable (Ferguson and Gavis, 1972, Robertson, 1989; Smith, 1998). However, it also tends to be less mobile than arsenite due to the tendency of arsenate to adsorb strongly to oxy-hydroxides of iron (Drever, 1997).

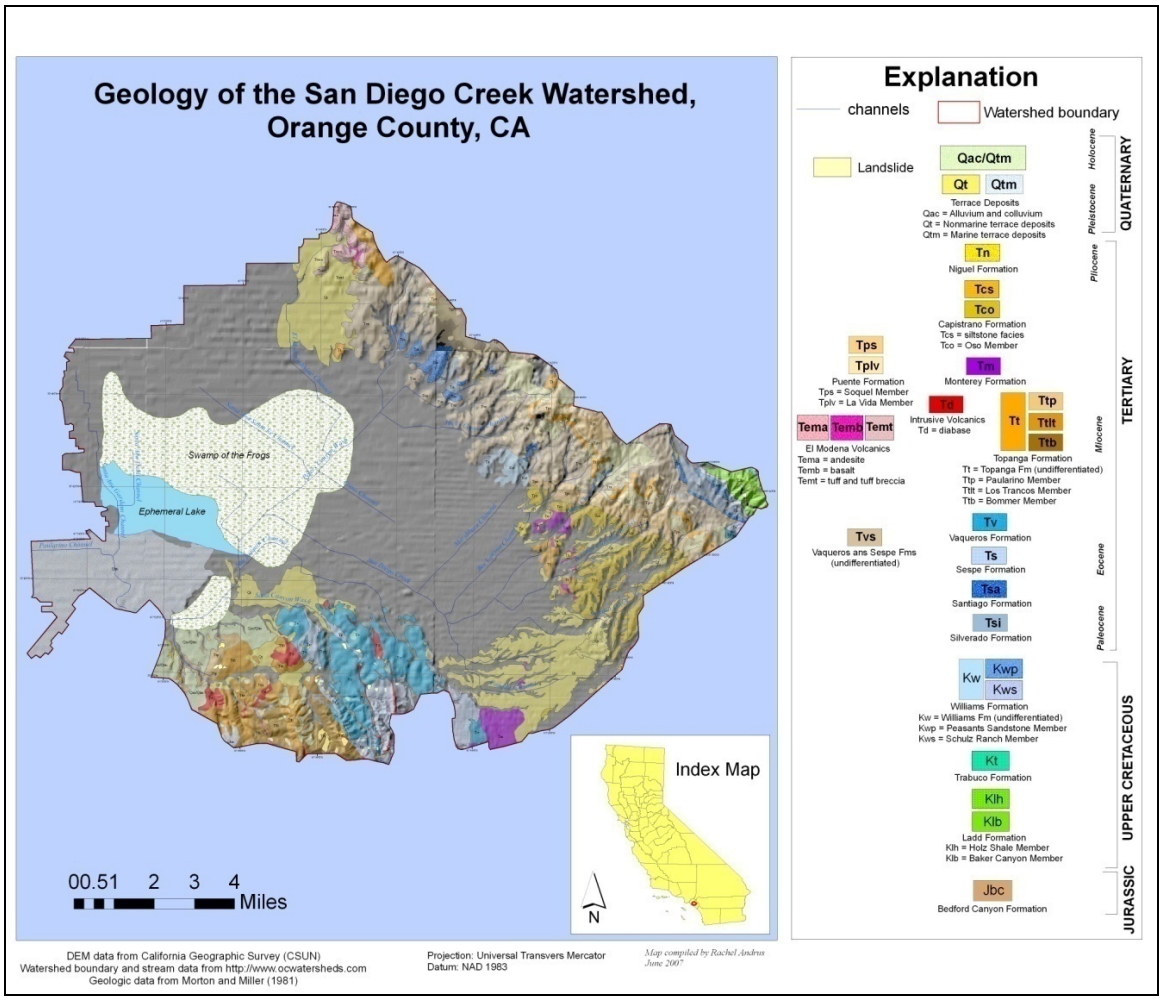


Figure 2.0.1. Map showing the geology of the San Diego Creek Watershed with the boundary of the historic "Swamp of the Frogs" Marsh shown, as determined by Trimble (2003).

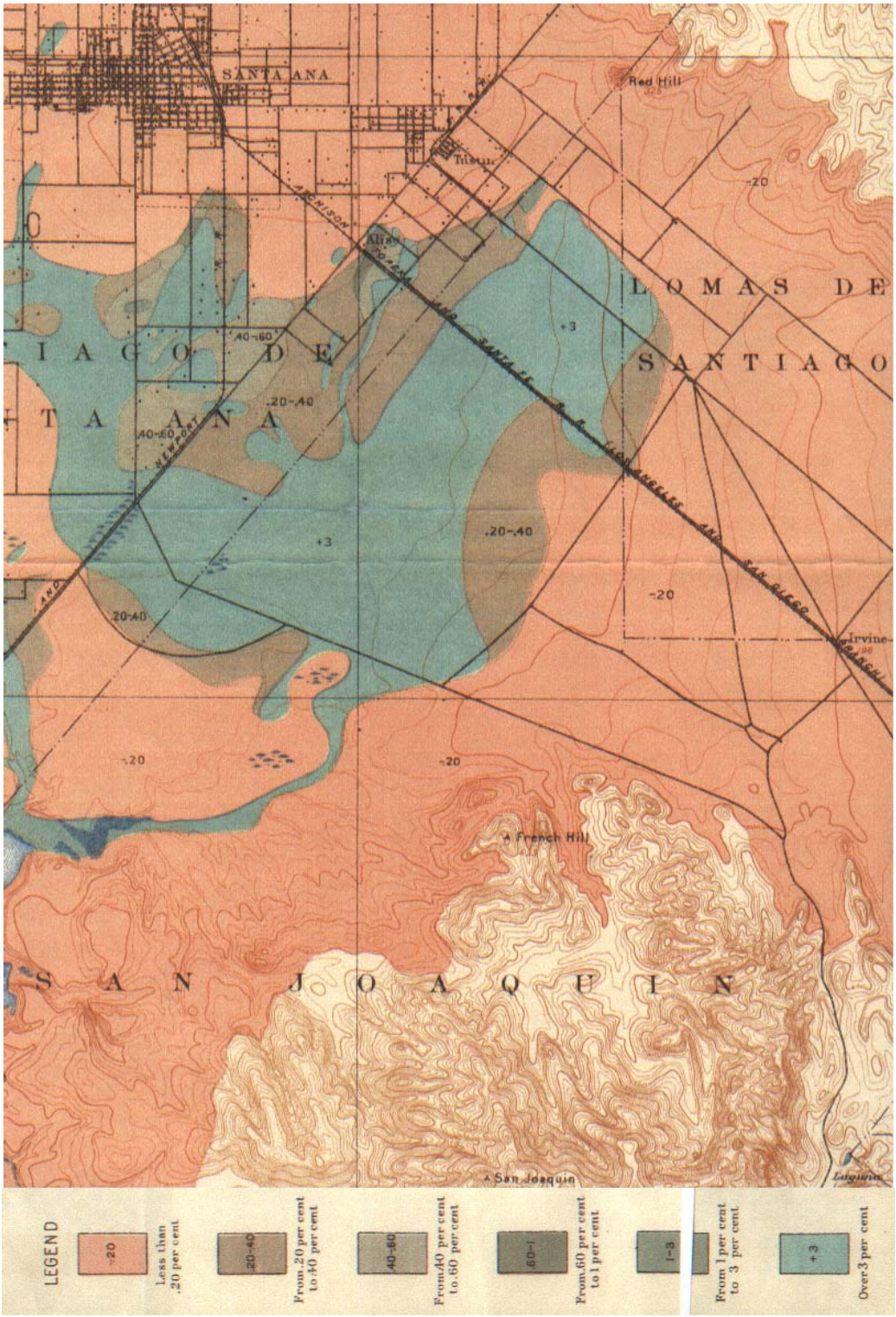


Figure 2.0.2. U.S. Department of Agriculture1900 Alkali map of the San Diego Creek area (from Holmes, 1901). Alkali develops at or near land surface when evaporating groundwater from shallow water tables leaves salts behind. Map is a proxy indicator of the geographic limits of the Swamp of the Frogs marsh.

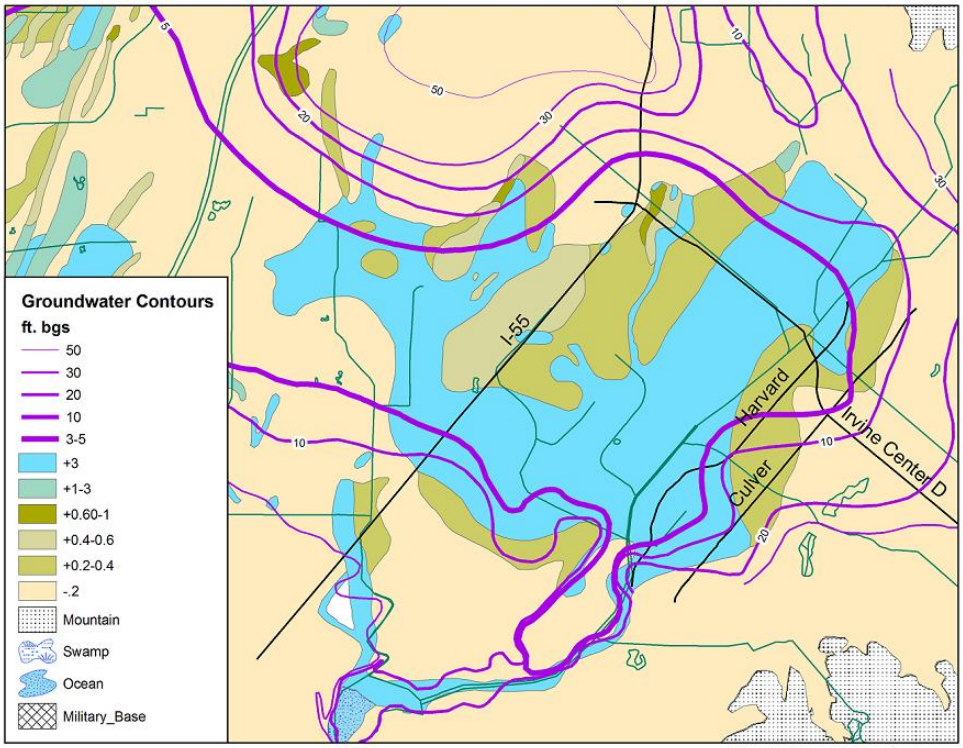


Figure 2.0.3. Depth to shallow groundwater contours superimposed on 1900 alkali map (from Holmes, 1901). The thickest internal contour shows a groundwater depth that is only 3 to 5 ft below ground surface. Depth to groundwater contours extracted from seismic zonation study by Sprotte and others (1980).

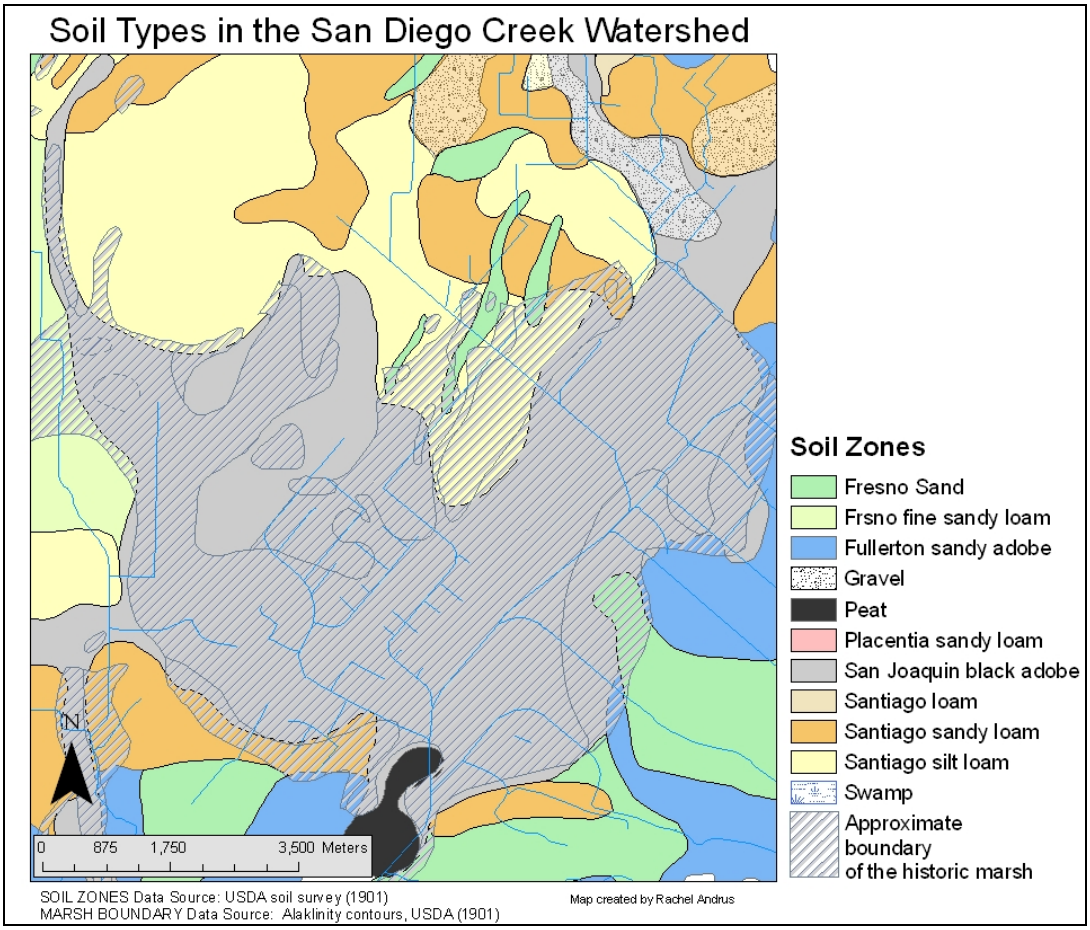


Figure 2.0.4. Map showing the distribution of soil types in the San Diego Creek Watershed, including overlapping area of heaviest alkali (stipple pattern) (from Holmes, 1901).

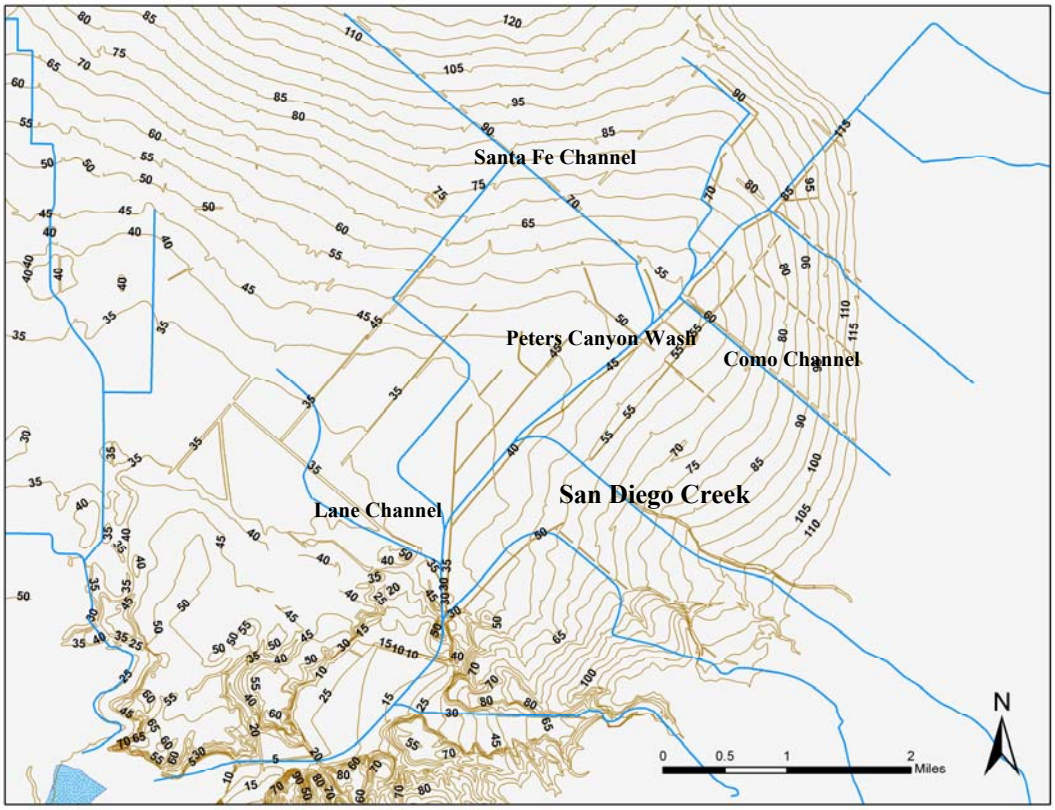


Figure 2.0.5. USGS topographic map from the 1940s showing land surface topography in feet above sea level. The Swamp of the Frogs Marsh covers many areas below the 70 ft contour line, except near Upper Newport Bay. Very flat land areas had sluggish groundwater movement in predevelopment times because the water table was at land surface. Groundwater moves very slowly where hydraulic gradients are nearly flat. This led to heaviest accumulation of alkali-salt crusts where land surface is flat, because these areas are groundwater evaporation/discharge areas where groundwater movement is sluggish. When groundwater evaporates at land surface, dissolved salts are precipitated in soils. This map is highly relevant to sections covering development of alkali-salt flats (e.g., Edinger Underground Circular Drain Studies, Lane Channel Studies, Barranca Underground Circular Drain Studies).

Figure 2.0.6. Last of the lima bean crop from site used to build the Tustin Marine Corps Air Station, 1942 (from www.tustinhistory.com).

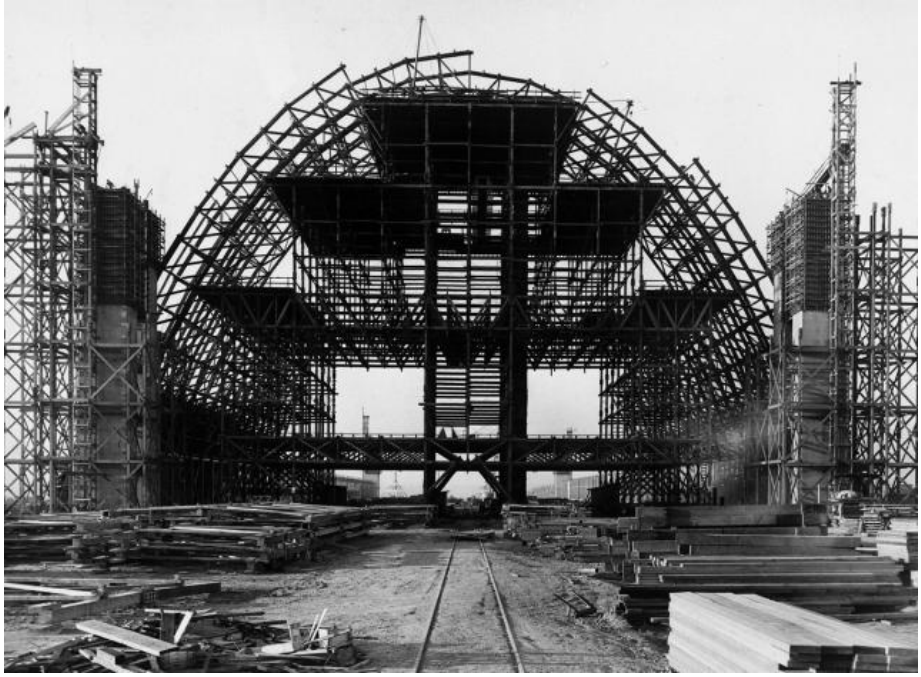


Figure 2.0.7. Hangar construction, Tustin Marine Corps Air Station, 1943 (from www.tustinhistory.com).

2.1. ANALYSIS OF SELENIUM AND NITRATE - A REGIONAL CONCEPTUAL MODEL

Selenium concentrations in shallow groundwater in San Diego Creek Watershed are presented in regional context in map form (Figure 2.1.1). These data are color coded by ranges of selenium concentration, with blue being the lowest range and red being the highest range. These data are developed mostly from information collected during the prop-13 study and from historical 1990s base closure data collected at the Tustin Marine Corps Air Station. A very small set of data were integrated from Hibbs and Lee (2000). The information in the maps represents a compilation data set, covering nearly a decade. However, most of the data in the vicinity of Tustin Air Station were collected during a two year period, and most of the other data were collected from 2004 to 2007.

The 70 and 50 foot land surface contours are plotted on the map (Figure 2.1.1). The area above the 70 ft contour is located above the Swamp of the Frogs Marsh. The area between the 70 and 50 ft land surface contours occupies the outer fringe of the historic marsh, but it is a zone within the marsh. Most of the area below the 50 ft land surface contour occupies the interior of the historic marsh. The patterns indicate generally low selenium concentrations above the 70 ft land surface contour, very high selenium concentrations between or near the 50 and 70 ft land surface contours, and generally low concentrations at elevations below the 50 ft land surface contour. These same data are plotted in scatter plot form, showing selenium concentrations above, within, and below the 50 to 70 ft contour zone (Figure 2.1.2). The results reveal strikingly elevated selenium concentrations within the historic swamp fringe (50 to 70 ft).

A spatial map of total dissolved solids (TDS) shows almost opposite results, where TDS concentrations are lowest within the outer fringe of the historic swamp and above the swamp, while TDS is highest in the interior portion of the marsh, below the 50 ft contour (Figure 2.1.3; also see Figure 2.0.5). A reasonable interpretation of selenium and TDS data suggests that selenium accumulated primarily in the outer swamp fringe where vegetation and anoxic sediments stripped dissolved selenium from the incoming runoff waters and groundwaters. In the interior of the swamp, salts accumulated in the alluvial salt flats due to high evaporation rates. In the salt flats region, less selenium may have accumulated because it had already been removed from groundwater (and possibly from overland flow, to some extent) in the outer fringe of the swamp. Also, the sparse and different varieties of vegetation in the interior salt flats of the historic swamp may not have sequestered selenium as readily (Figure 2.1.4).

Nitrate-nitrogen concentration in shallow groundwater is presented in map form (Figure 2.1.5). This map also shows the relationship between nitrate and the 70 ft and 50 ft land surface contours within the Swamp of the Frogs Marsh (outer fringe of the marsh) (Figure 2.1.5). Notice also the spatial distribution of orchards, circa 1950, surrounding the outer limits of the Swamp of the Frogs Marsh, as indicated by the 70 ft topographic contour. As explained in the last section, deep rooted orchards were not planted in areas once occupied by the Swamp of the Frogs Marsh, where soils were fine textured and poorly drained, and where water tables were shallow, even after drainage of the swamp. High nitrate concentrations in shallow groundwater are found in the orchards area above the historic swamp.

Nitrate is also high in the swamp fringe area between the 50 and 70 ft land surface contours. Nitrate obviously moved with groundwater into the swamp fringe (Figure 2.1.8). However, in areas of high total dissolved solids, nitrate-nitrogen is usually low (compare Figures 2.1.3 and 2.1.5).

In scatter plot form, it is evident that nitrate is highest in the area above the historic swamp (above 70 ft) where the orchard coverages were once dense (Figure 2.1.6). Nitrate is also elevated between and near the 70 and 50 ft land surface contours, within the swamp, where selenium concentrations are most elevated (see Figures 2.1.1, 2.1.2, and 2.1.7). Average nitrate concentrations diminish below the 70 ft contour, as shown by the trend line in Figure 2.1.6B. Despite much variation in nitrate near and below the 50 ft land surface contour, the overall nitrate concentration trends to a lower average concentration below the 50 ft land surface contour line (Figure 2.1.6B). This may be due to nitrate loss through denitrification, and associated oxidation of organic matter, sulfur, and selenium along with dilution recharge through unsaturated soils within the swamp region. Dilution recharge within the swamp also should contain lower nitrate, due to limited historic use of synthetic fertilizer (Figure 2.1.5).

Later in our discussion of channels and drains, we report additional evidence from nitrogen isotopes and other hydrochemical and isotopic tracers that nitrate may be an oxidant for bound and reduced forms of selenium in soils formed within the historic Swamp of the Frogs Marsh. Summary details are provided for regional context in this section. The following reaction applies:

$$5FeSe_2 + 14NO_3^- + 4H^+ \rightarrow 7N_2 + 10SeO_4^{2-} + 5Fe^{2+} + 2H_2O \quad \text{(equation 2.1.1)}$$

In this reaction, metal selenides in soils are oxidized to selenate (+VI) by dissolved nitrate, while nitrate is reduced by denitrification. Selenides (-II) are much reduced forms of selenium. Elemental selenium and selenite can also be oxidized by nitrate, to release selenate into ground water, while the nitrate is simultaneously denitrified. Selenite (+IV) is an intermediate oxidation form of selenium that is often bound or sorbed onto clay particles and organic material.

Wright (1999) found that selenium can be oxidized by nitrate from irrigation on Cretaceous marine shale. Dissolved selenium concentrations are positively correlated with dissolved nitrate concentrations in both surface water and ground water samples from irrigated areas in Wright's study area. Theoretical calculations done by Wright (1990) for the oxidation of selenium show favorable Gibbs free energies for the oxidation of selenium by nitrate, indicating nitrate can act as an electron acceptor for the oxidation of selenium. Laboratory batch experiments with selenium-bearing shale and zero-dissolved-oxygen water containing nitrate showed increased selenium concentrations over time with increased nitrate concentrations (Wright, 1990). Wright concluded that careful management of nitrogen-fertilizer applications in Cretaceous shale settings might help to control the oxidation and mobilization of selenium into surface water and groundwater. The same management practices might prove fruitful in San Diego Creek Watershed.

In subsequent sections, a covariate relationship will be shown for selenium, nitrate, and salinity in specific parts of the San Diego Creek Watershed (e.g., El Modena Channel Studies, Santa Ana Delhi Channel Studies, and Alton Drain

Studies). We will show a clear positive correlation between selenium and nitrate concentrations, and a negative correlation between nitrate/TDS and selenium/TDS. These relationships are also shown in the regional maps and figures (Figure 2.1.1 to 2.1.8). A possible set of hypotheses for the correlative relationships between selenium, nitrate, and TDS (salinity) are as follows:

- Oxidation of selenium by nitrate produces a positive correlation between high nitrate and high selenium. The higher the nitrate concentration, the higher the selenium concentration. In fact, dissolved oxygen in groundwater, when not completely consumed during recharge, acts in tandem with nitrate to raise oxidation potential in groundwater. However, this process only applies in areas where bound forms of selenium in soils are concentrated, such as in the outer swamp fringe, where selenium was sequestered when it entered the historic swamp. Where selenium concentration in soils is not high, such as above the 70 ft contour line (above the swamp fringe), selenium is low, even when nitrate concentration is high (Figure 2.1.7).

- Though nitrate is consumed in the oxidation/reduction process, nitrate does not diminish completely due to the stoichiometric relationships between ppb (ug/L) concentrations of selenium, and ppm (mg/L) concentrations of nitrate. Some dilution recharge in the Swamp of the Frogs Marsh could also dilute nitrate concentrations due to percolation recharge through nitrate-limited soils in the unsaturated zone that had limited orchard and other synthetically fertilized crops.

- Groundwaters with high salinity are found in topographically flat and low lying areas, where groundwater (mostly) and surface water collected and evaporated, to create salt crusts in the interior of Swamp of the Frogs Marsh. Because these soils tend to be low-permeability, they do not drain well and they continued to contain high salt content after the Swamp of the Frogs Marsh was drained. Accordingly, nitrate is low and salt content is high in the groundwater beneath these historic salt flats. In these historic salt flats, agriculture was not practiced much historically.

- A low selenium, high salinity, low nitrate correlation is consequently observed in the data set. The soils with high salinity within the Swamp of the Frogs Marsh boundary may contain

moderate selenium. Or they may contain low selenium, because in historic times selenium in groundwater may have been removed from waters in the outer Swamp of Frogs Marsh fringe before these waters reached the low lying interior of the swamp (this same scenario does not apply to sulfur because sulfur [sulfate] is ubiquitous in incoming waters).

● Without the presence of nitrate needed to oxidize selenium from soils, the selenium concentration may remain low in nitrate-deficient groundwater. Thus, nitrate could be an important factor in selenium mobility.

According to this model, nitrate-enriched groundwater moves from the areas once occupied by orchards into the outer swamp fringe where selenium-enriched soils are oxidized by nitrate to produce high concentrations of selenium in shallow groundwater (Figures 2.1.7 and 2.1.8). The ramifications of these processes could be profound. If nitrate continues to be added to the shallow aquifer via application of nitrogen to urban landscapes (by household application, treated wastewater, etc.); or if substantial amounts of nitrate are left over in soils from the historic period of agriculture in the region, the selenium in soils could be mobilized by nitrate in greater concentrations than would naturally occur.

<u>We do not exclude oxidation of reduced forms of selenium by dissolved oxygen as a process to explain high selenium in shallow groundwater</u>. This common process was first suggested as the dominant factor by Hibbs and Lee (2000). However, we feel that nitrate as an oxidant of reduced forms of selenium is probably as important as dissolved oxygen. This is because dissolved oxygen is often depleted to suboxic concentrations (<0.3 mg/L) during aquifer recharge through organic rich topsoils and aquifer matrix. We believe dissolved oxygen and nitrate act together to raise oxidation potential in shallow groundwater and both

help to oxidize reduced forms of selenium. When dissolved oxygen is near depletion, nitrate continues to keep oxidation potential high.

The model described above is a generically applicable model operating on a regional scale. The model does not integrate the concepts of "perennially wetted" and "ephemerally wetted" soils in predevelopment times, discussed by Meixner and others (2004). In these local areas, intricacies in groundwater redox conditions, both historically and in contemporary times, cause deviation from our regional generic model. These intricacies are discussed at length in other sections in this chapter.

Alternative Conceptual Model

An alternative conceptual model involves the presence of contemporary reducing conditions in sediments and aquifer material in the interior flatlands of the Swamp of the Frogs Marsh. Overall, the sediments beneath the historic salt flats tend to be finer textured and lower permeability than sediments within the outer swamp fringe. This is because active channels, such as the antecedent washes to Peters Canyon Wash and San Diego Creek, deposited blankets or seams of sand in the outer swamp fringe during occasional heavy floods in the times that predated channelization of San Diego Creek Watershed.

Sediments within the outer swamp fringe (50 to 70 ft contour) have mixed clay/silt/fine sand lithologies, because occasional floods laid down fine sand along the fringes of the historic marsh. If finer sediments within the interior of the swamp have a lot of undecomposed organic matter today, these soils could create anoxic

groundwaters. In such a scenario, the anoxic sediments could deplete nitrate and selenium in groundwater through the processes of denitrification and selenium reduction.

The two regional conceptual models discussed above are not mutually exclusive, and both may operate together to produce the selenium and nitrate distributions we observe in San Diego Creek Watershed. The local studies discussed in the next sections provide several additional insights on these processes and concepts.

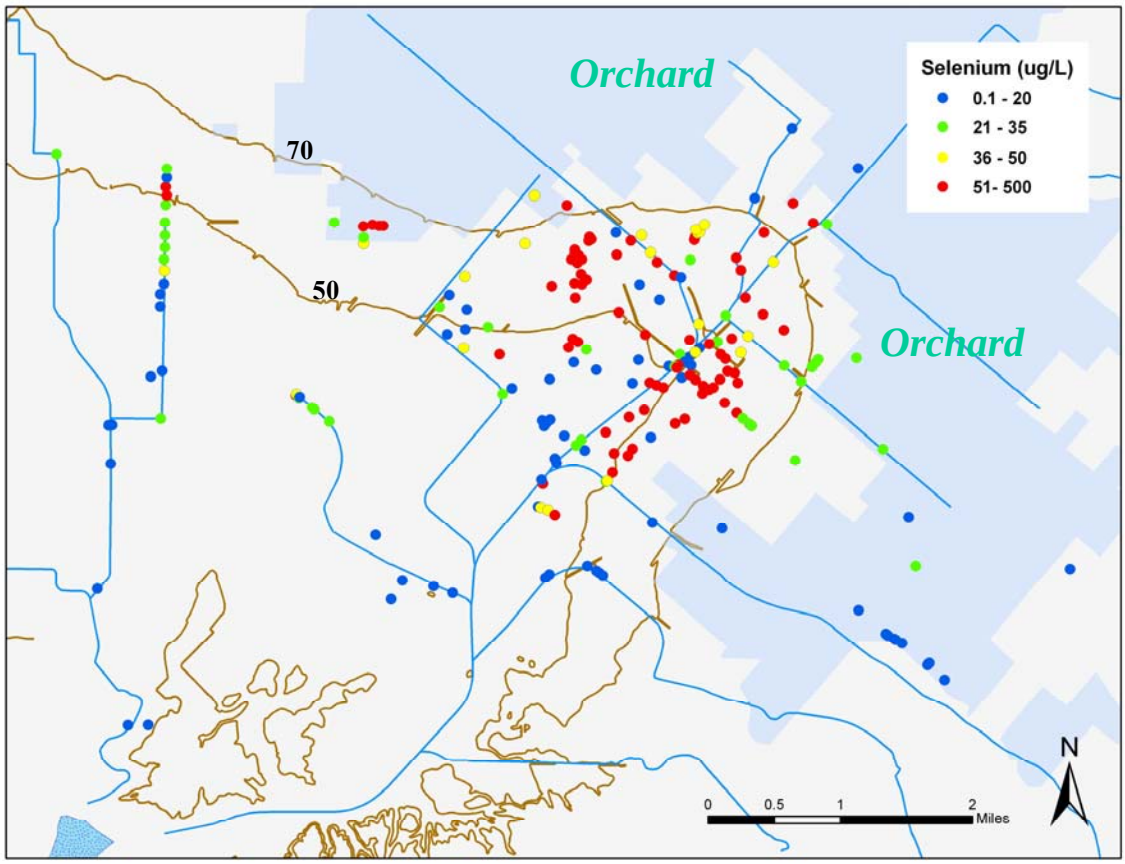
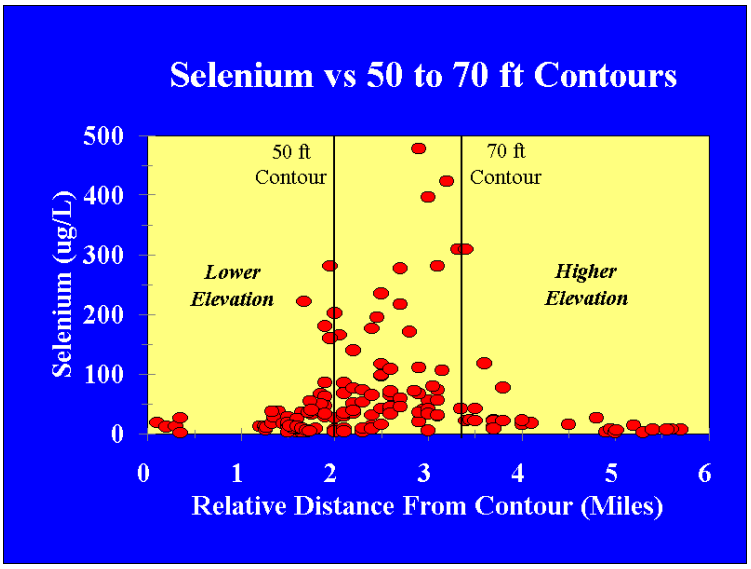
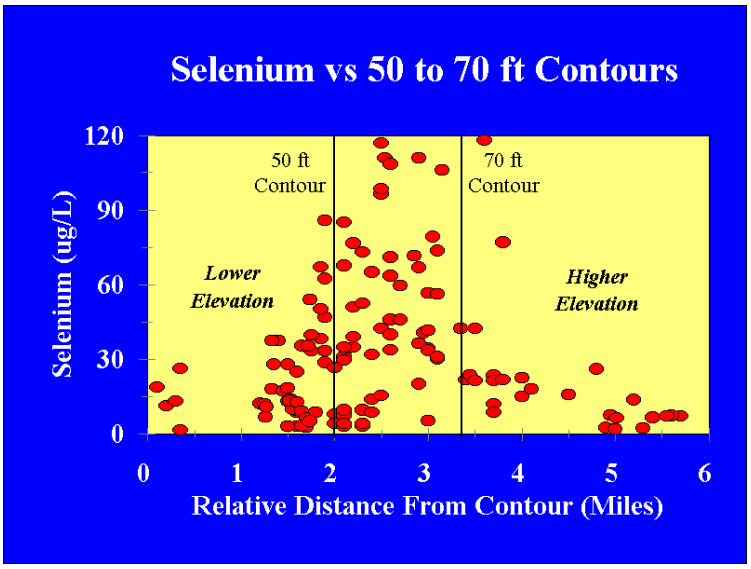


Figure 2.1.1 Selenium concentration in shallow groundwater, showing relationship between the 70 ft and 50 ft land surface contours, within the Swamp of the Frogs Marsh (outer fringe of the marsh). High selenium concentrations in this area suggest selenium was precipitated and sorbed in this outer-swamp area in large amounts. Below the 50 ft contour line, most of the land region is occupied by the Swamp of the Frogs Marsh, but selenium concentrations are generally lower in the other parts of the marsh (exhibited by many blue points). Notice also the spatial distribution of orchards, circa 1950, surrounding the outer limits of the Swamp of the Frogs Marsh, as indicated by the 70 ft topographic contour. Orchards did not flourish in areas once occupied by the Swamp of the Frogs Marsh, where soils were fine textured and poorly drained, and where water tables were shallow, even after drainage of the swamp.



A.



B.

Figure 2.1.2 Selenium concentration in shallow groundwater, showing relationship between the 70 ft and 50 ft land surface contours. Selenium concentrations are ranged from 0 to 500 ug/L in plot A and from 0 to 120 ug/L in plot B. In particular, plot B shows that selenium concentrations above the 70 ft contour (higher elevation above Swamp of the Frogs Marsh) are relatively low. Within or near the 50 to 70 ft land surface elevation, along the outer fringe of Swamp of the Frogs Marsh, selenium concentration is highest. Below the 50 ft contour line, within the interior of the Swamp of the Frogs Marsh, selenium concentration decreases considerably.

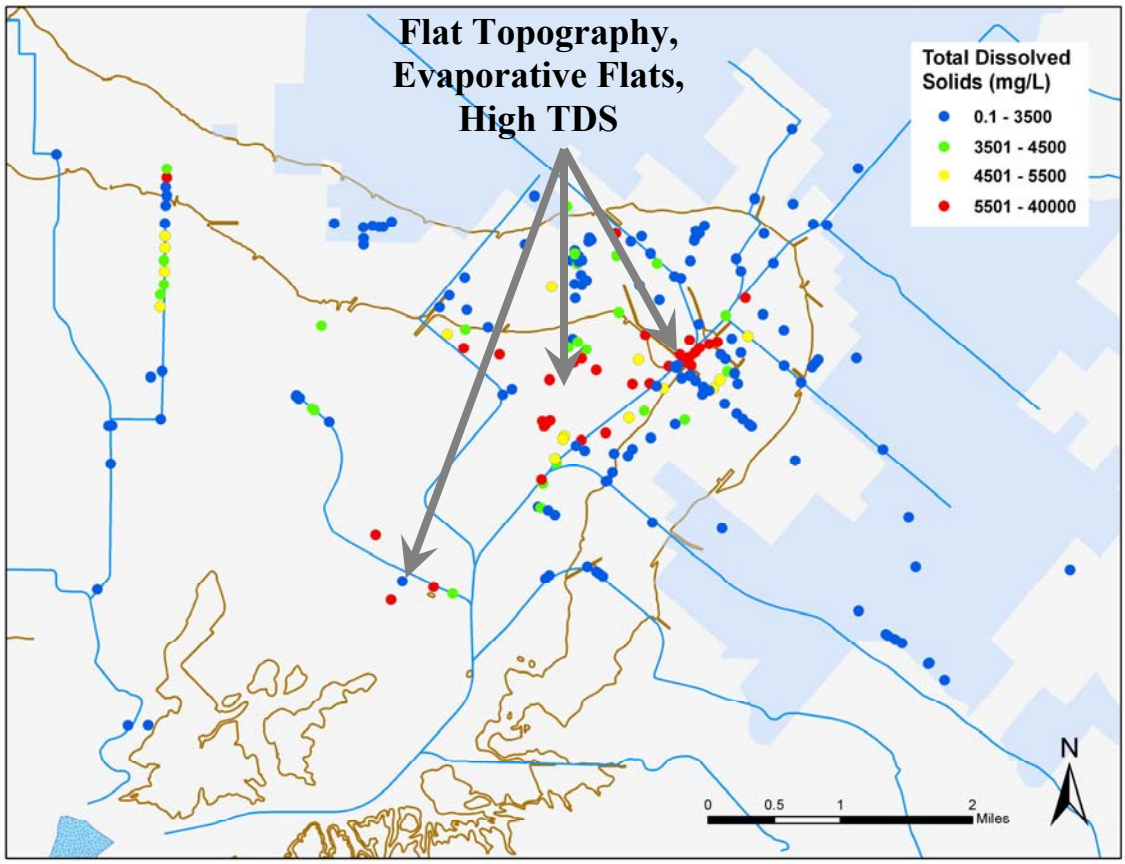


Figure 2.1.3. Total Dissolved Solids (TDS) concentration in shallow groundwater, showing relationship between the 70 ft and 50 ft land surface contours, within the Swamp of the Frogs Marsh (outer fringe of the marsh). TDS is low above the Swamp of the Frogs Marsh (above 70 ft contour line) and is highest in topographically flat areas (also see Figure 2.0.5).

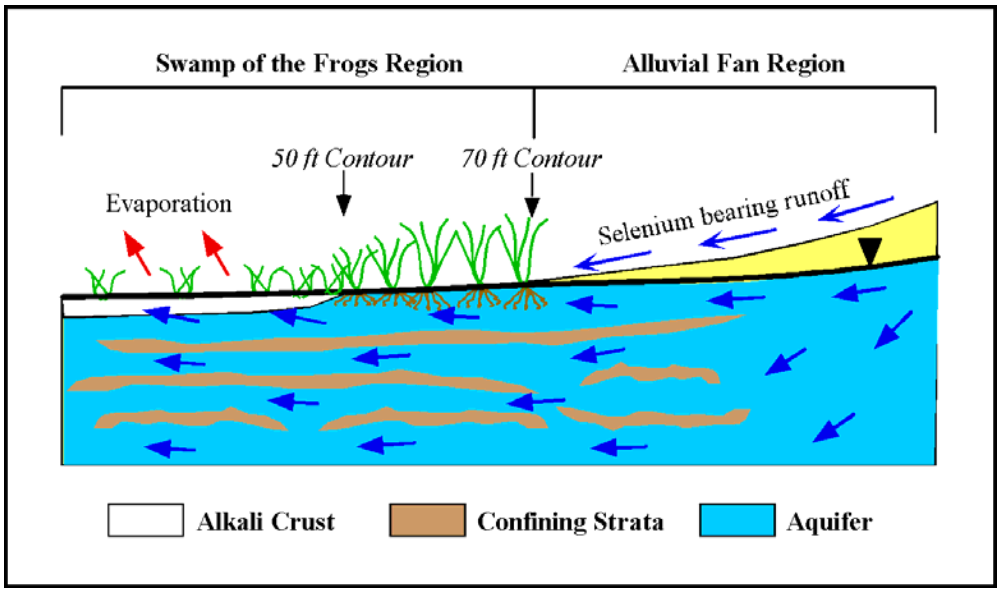


Figure 2.1.4. Conceptual model showing the alluvial fan region above the Swamp of the Frogs Marsh and two areas within the Swamp of the Frogs Marsh. Areas include the outer swamp fringe area between the 50 and 70 ft land surface contours and the alluvial/salt flats region toward the interior of the Swamp of the Frogs Marsh. Selenium accumulation was probably greatest in the outer swamp fringe where vegetation and anoxic sediments stripped dissolved selenium from groundwater and possibly from runoff waters. Further in the interior of the swamp, salts accumulated in alluvial flats due to high groundwater evaporation rates, but less selenium accumulated because it may have already been removed from waters passing through the fringe of the swamp where dense vegetation existed.

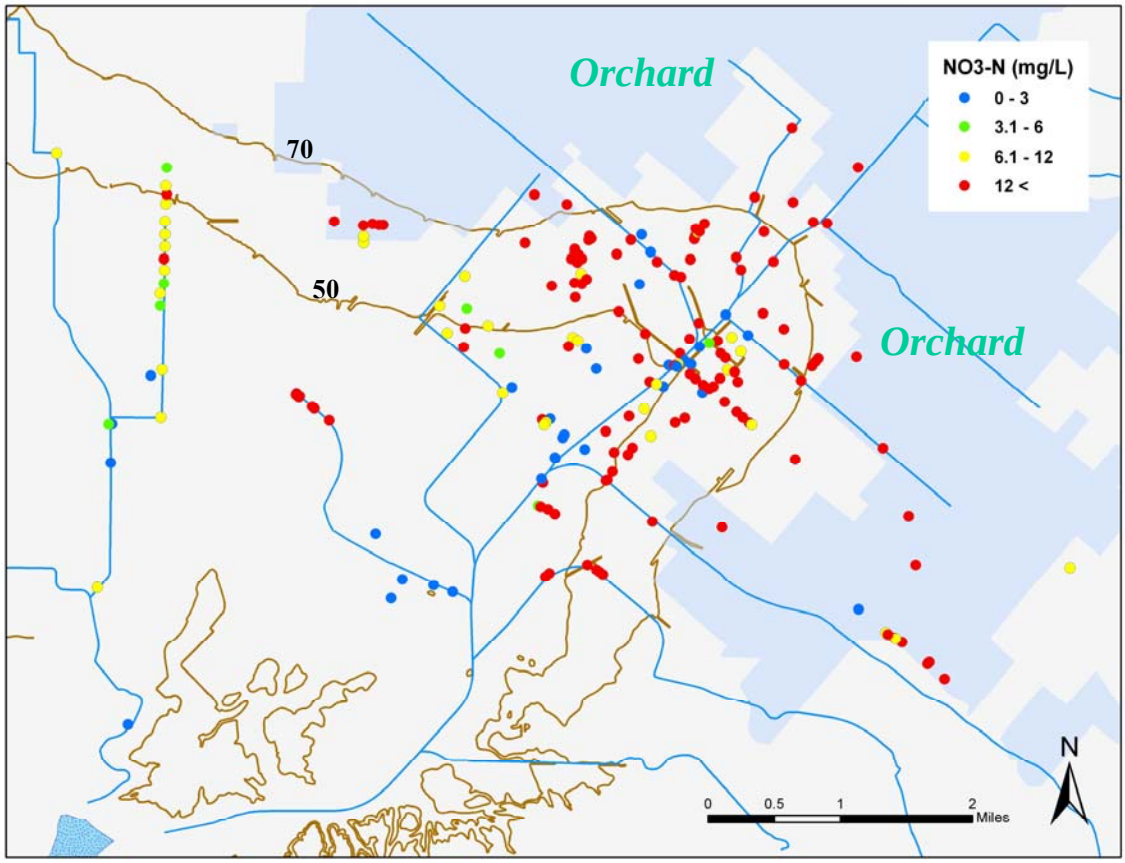
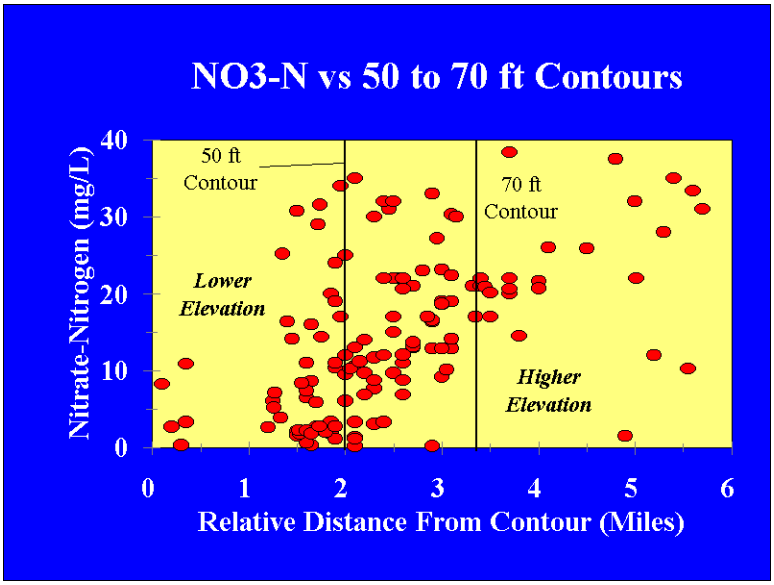
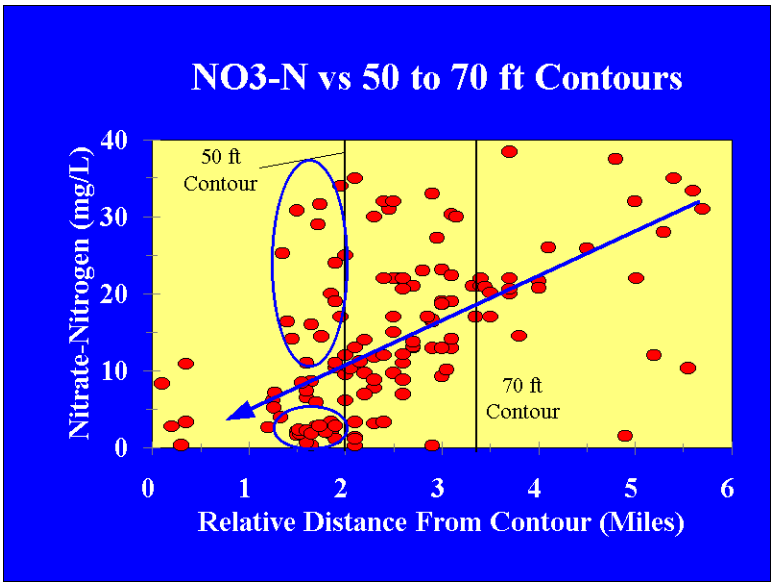


Figure 2.1.5. Nitrate-nitrogen concentration in shallow groundwater, showing relationship between the 70 ft and 50 ft land surface contours within the Swamp of the Frogs Marsh (outer fringe of the marsh). Notice also the spatial distribution of orchards, circa 1950, surrounding the outer limits of the Swamp of the Frogs Marsh, as indicated by the 70 ft topographic contour. Orchards did not flourish in areas once occupied by the Swamp of the Frogs Marsh, where soils were fine textured and poorly drained, and where water tables were shallow, even after drainage of the swamp. High nitrate concentrations in shallow groundwater (red dots, > 12 mg/L NO3-N) are found in the orchards area above the historic swamp, and in the swamp area between the 50 and 70 ft land surface contours. Nitrate moves with groundwater into the swamp fringe (Figure 2.1.8). In areas of high total dissolved solids, nitrate-nitrogen is usually low (blue dots, compare Figures 2.1.3 and 2.1.5).



A.



B.

Figure 2.1.6. Nitrate-nitrogen concentrations in shallow groundwater, showing relationship between the 70 ft and 50 ft land surface contours. Nitrate is highest in the area above the historic swamp (above 70 ft) where orchards were dense (see Figure 2.1.5). Nitrate is also high between and near the 70 and 50 ft land surface contours, within the swamp, where selenium is elevated (see Figures 2.1.1 and 2.1.2). Average nitrate diminishes below the 70 ft contour, as shown by the trend line in B. Despite much variation in nitrate near and below the 50 ft land surface contour, the overall nitrate concentration trends to a lower average concentration below the 50 ft land surface contour line. This may be due to denitrification and oxidation of organic matter, sulfur, and selenium, along with dilution recharge through unsaturated soils within the swamp region that contains limited nitrogen, due to lack of orchards within the swamp region historically.

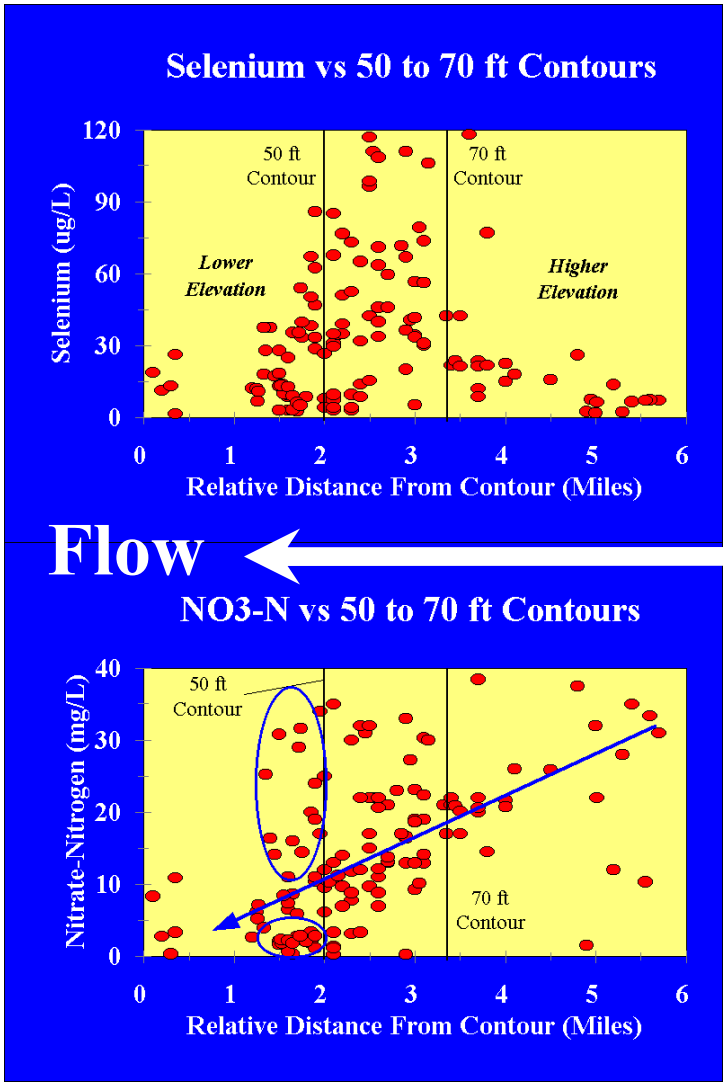


Figure 2.1.7 Side by side comparison of Figures 2.1.2 and 2.1.6, showing selenium and nitrate concentrations in relation to the 70 ft and 50 ft land surface contours. This data supports a model of leaching of nitrate into groundwater above the historic marsh (above 70 ft), where orchard density was high. Nitrate-enriched groundwater moves into the outer swamp fringe, between and near the 50 and 70 ft land surface contours. In this region, nitrate probably helps to oxidize selenium (and sulfur) and nitrate is depleted by the complementary redox process of denitrification. Below the 50 ft land surface contour, nitrate concentrations and selenium concentrations diminish.

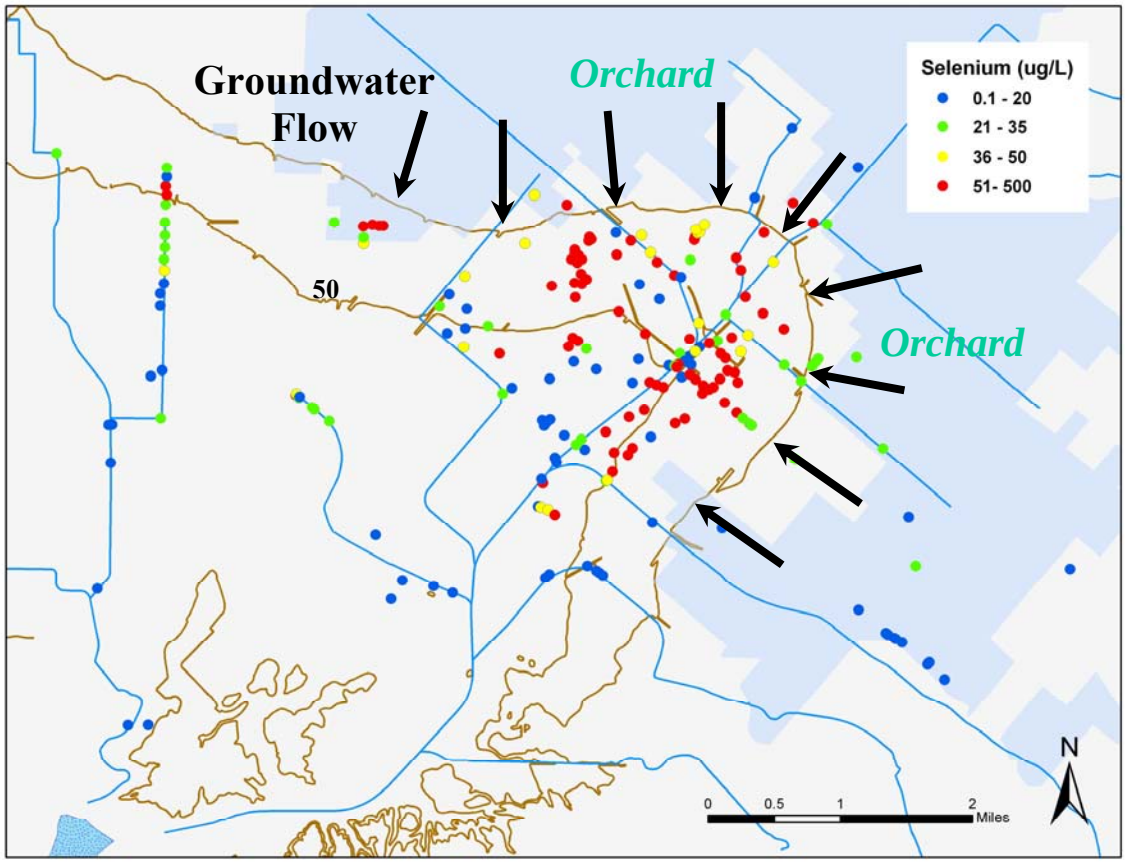


Figure 2.1.8. Groundwater presently moving into the outer fringe area of the historic Swamp of the Frogs Marsh carries large masses of dissolved nitrate into the fringe. Nitrate probably oxidizes selenium that is most concentrated in the sediments of the fringe area (within and near the 50 to 70 ft land surface contour interval, Figure 2.1.4).

2.2. EL MODENA CHANNEL STUDIES

El Modena Channel is a concrete lined channel flowing into Peters Canyon Wash below Walnut Avenue and near Harvard Park (Figures 2.2.1 and 2.2.2). One of the most important data sets that led to the hypothesis of the historic Swamp of the Frogs Marsh as the major source of selenium in San Diego Creek Watershed was provided by the El Modena Channel local groundwater data collected by Hibbs and Lee (2000) (Figure 2.2.2). Sample points included four weepholes along El Modena Channel (EMW-1weep, EMW-2weep, EMW-4weep, EMW-Wweep) and a shallow water well in the dividing area between Peters Canyon Wash and El Modena Channel (CW1-2D). These weepholes and water wells are oriented along a groundwater flowpath that moves subparallel to the direction of surface water flow in Peters Canyon Wash and El Modena Channel.

The chloride, sulfate, and selenium data from weepholes and from a water well are plotted as bar graphs (Figure 2.2.2). The graphs indicate that selenium and sulfate increase significantly between Bryan Ave and Walnut Ave. In this region, selenium increases from a low value of 20 µg/L (weephole EMW-2) to a high value of 178 µg/L (weephole EMW-W) along the groundwater flowpath. Sulfate increases simultaneously from a low value of 458 mg/L (weephole EMW-2) to a high value of 1430 mg/L (weephole EMW-W) as groundwater flowed down the hydraulic gradient. Hibbs and Lee (2000) noted that the chloride concentrations did not increase proportionately to sulfate and selenium concentrations along the hydraulic gradient. Chloride varies from a low of 189 mg/L (weephole EMW-2) to a high of 251 mg/L (weephole WEMW-weep) in the other wells and weepholes.

Hibbs and Lee (2000) speculated that groundwater evaporation alone could not explain selenium enrichment in groundwater, otherwise, the chloride (the most conservative of the three ions) in groundwater would become similarly enriched. Chloride concentrations are fairly constant in most water wells and weepholes. Therefore, evaporation could not be the primary agent enriching sulfate and selenium along the groundwater flowpath. This led them to develop the hypothesis of selenium remobilization from reduced forms in the Swamp of the Frogs Marsh region. Hibbs and Lee (2000) discuss a geologic source of selenium and sulfate in shallow groundwater:

> *"During the historic period of the Swamp of the Frogs Marsh, any forms of selenium and sulfur that flowed into the marsh were probably derived from surface runoff from the highlands in the oxidized forms (SeO_4^{2-} and SO_4^{2-}). Once the oxidized forms of selenium and sulfur reached the anoxic waters of the marsh, these oxidized species were probably reduced to SeO_3^{2-}, elemental Se(0), Se^{2-}, H_2S, and HS^-. These forms would be expected to be removed from the waters in the marsh and sorbed onto solid particles, precipitated as crystalline and amorphous polymorphs, or transformed into volatile gases.*
>
> *Once immobilized in solid forms, the selenium and sulfur solids would tend to remain stable in the soil substrate as new sediments and organic matter in the marsh continued to accumulate. Cores extracted from old marsh sediments reveal sedimentary facies consistent with anoxic environments, including thick sequences of olive-gray clay, dark gray to dark brown silt and silty clay, and sandy clay and clayey sand that is usually medium to dark brown. Some of the core logs show traces of carbonized fragments indicative of decaying plant material.*
>
> *When the Swamp of the Frogs Marsh was drained in the late 1800's and early 1900's, the shallow subsurface was transformed into an oxic environment. In fact, the shallow groundwater flow system today is being recharged by oxygen-enriched water that retains some dissolved oxygen as it flows through the old marsh deposits. The groundwater data collected during this study, along with other groundwater data (Silverado, 1997) indicate that groundwater contains relatively high*

concentrations of dissolved oxygen (usually 0.3 to 5 mg/L), very high ratios of dissolved nitrate to nitrite, and the general absence of iron and manganese. These hydrochemical signatures indicate a highly oxic groundwater flow system.

Oxidizing groundwaters flowing through the old marsh sediments today remobilizes the bound forms of selenium and sulfur into their oxidized and mobile forms (SeO_4^{2-} and SO_4^{2-}). Thus, we can account for high sulfate and selenium in groundwaters in large part from remobilization of reduced forms of selenium and sulfur as oxic waters flow through the historic marsh sediments."

In late 2002, the weepholes in El Modena Channel dried up and didn't start flowing again until heavy sustained rains in February 2005. Rising water tables and reactivation of weepholes in El Modena Channel provided the prop 13 research group with an opportunity to sample weepholes for sulfate isotopes. Sulfate isotopes can help determine sources of sulfur in groundwater. Positive sulfate isotope $\delta^{34}S[SO_4^{2-}]$ values in local groundwaters may indicate multiple sulfate sources and mixtures, including fertilizers, organic matter, marine salts, and atmospheric deposition (Clark and Fritz, 1997). Negative sulfur isotope values are consistent with oxidation of Fe-sulfides and dissolution of second-cycle terrestrial evaporitic salts that may have been derived originally from oxidation of metal sulfides (e.g., Thernardite or Mirabolite salts). This mechanism of sulfate and selenium remobilization from reduced forms (metallic sulfides and metallic selenides) was first postulated by Hibbs and Lee (2000). The lighter $\delta^{34}S[SO_4^{2-}]$ signature often develops as a result of the lower energy required by bacteria to break ^{32}S – Fe bonds, resulting in a negative sulfur isotope signature (Clark and Fritz, 1997). Sulfur and selenium species behave very much alike in groundwater

and marshes, so the sulfur isotope data is proxy information for selenium immobilization and remobilization.

Results of Subsequent Studies in El Modena Channel

As predicted by the Hibbs and Lee model (2000), sulfur isotopes become increasingly negative along the groundwater flowpath that was resampled by the prop 13 team in El Modena Channel (Figure 2.2.3). Once groundwater enters the historic marsh region, the sulfate isotope signatures decrease from -0.6 to -15.9 $\delta^{34}S[SO_4^{2-}]$ (Figure 2.2.3). This is a very significant change in the sulfur isotope signature that points to a local geologic source of sulfate, and by association, a geologic source of selenium. In light of the observations provided by sulfate isotopes, El Modena Channel was studied extensively with a variety of hydrochemical parameters to examine the possibility of selenium and sulfur oxidation. Four weephole samples were collected along a flowpath during two sample intervals, in 2005 and 2006. These data are compared to the 1999 data from Hibbs and Lee (2000) (Figures 2.2.2 and 2.2.4; Table 2.2.1). Additional steps included collection of nitrogen isotopes in 2006, collection of stable isotopes of oxygen and hydrogen in 2005 and 2006, and recollection of sulfate isotopes collected in 2006 (Table 2.2.2).

Sample points reported by Hibbs and Lee (2000) included four weepholes along El Modena Channel (EMW-1weep, EMW-2weep, EMW-4weep, EMW-Wweep) (Figure 2.2.2). Sample points collected in 2005 and 2006 included all of the above except EMW-1weep, which hasn't flowed since 1999, plus a new

weephole (EMW-5weep). These weepholes are oriented along the groundwater flowpath that moves subparallel to the direction of surface water flow in Peters Canyon Wash and El Modena Channel (Figure 2.2.4).

The chloride, sulfate, and selenium data from each weephole are presented in Table 2.2.1. The data indicate that selenium and sulfate increase significantly between Interstate-5 and Walnut Ave, whereas chloride doesn't increase substantially during any year. Nitrate and selenium concentrations seem to have decreased from 1999 to 2006. Sulfate concentrations increase consistently along the flowpath during all years, whereas nitrate and selenium concentrations vary along the flowpath, despite overall enrichment downgradient of EMW-2weep.

As mentioned earlier, Hibbs and Lee (2000) speculated that groundwater evaporation alone could not explain selenium and sulfate enrichment in groundwater, otherwise the chloride (the most conservative ion) in groundwater would become enriched along the flowpath. Chloride concentrations are fairly constant in most water wells and weepholes (Table 2.2.1). Therefore, evaporation cannot be the primary process that enriches sulfate and selenium along the flowpath. Stable isotopes of oxygen and hydrogen collected in 2005 and 2006 also point to lack of enrichment of ions from evaporation, because stable isotopes plot in the same general cluster (Table 2.2.2 and Figure 2.2.5). This cluster effect in samples with strong contrasts in salinity indicates that there is little systematic evaporation of groundwater moving downgradient from Interstate-5 (Figure 2.2.5).

Sulfur isotopes collected in 2006 show trends of isotopic depletion down the hydraulic gradient (i.e., more negative values) just as they did in 2005 (Table 2.2.2).

In 2005 and 2006 data sets, sulfur isotopes became increasingly negative along the groundwater flowpath. Once groundwater enters the historic marsh region, the sulfate isotope signatures decreased by more than 15 per mil in 2005 (from -0.6 to -15.9 per mil $\delta^{34}S[SO_4^{2-}]$) and by more than 17 per mil in 2006 (from 0.1 to -17.2 per mil $\delta^{34}S[SO_4^{2-}]$) (Table 2.2.2).

Based on research by the US Geological Survey (Wright, 1999), the prop 13 team believes that nitrate may be an oxidant for bound and reduced forms of selenium and sulfur in soils formed within the historic Swamp of the Frogs Marsh. This was discussed in Section 2.1. Other details are provided here. The team decided to test that hypothesis by collecting samples for nitrogen isotope analysis. Nitrogen isotopes can be powerful tools for determining sources of nitrate contamination (e.g., septic tanks, feedlots, fertilizers, Figure 2.2.6). Nitrogen isotopes can also be very useful for determining denitrification by oxidation of metal sulfides. The reaction shown in equation 2.1.1, Section 2.1 applies.

When nitrate undergoes this oxidation-reduction reaction, the residual nitrate becomes isotopically heavier with respect to both the $\delta^{15}N[NO_3]$ (the nitrogen in the nitrate) and the $\delta^{18}O[NO_3]$ (the oxygen in the nitrate). A shift of isotopically heavier values results from this progressive denitrification along a flowpath (Figure 2.2.6). Along this trend, the oxygen and nitrogen in the residual (non-reduced) nitrate become progressively more positive. The reaction (equation 2.1.1, Section 2.1) is dependent on several factors, including the presence of nitrogen reducing bacteria, a sufficient quantity of oxidizable sulfur, and appropriate redox conditions along the flowpath (Fritz and Clark, 1997). The result

is a isotopically heavier (more positive) residual nitrate and an isotopically lighter (more negative) oxidized sulfate.

These trends are quite obviously observed along El Modena channel, where nitrate becomes isotopically heavier while sulfur becomes isotopically lighter (Figure 2.2.7). The isotope data fit the reactions shown in equation 2.1.1 and provide robust evidence for oxidation of metal sulfides by nitrate. The data also points to mineralized nitrogen fertilizer as the source of nitrate in shallow groundwater, at least along El Modena Channel. We propose that the same mechanism also applies to selenium oxidation. The groundwater data indicate that selenium is already in the oxidized form in El Modena Channel area (Table 2.2.3). El Modena Channel groundwater samples consist mainly of selenium-VI with little selenium-IV and no detectable organic selenium.

In a closed system, the reaction shown in equation 2.2.1 would exhaust the available supply of nitrate as sulfate was simultaneously oxidized. The fact that nitrate is not exhausted along the flowpath (Table 2.2.1) must mean that nitrate is being added continuously to the flow system, even as sulfur is being oxidized and released from sediments. A possible explanation for this "open system model" is by continuous addition of nitrate from the vadose zone along the flowpath (Figure 2.2.8). In this proposed model, the nitrate in the vadose zone percolates into groundwater and mixes with isotopically heavier (partially denitrified) nitrate in groundwater that has moved down the hydraulic gradient.

A caveat to this model is that we have indicated that nitrogen fertilizer was not applied in great quantities historically within the boundaries of the Swamp of

the Frogs Marsh. This is particularly true within the Tustin Marine Corps Air Station (though some crops were eventually raised within the base boundaries). However, El Modena Channel groundwater appears to occupy a unique flowpath system, in that a few orchards and several row crops were grown very close to El Modena Channel (USGS topographic maps, 1960s). Nitrogen fertilizer was probably applied heavily in the vicinity of El Modena Channel.

In another possible model, the incomplete reduction of nitrate, oxidation of sulfur, and (probable) oxidation of selenium all occurs in the vadose zone. In this second case, vadose zone recharge waters carry heavier nitrate and lighter sulfate (and probably) lighter selenium into groundwater within the interior of the Swamp of the Frogs Marsh area. We also observe positive correlation between nitrate and selenium in these data sets (Figure 2.2.9).

In conclusion, the El Modena Channel studies provide robust evidence of oxidation of sulfur and selenium by nitrate. This is the area of perennially wetted soils in predevelopment times (Meixner and others, 2004). We do not yet know if the selenium that was sequestered in the Swamp of the Frogs Marsh was reduced primarily to its intermediate oxidation states (i.e., selenite-IV), or if it speciated to lower oxidation states, such as elemental selenium (0) and selenide (-II). We do know that nitrate is an oxidant of metal sulfides along the El Modena Channel flowpath, and nitrate is probably equally important in oxidizing one of the reduced forms of selenium in soils near El Modena Channel. This proposed model depends upon bound selenium being oxidized by nitrate in a manner analogous to sulfur oxidation. Selenium isotopes should be analyzed to test this hypothesis.

Table 2.2.1: Selenium, Nitrate, Sulfate, and Chloride Data for El Modena Channel Groundwater Flows, 1999, 2005, 2006

Sample ID	Selenium (ug/L)	Total Nitrate (mg/L)	Sulfate (mg/L)	Chloride (mg/L)
May 1999 (Hibbs and Lee, 2000)				
Weephole EMW-1	23	96	477	194
Weephole EMW-2	20	86	458	189
Weephole EMW-4	96	184	929	212
Weephole EMW-5	--	--	--	--
Weephole EMW-W	178	198	1430	251
March 2005 (prop 13)				
Weephole EMW-1	--	--	--	--
Weephole EMW-2	10	55	371	168
Weephole EMW-4	176	126	573	148
Weephole EMW-5	63	123	1019	181
Weephole EMW-W	82	65	1346	177
February 2006 (prop 13)				
Weephole EMW-1	--	--	--	--
Weephole EMW-2	12	87	409	195
Weephole EMW-4	80	127	665	187
Weephole EMW-5	53	117	1144	196
Weephole EMW-W	77	73	1527	197

Table 2.2.2: Sulfur, Oxygen, and Deuterium Isotope Data for El Modena Channel Groundwater Flows, 2005 and 2006

Sample ID	Sulfur Isotope (del 34S, per mil)	Oxygen Isotope (del 18O, per mil)	Deuterium Isotope (del 2H, per mil)
March 2005 (prop 13)			
Weephole EMW-1	--	--	--
Weephole EMW-2	-0.6	-6.6	-49
Weephole EMW-4	-4.8	-6.9	-48
Weephole EMW-5	-15.9	-6.4	-47
Weephole EMW-W	-12.3	-6.7	-48
February 2006 (prop 13)			
Weephole EMW-1	--	--	--
Weephole EMW-2	0.1	-6.8	-51
Weephole EMW-4	-3.2	-7.6	-48
Weephole EMW-5	-17.2	-6.6	-48
Weephole EMW-W	-12.7	-6.8	-47

Table 2.2.3: Selenium Speciation Data for El Modena Channel Groundwater Flows, 2006

Sample ID	Se VI (ug/L)	Se IV (ug/L)	Organic Se (ug/L)	Total Dissolved Se (ug/L)
February 2006 (prop 13)				
Weephole EMW-1	--	--	--	--
Weephole EMW-2	11.2	0.8	<0.2	12.0
Weephole EMW-4	79.3	0.8	<0.2	80.1
Weephole EMW-5	51.4	1.3	<0.2	52.7
Weephole EMW-W	75.5	1.3	<0.2	76.8

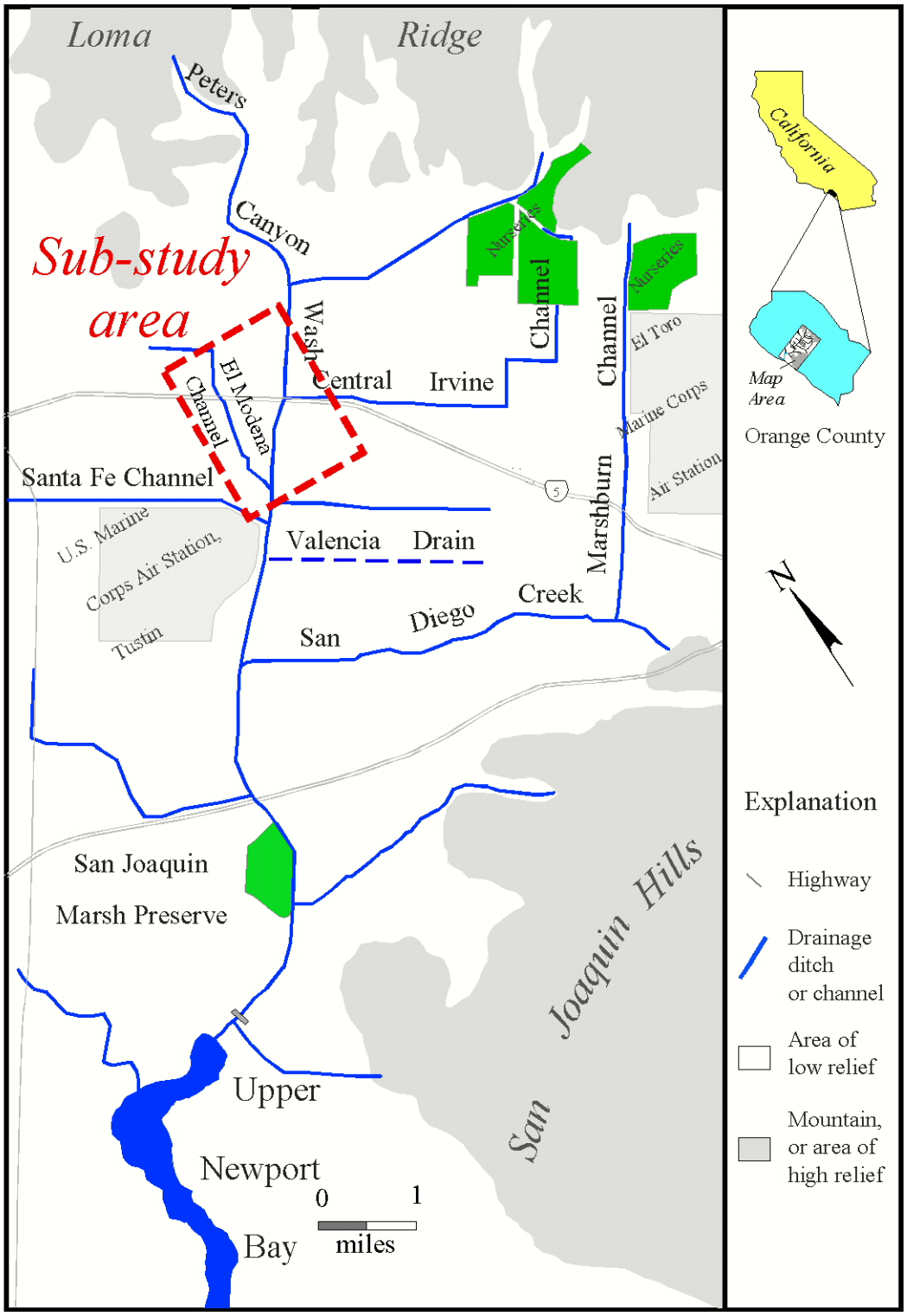


Figure 2.2.1. Location of El Modena Channel sub-study area.

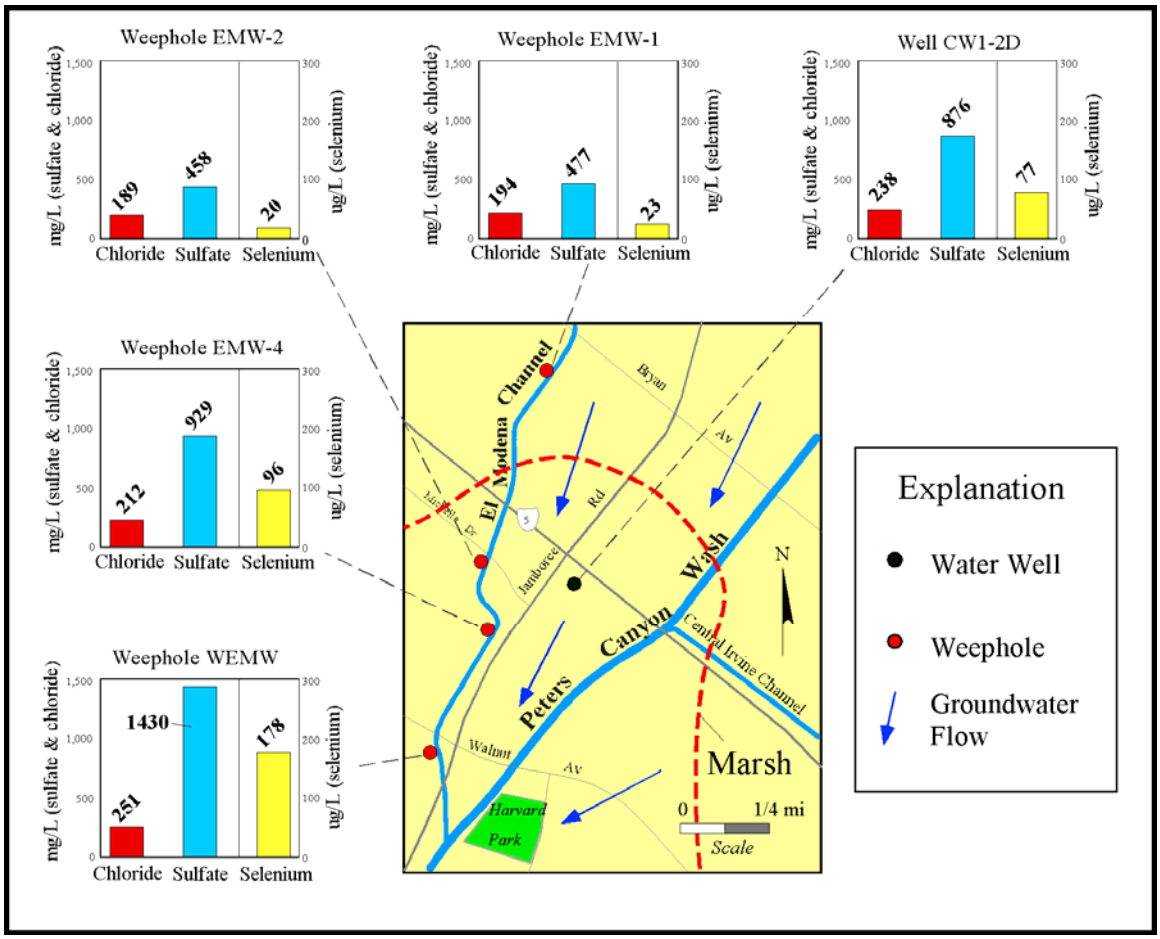


Figure 2.2.2. Bar graphs showing chloride, sulfate, and selenium concentrations in water wells and weepholes in El Modena Channel area (from Hibbs and Lee, 2000). The diagram indicates that sulfate and selenium concentrations increase continuously along the hydraulic gradient, but chloride does not increase significantly in wells and weepholes. These data suggested to Hibbs and Lee (2000) that selenium enrichment did not result from evaporation alone, but that there was a likely geological source associated with the historic Swamp of the Frogs Marsh.

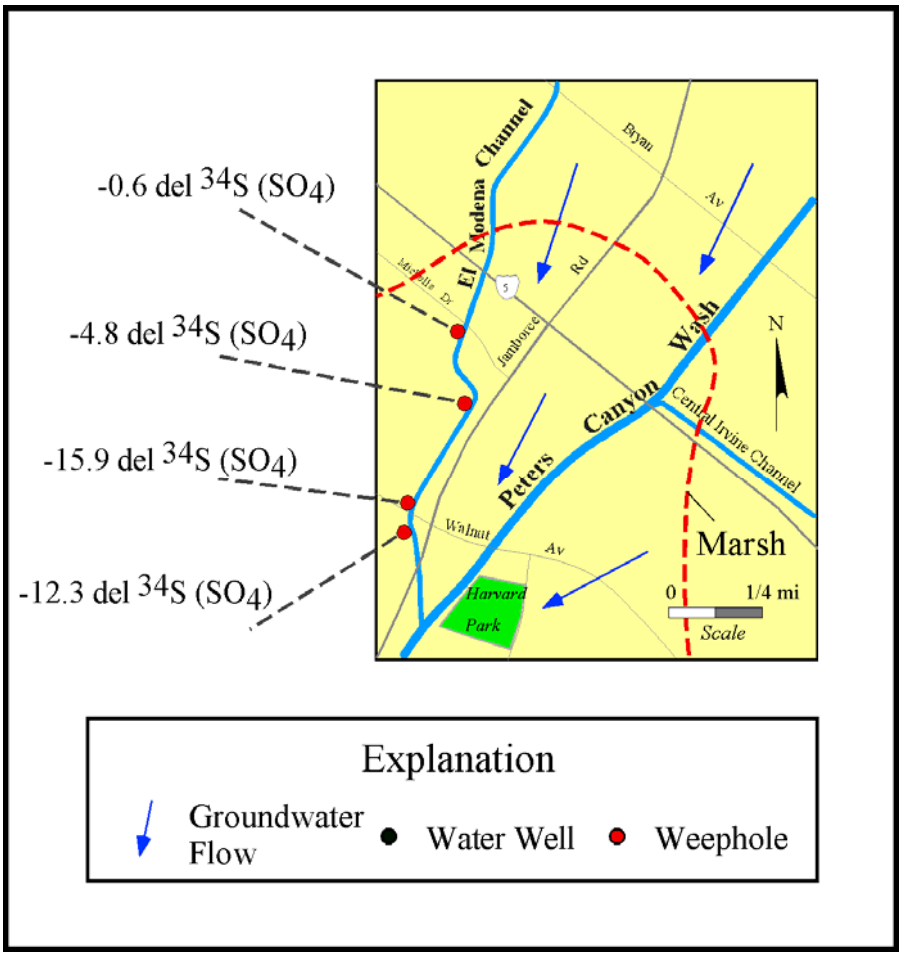


Figure 2.2.3. Sulfur isotope data for local groundwater samples collected in El Modena Channel, 2005. Once groundwater enters the historic marsh region (red dashed line), the sulfate isotope signatures decrease from -0.6 to -15.9 $\delta^{34}S[SO_4^{2-}]$. This is a very significant change in the sulfur isotope signature that points to a local geologic source of sulfate, and by association, a geologic source of selenium.

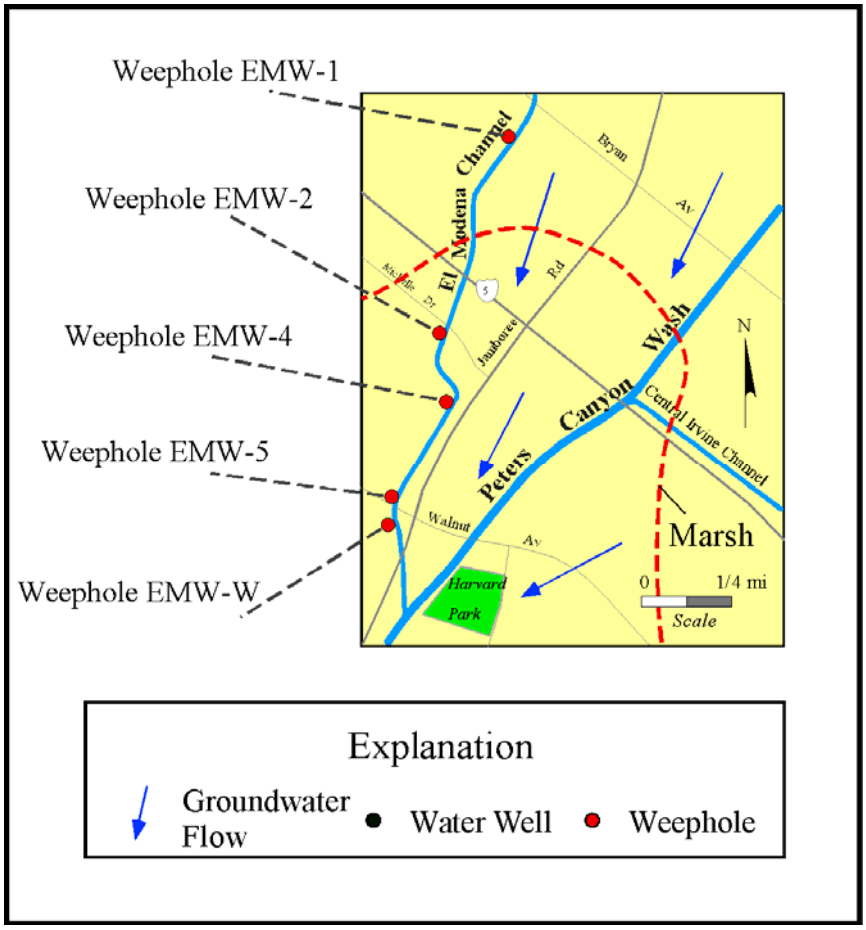


Figure 2.2.4. El Modena Channel groundwater sampling locations, 1999, 2005 and 2006.

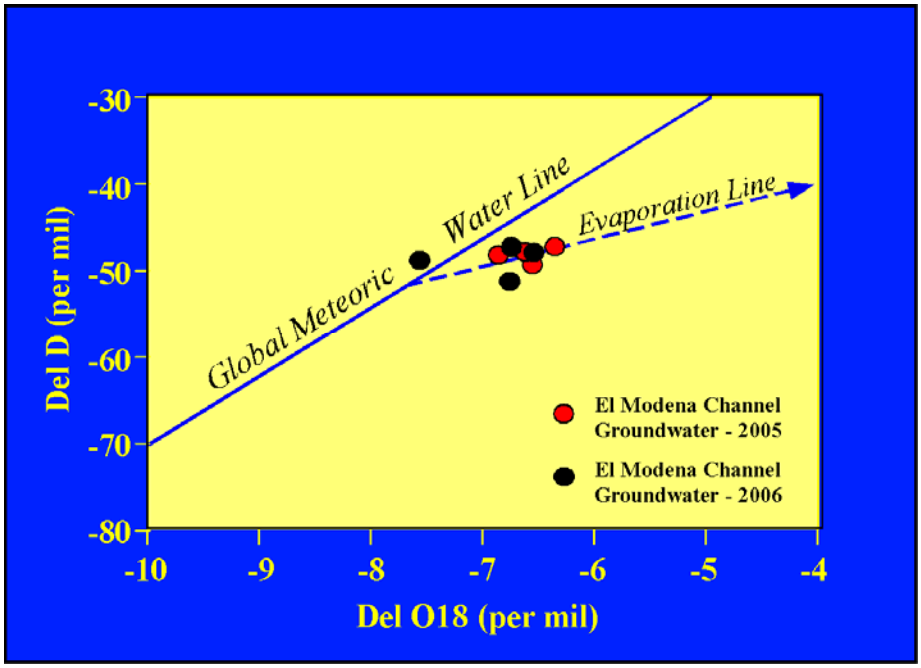


Figure 2.2.5. Oxygen and hydrogen isotope data for local groundwater samples collected in El Modena Channel, 2005 and 2006. The cluster of samples indicates that groundwaters are isotopically similar. Though all except one sample plot along the shallow aquifer evaporation line, most of the waters cluster at the same location on the evaporation line. This indicates little or no evaporative enrichment of groundwaters along a flowpath, where groundwaters are observed to evolve to higher salinities. A geologic dissolution source of sulfate (and selenium) is indicated instead of simple evaporative concentration of groundwater.

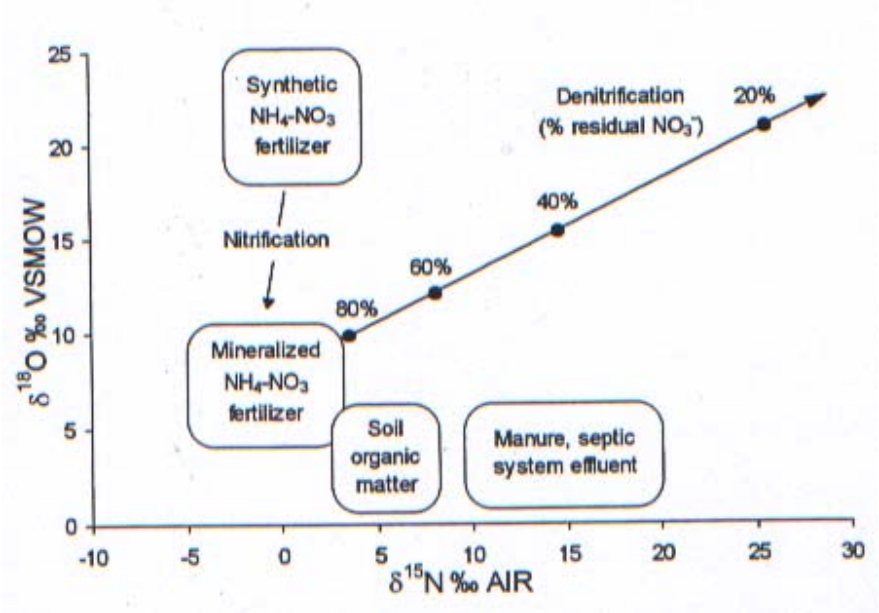


Figure 2.2.6. The isotopic composition of various sources of nitrate. The enrichment trend for nitrate during denitrification is shown with % of original concentration remaining (from Clark and Fritz, 1997).

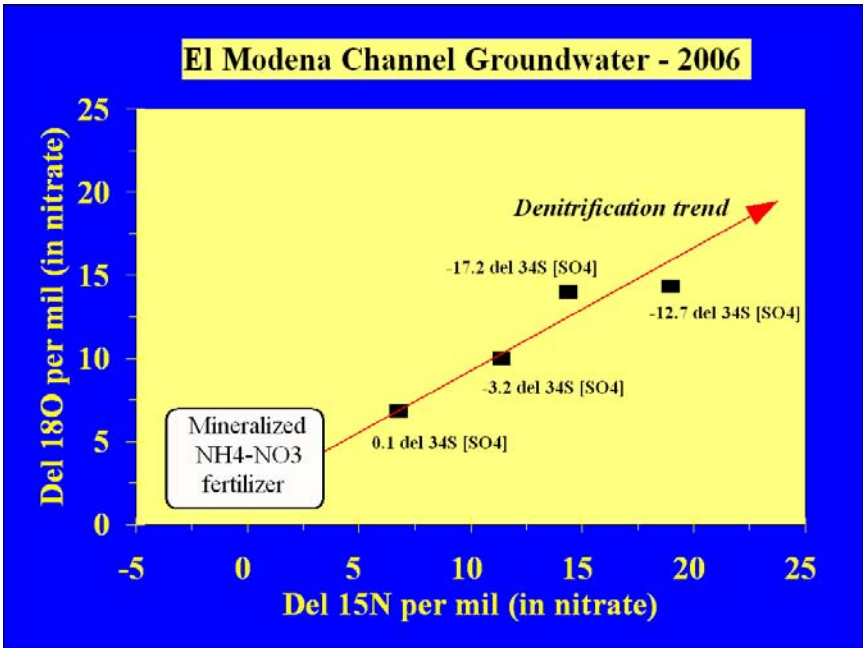


Figure 2.2.7. The isotopic composition of nitrate in El Modena Channel Groundwater. The denitrification trend shown in El Modena Channel groundwater, along with the increasingly negative isotopic signature of sulfate in samples, strongly suggests that metal sulfides are oxidized by nitrate along the El Modena Channel groundwater flowpath (equation 2.1.1, Section 2.1).

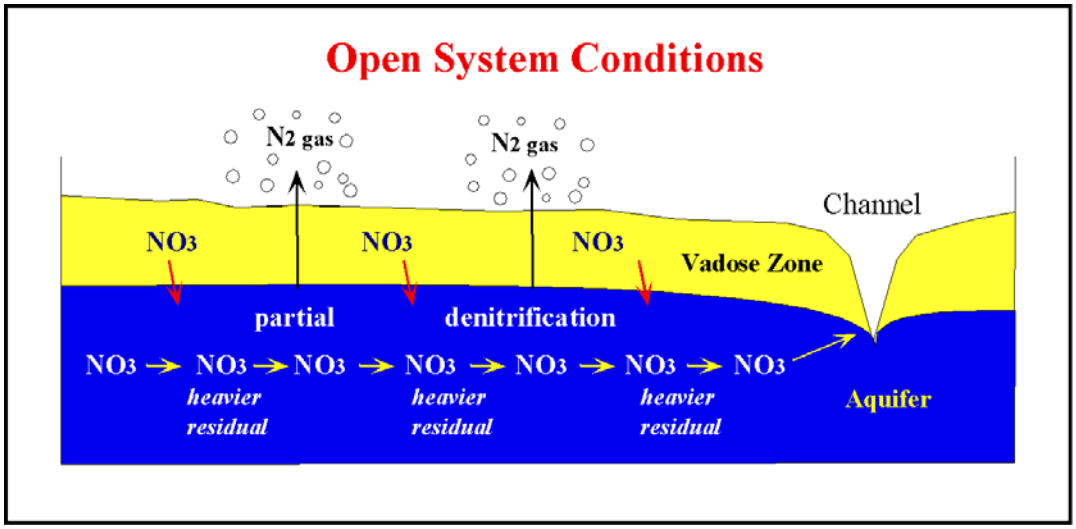


Figure 2.2.8. In a closed system, the reaction shown in equation 2.1.1 would exhaust the available supply of nitrate as sulfate was simultaneously oxidized. The fact that nitrate is not exhausted along the El Modena Channel flowpath (Table 2.2.1) must mean that nitrate is being added continuously to the flow system, even as sulfur is being oxidized and released from sediments. A possible explanation for this "open system model" is by continuous addition of nitrate from the vadose zone along the flowpath. In this model, the nitrate in the vadose zone percolates into groundwater and mixes with isotopically heavier (partially denitrified) nitrate in groundwater that has moved down the hydraulic gradient.

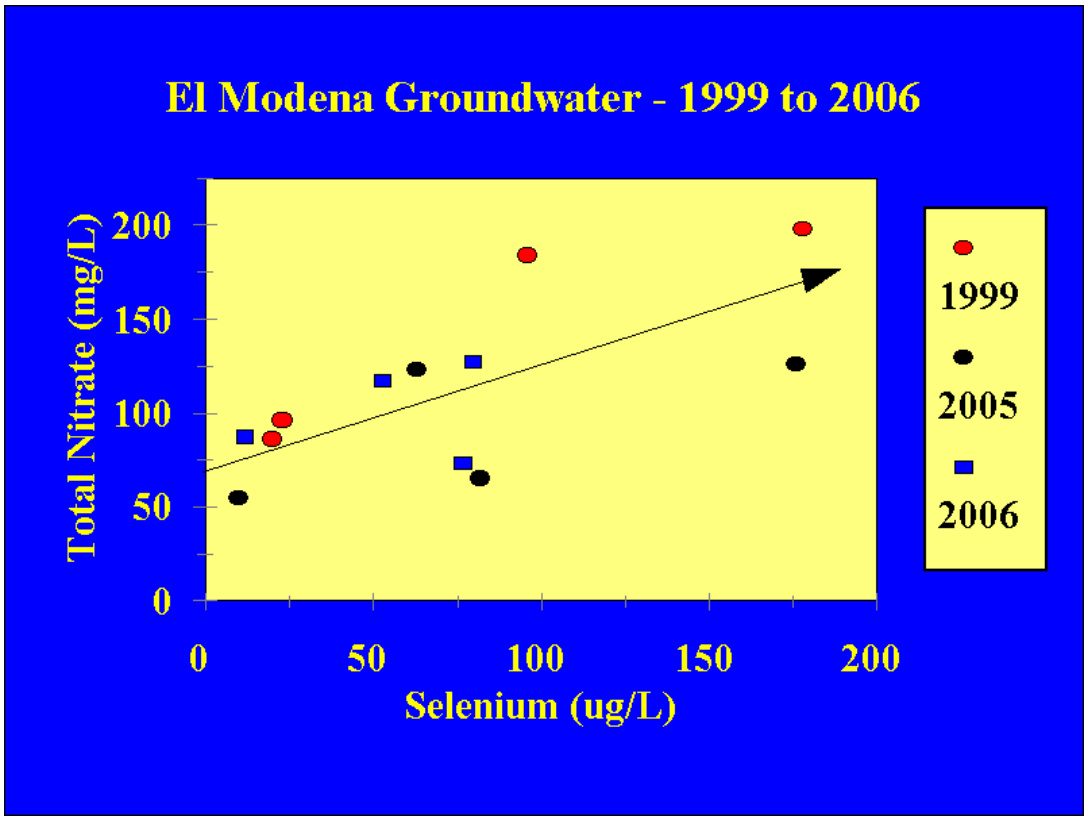


Figure 2.2.9. Positive correlation between nitrate and selenium in El Modena Channel area groundwater.

2.3. SANTA ANA DELHI CHANNEL STUDIES

Previous investigations by Hibbs and Lee (2000) and Meixner and others (2004) did not include detailed investigations of Santa Ana Delhi Channel, and vicinity (Figure 2.3.1). It is important to determine the relationship between surface water and groundwater in this part of the watershed to determine concentrations of selenium and other hydrochemical parameters. Therefore, the research group investigated Santa Ana Delhi Channel in January 2004 and March 2005. The purpose of this sub-study was to determine if groundwater baseflow conditions dominated in certain areas, and to determine the extent to which loading of selenium and other constituents occurred as a result of groundwater seepage. Surface and groundwater samples from the Santa Ana Delhi Channel area were therefore collected and analyzed for index parameters, general minerals, selenium, select trace elements, and nitrate.

Our investigations discovered a number of groundwater flows (weepholes and flowing seams) along several portions of Santa Ana Delhi Channel (Figures 2.3.1 and 2.3.2). Conductivity measurements and analysis of general minerals indicated that these flows were definitively groundwater. The analysis indicates that Santa Ana Delhi Channel has a strong baseflow component. Groundwater contained moderate to small amounts of selenium and very small amounts of arsenic relative to concentrations observed in other parts of the watershed (Figure 2.3.1). With respect to surface flows, selenium is highest in Santa Ana Delhi Channel above the confluence with Santa Ana Gardens Channel (13.4 ug/L Se) and is lowest in Santa Ana Gardens Channel (7.1 ug/L Se) (Figure 2.3.1).

The reason for low selenium concentrations in Santa Ana Gardens Channel and its weepholes is shown by inspection of the USDA salinity map (Figures 2.0.2 and 2.0.3). The 1900 USDA alkali map of the Santa Ana-Irvine-Tustin area shows a distinctive alkali pattern, mimicking the spatial limits of the historic Swamp of the Frogs Marsh (Figure 2.0.2). Heaviest alkali concentrations correspond to areas of shallow groundwater, where water evaporated in predevelopment times to produce sodium-sulfate salts at land surface. A depth to groundwater map prepared by Sprotte and others (1980) (Figure 2.0.3) shows a remarkable correlation between shallowest groundwater depth and heavy alkali concentrations in the watershed. Our investigations show areas of high groundwater salinity concentrations match up reasonably well with the 1900 alkali map. High selenium concentrations in shallow groundwater also correspond to patterns of alkali concentration in the watershed.

The regions in the 1900 alkali map with orange pattern had the lowest alkali concentrations in 1900 (Figure 2.0.2). Today, these areas have the lowest selenium concentrations in groundwater in San Diego Creek Watershed. Areas near the Tustin Marine Corps Air Station and near Harvard Ave and Irvine Center Drive (Figure 2.0.3) contained moderate alkali concentrations in the 1900 map (green patterns). These same regions of moderate alkali have the highest selenium concentrations in groundwater today (frequently 50 to 350 ug/L selenium) (Bechtel basewide groundwater geochemistry data, 1996 to 2000; Hibbs and Lee, 2000; Meixner and others, 2004).

It appears from the alkali map that the areas of highest selenium contained moderate alkali concentrations at the outer edges of the historic Swamp of the Frogs

Marsh. Along the margins of the marsh, prolific vegetation and wetland plant growth may have hastened selenium removal from the water column in a perennially wetted environment (see Section 2.1). Within the interior of the marsh, where alkali and salinity concentrations were higher, much of the selenium may have already been removed from percolating surface water and groundwater before it reached the interior regions on the map where alkali concentrations were higher (Figure 2.0.3). It is also likely that the interior, saline regions of the marsh supported less prolific varieties of vegetation that did not sequester the larger amounts of selenium seen along the margins of the marsh. The boundaries of the high alkali areas in the USDA map mark the limits of the historic Swamp of the Frogs Marsh. By comparison, the location of the groundwater data obtained from Santa Ana Gardens Channel do not overlap with the region once occupied by the historic swamp (compare Figures 2.3.1 and 2.0.3 spatially, just left of center of Figure 2.0.3). Typically, little selenium is found in groundwater outside of the limits of the Swamp of the Frogs Marsh.

One data point shown in Figure 2.3.1 is located within the historic swamp boundaries. This sample was collected from a weephole in Santa Ana Delhi Channel. It contained 27 ug/L selenium, a concentration that is much higher than in groundwater collected in Santa Ana Gardens Channel. This shows again how important are the boundaries of the Swamp of the Frogs Marsh on controlling selenium concentrations in local groundwater.

The portion of Santa Ana Delhi Channel upstream of this data point (27 ug/L) flows entirely within the boundaries of the historic Swamp of the Frogs

Marsh (Figure 2.3.1). Therefore, the research team investigated this channel more intensively in March 2005. This was done to test apriori predictions of high selenium concentrations in the upper part of Santa Ana Delhi Channel. Data collected from Santa Ana Delhi Channel show mostly moderate to moderately high concentrations of selenium in groundwater (25 to 55 ug/L Se; Figure 2.3.2). A few samples are well below 25 ug/L Se however. One groundwater sample contained only 1.2 ug/L Se. This sample also contained a non-detect concentration of nitrate (<0.5 mg/L NO3-N) and a very high salinity value (9260 uS/cm) (Figures 2.3.3 and 2.3.4). Other analysis by the research team showed that highly saline ground waters (> 10,000 uS/cm) seldom contain high concentrations of selenium (<15 ug/L Se), even within the historic Swamp of the Frogs Marsh region (see Section 2.8. Lane Channel Studies and Section 2.9. Barranca Underground Circular Drain Studies). Nitrate may be a correlative to elevated selenium in groundwater relative to salinity.

As mentioned in Section 2.2. El Modena Channel Studies, nitrate and dissolved oxygen are known to oxidize reduced forms of selenium (Wright, 1999). Thermodynamic relations for selenium oxidation indicate that elemental selenium and selenite can be oxidized to selenate (Se-VI) by nitrate. Theoretical energies for these oxidation reactions nearly equal the energy available for oxidation of selenium by oxygen (Wright, 1999).

A covariate visual relationship is shown for selenium, nitrate, and salinity in groundwaters from Santa Ana Delhi Channel (Figures 2.3.5, 2.3.6, and 2.3.7). Despite wide scatter, there is a clear positive correlation (visual) shown between

selenium and nitrate concentrations, and a negative correlation between nitrate/specific conductance and selenium/specific conductance.

A possible set of hypotheses for the correlative relationships between selenium, nitrate, and salinity (specific conductance) are as follows:

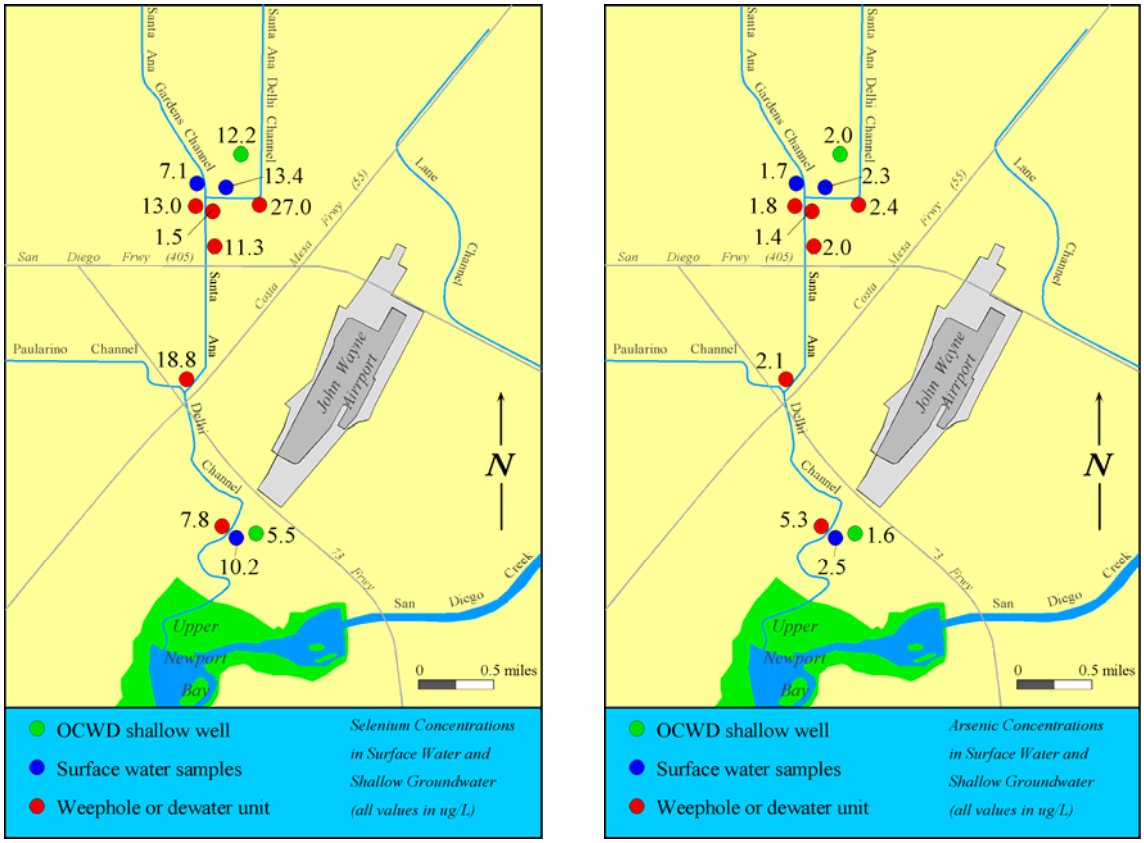
- Oxidation of selenium by nitrate produces a positive correlation between high nitrate and high selenium. The higher the nitrate concentration, the higher the selenium concentration. Though nitrate is consumed in the oxidation/reduction process, nitrate does not diminish substantially in Santa Ana Delhi Channel due to the stoichiometric relationships between ppb (ug/L) concentrations of selenium, and ppm (mg/L) concentrations of nitrate. This results in a positive correlation between selenium and nitrate (Figure 2.3.5).

- Nitrate also oxidizes sulfide to produce sulfate in El Modena Channel area groundwater (see Section 2.2), and nitrate is added as an open system model faster than it is consumed by denitrification. We don't know if nitrate oxidizes sulfide in Santa Ana Delhi Channel area groundwater. Selenium in soils may be mostly in intermediate oxidation states (i.e., selenite-IV), or may exist in lower oxidation states, such as elemental selenium (0) or selenide (-II). If selenium exists in lower oxidation states in soils and aquifer matrix near Santa Ana Delhi Channel, then sulfide is probably oxidized from these soils as well.

- Groundwaters with highest salinity in the local areas near Santa Ana Delhi Channel are sourced from lower permeability alkali soils (clays, clayey silts). Fine textured soils were not leached as effectively historically, and retained more salt during leaching. Leaching of salts was important when the alkali soils of the Swamp of the Frogs Marsh region were developed for eventual crop agriculture (1890 to 1960). Leaching was first accomplished simply by draining the water table to allow livestock grazing. Leaching occurred naturally by rainfall infiltration and by percolation of overland flows. Later, as soils started to be leached of salts naturally, alkali resistant crops were planted and irrigated, which increased the rate of leaching. The finer textured, poorly drained soils (clays, clayey silts) contain organics that consume nitrate (reducing conditions), retain ammonium, and respond to leaching sluggishly. This set of conditions may create an inverse correlation between salinity and nitrate in the data set (Figure 2.3.6).

- A low selenium, high salinity, low nitrate correlation is consequently observed in the data set (Figure 2.3.5, 2.3.6, 2.3.7). The soils with high salinity may contain abundant selenium. However, without the presence of abundant nitrate to oxidize selenium from soils, the selenium concentration remains low in shallow groundwater beneath the soils that are leached by rain or by applied water. Thus, nitrate availability is shown again to be a likely factor in selenium mobility.

If nitrate continues to be added to the shallow aquifer via application of nitrogen to urban landscapes (by household application, treated wastewater, etc.); or if substantial amount of nitrate is left over in soils from the historical period of agriculture in the region, the selenium in soils could be mobilized by nitrate in greater concentrations than would naturally occur. Thus, site specific studies in El Modena Channel and Santa Ana Delhi Channel support the regional analysis presented in Section 2.1.



A. B.

Figure 2.3.1. Location of sub-study area in the vicinity of Santa Ana Gardens Channel and Santa Ana Delhi Channel. Results of sampling in Santa Ana Delhi and Santa Ana Gardens Channel showing (A) selenium and (B) arsenic concentrations in weepholes, shallow water wells, and surface flows, January 2004.

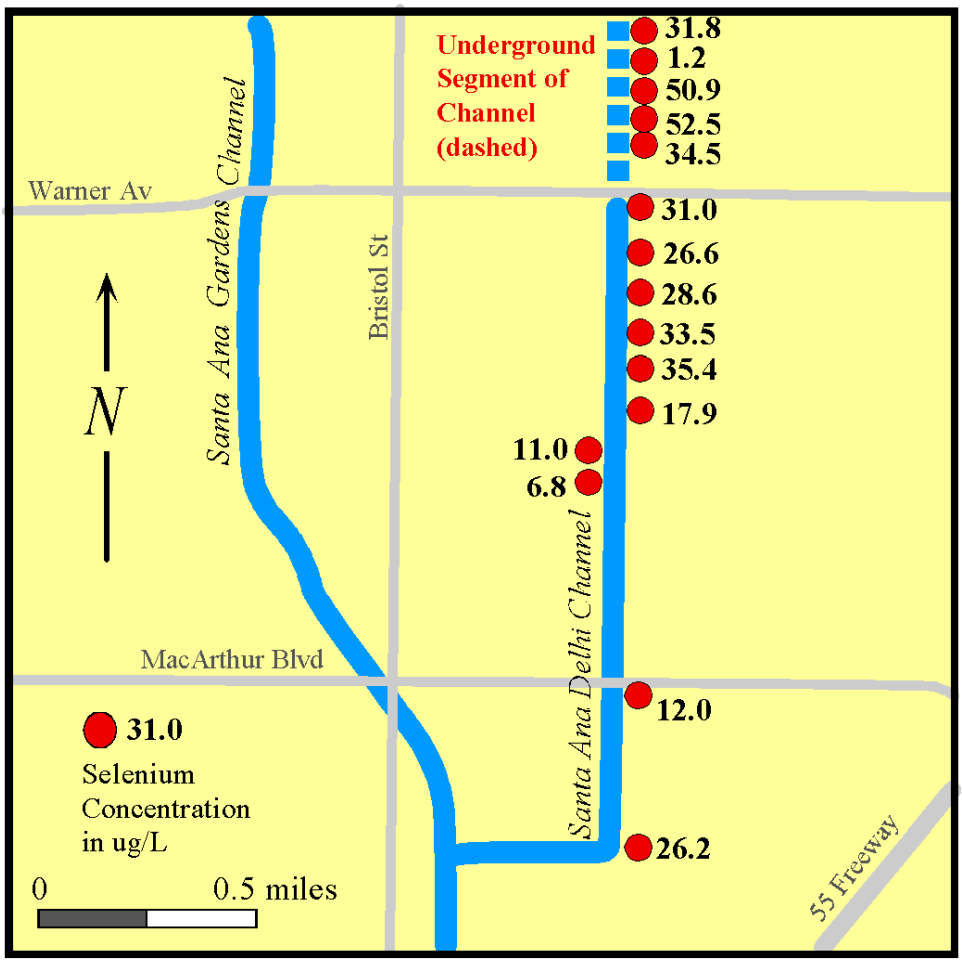


Figure 2.3.2. Selenium concentrations in groundwater in upper Santa Ana Delhi Channel, March 2005.

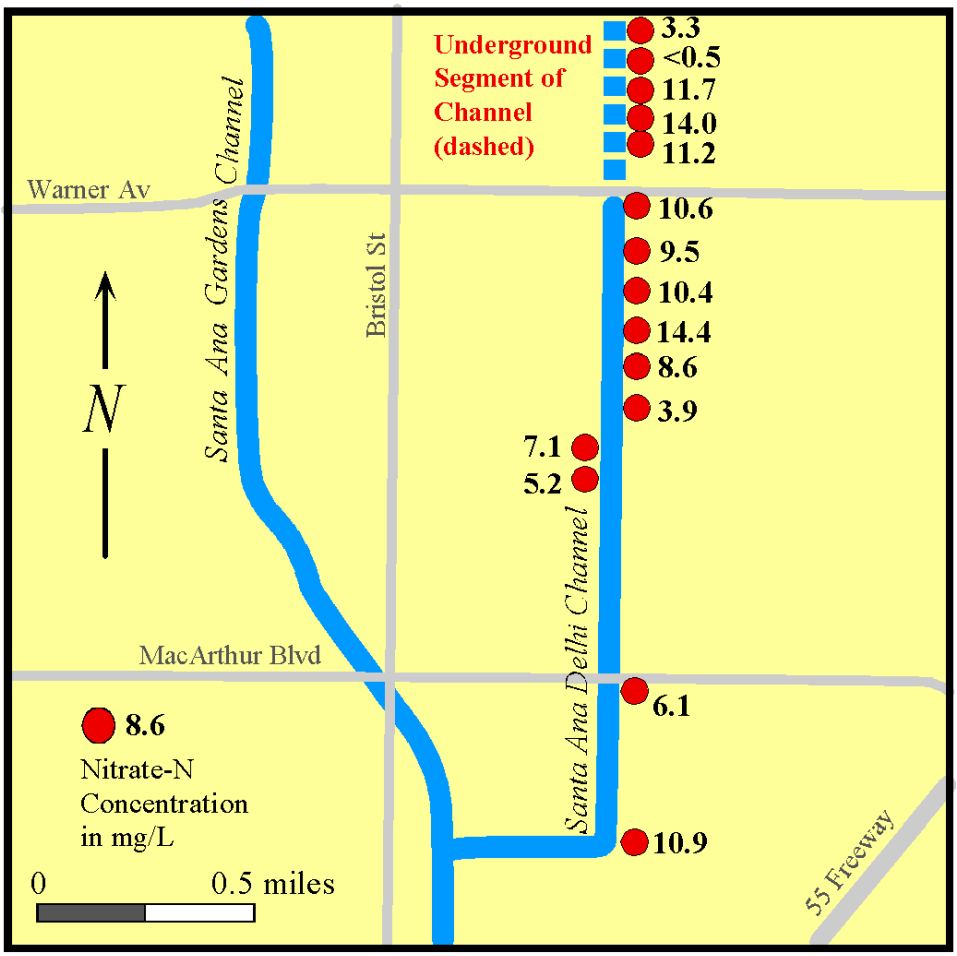


Figure 2.3.3. Nitrate-nitrogen concentrations in groundwater in upper Santa Ana Delhi Channel, March 2005.

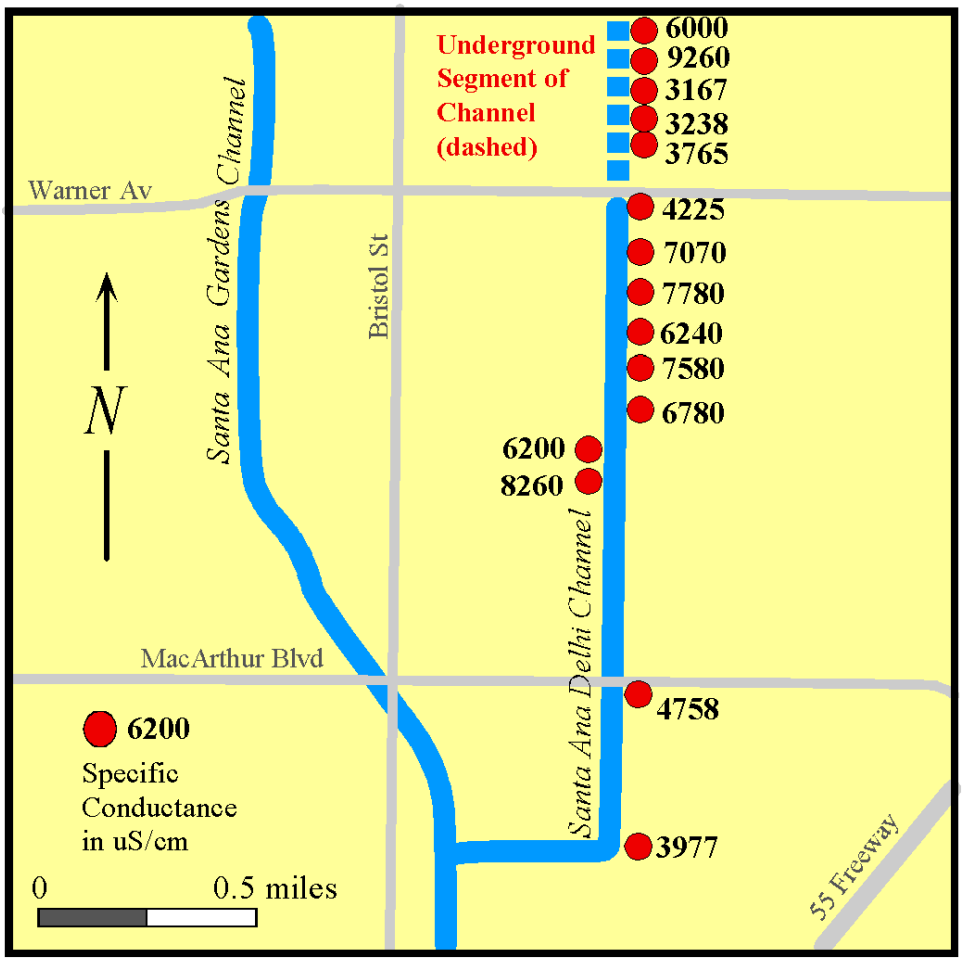


Figure 2.3.4. Specific conductance values in groundwater in upper Santa Ana Delhi Channel, March 2005.

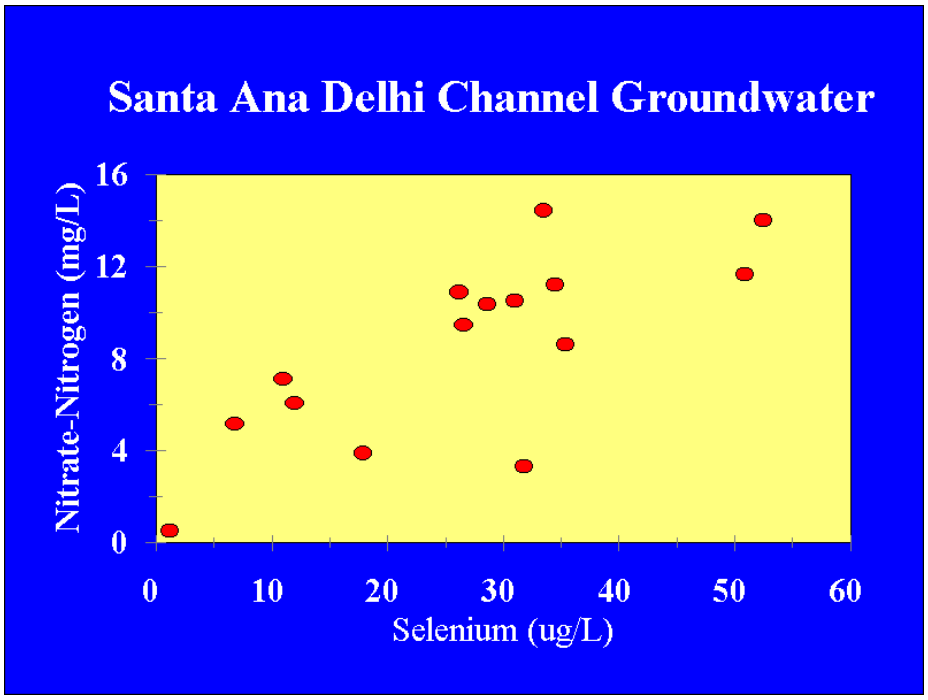


Figure 2.3.5. Santa Ana Delhi Channel groundwater data, showing a positive correlation between selenium and nitrate.

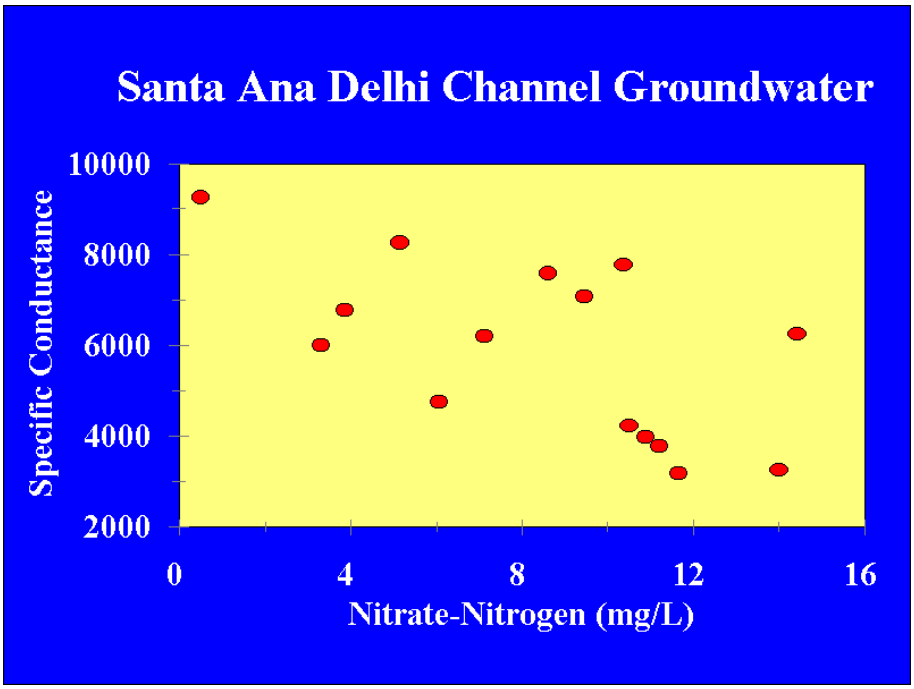


Figure 2.3.6. Santa Ana Delhi Channel groundwater data, showing a negative correlation between nitrate and specific conductance.

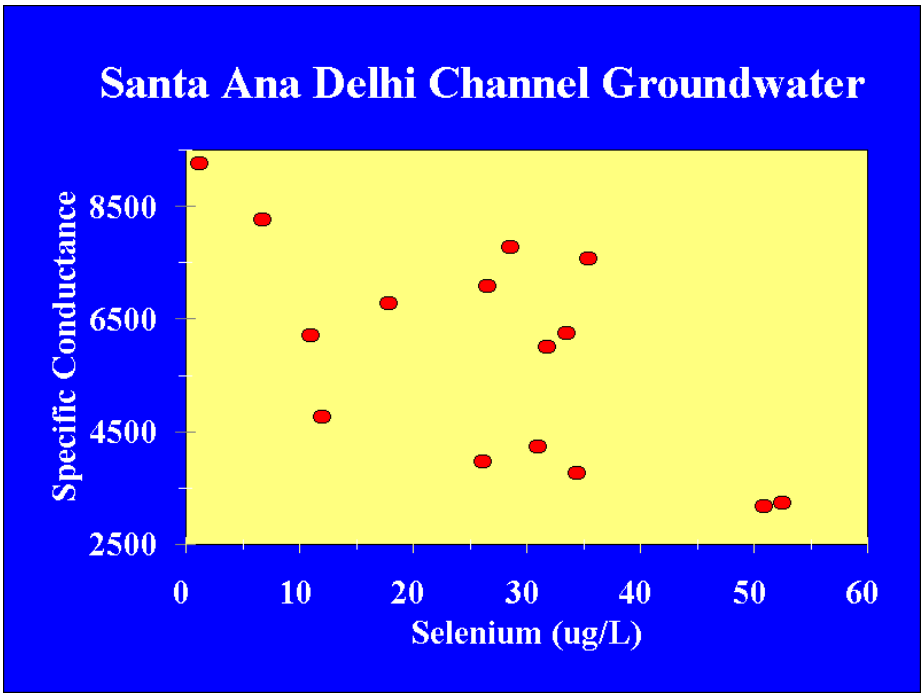


Figure 2.3.7. Santa Ana Delhi Channel groundwater data, showing a negative correlation between selenium and specific conductance.

2.4. ALTON DRAIN STUDIES

Alton Drain is a concrete lined circular drain that flows into San Diego Creek directly below the confluence with Peters Canyon Wash (Figure 2.4.1). Four seepages were identified in Alton Drain (Figure 2.4.2). Three of the seepages occurred where segments of concrete pipe are joined together (Alton Drain Ground Water 4, 3, and 2). Alton Drain Ground Water 1 originated from a small, free-flowing dewatering pipe inside of Alton Drain.

The research team sampled all four seepages within Alton Drain in February 2005 (Figure 2.4.2). The sample locations are just above the outlet of Alton Drain to Peters Canyon Wash in a northwest orientation paralleling Alton Pkwy. Samples were collected and analyzed for index parameters (pH, temperature, specific conductance, dissolved oxygen); general ion analysis (Cl, SO_4, and NO_3); and trace elements (selenium and arsenic).

The groundwater samples collected in Alton Drain contained moderate to high concentrations of EC salinity (Table 2.4.1, Figure 2.4.2). The furthest upstream point (Alton Drain Ground Water 1) contained 54.0 μg/L total dissolved selenium. Further downstream, the selenium values decreased gradually to 35 μg/L and 40 μg/L total dissolved selenium. At the point closest to the outlet (Alton Drain Ground Water 4), the total dissolved selenium value decreased significantly to 5.0 μg/L (Figure 2.4.2).

Remobilization of sequestered selenium from soils in the immediate area of Alton Drain is believed to occur under oxidation conditions brought about by means of the introduction of oxidants into the groundwater. As described for El Modena

Channel and Santa Ana Delhi Channel, a likely species is nitrate, as well as dissolved oxygen. Nitrate analysis of the samples collected in Alton Drain show a strong correlation between nitrate and selenium concentrations (Figure 2.4.3). Nitrate-nitrogen concentrations in groundwater seeps generally decreased from upstream to downstream in Alton Drain (46 to 5.9 mg/L). The selenium values associated with them also decreased (54 to 5.0 µg/L). The upstream portion of Alton Drain is located beneath a well-landscaped residential area.

Historical fertilization of crops and past and current irrigation seems to be the most likely sources of nitrate in groundwater in this location. Exceptionally high nitrate concentrations in many samples (Table 2.4.1) probably increases the oxidation reactions between the soils and groundwater leading to increased amounts of leaching of sequestered selenium in soils and sediments. These data further support the oxidation/reduction model for selenium and nitrate discussed in previous sections.

Table 2.4.1. Selenium, Nitrate, and Specific Conductance Data for New Seeps Discovered in Alton Drain, February 2005

Sample ID	Dissolved Selenium (ug/L)	Nitrate-Nitrogen (mg/L)	Specific Conductance (uS/cm)
Alton Drain Ground Water 1	54	46	4516
Alton Drain Ground Water 2	35	29	5140
Alton Drain Ground Water 3	40	38	6640
Alton Drain Ground Water 4	5	5.9	2377

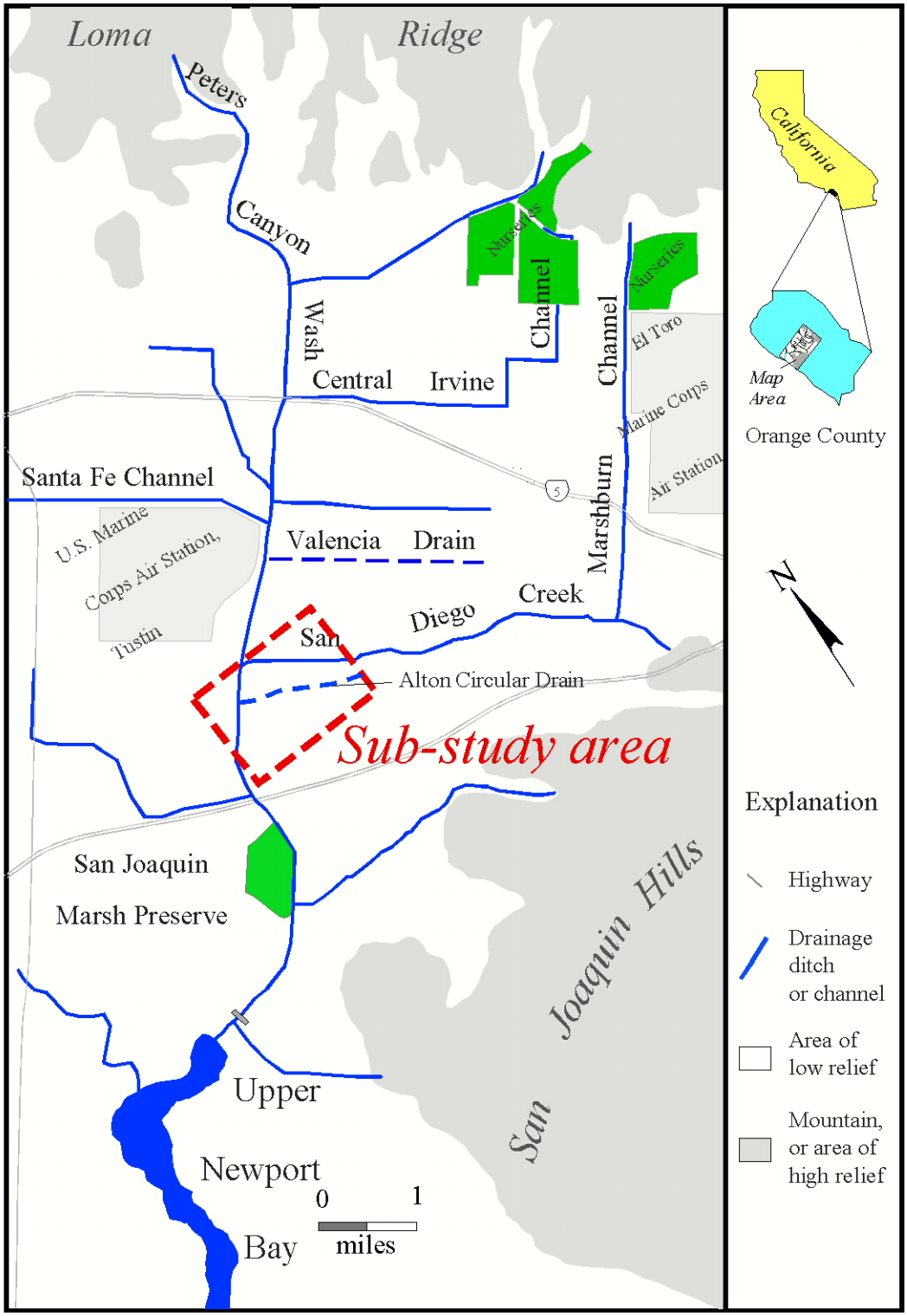
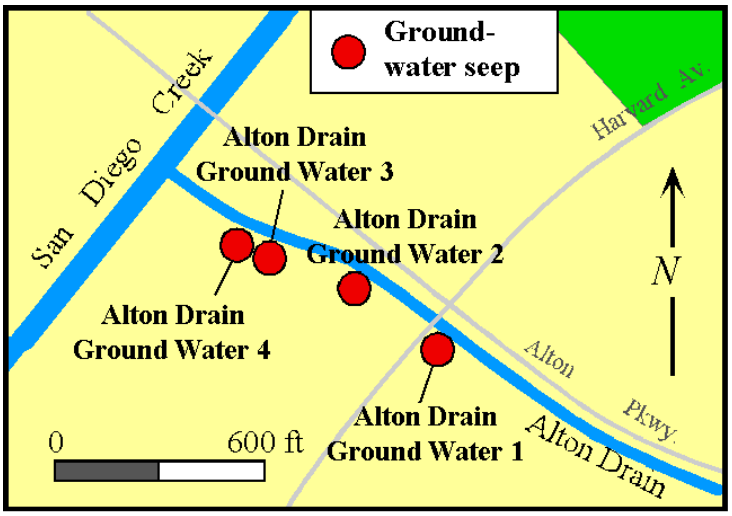
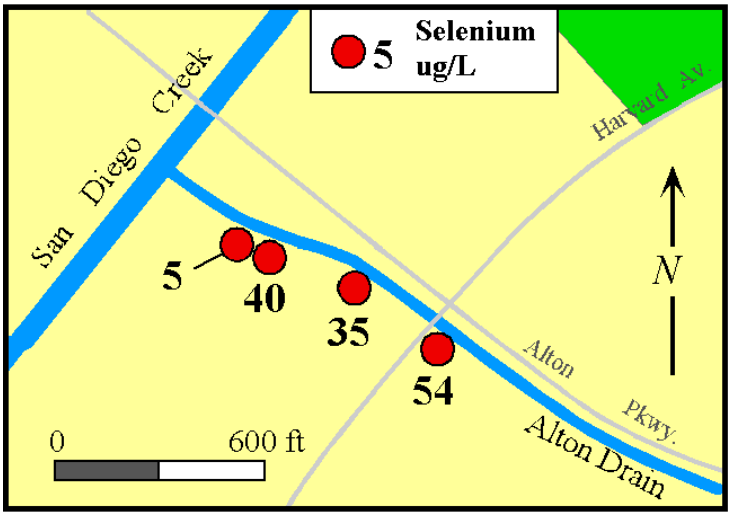


Figure 2.4.1. Location of Alton Circular Drain sub-study area.



A.



B.

Figure 2.4.2. Seeps where groundwater samples were collected in Alton Circular Drain (A); and selenium concentrations in the groundwater seeps, February 2005 (B).

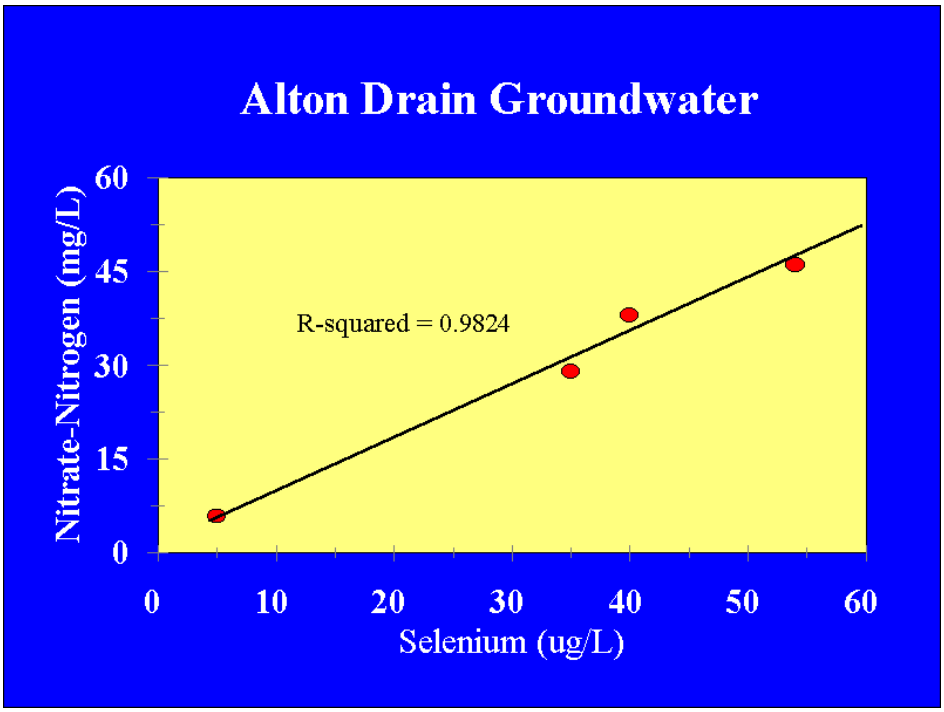


Figure 2.4.3. Nitrate vs. selenium concentrations in Alton Drain Groundwater. Notice the nearly linear correlation between nitrate and selenium concentrations. The R^2 value suggests a strong dependency between nitrate and selenium in the Alton Drain data set.

2.5. SANTA FE UNDERGROUND CIRCULAR DRAIN STUDIES

An underground drain feeding Santa Fe Channel contains a number of seeps and cracks where groundwater flows through concrete lining into the drain (Figure 2.5.1 and 2.5.2). The research team sampled seven of these flows in March, 2005. Most of the flows were located near Walnut Avenue (Figure 2.5.2).

Previous analysis by Hibbs and Lee (2000) and Meixner and others (2003) indicated high selenium concentrations (50 to 200 ug/L Se) in groundwater samples collected near Walnut Avenue and Peters Canyon Wash. Other areas of high selenium concentration in groundwater detected by Hibbs and Lee (2000) and in this report included El Modena-Irvine Channel and Walnut Avenue (Section 2.2). Santa Fe Underground Circular Drain is located at the outer fringe of the Swamp of the Frogs Marsh. The team anticipated potentially high selenium concentrations in the groundwater flows in Santa Fe Underground Circular Drain due to the proximity to Walnut Avenue, where high selenium concentrations have been observed in the past.

Specific conductance values in the groundwater flows in Santa Fe Underground Circular Drain were not particularly high, varying from 2000 to 2500 uS/cm (Figure 2.5.2). These values are near the lower range of salinity correlated with high selenium values in groundwater in this geographic part of San Diego Creek Watershed. Selenium values were moderate to moderately-high in groundwater, varying from 31 to 80 ug/L Se (Figure 2.5.3).

Selenium values are highest downgradient of Walnut Avenue, reaching values of 70 to 80 ug/L Se (Figure 2.5.3). This particular location is near the outer

fringe of the historic Swamp of the Frogs Marsh. Further down the hydraulic gradient, the next sampling point (920 ft) contained the lowest selenium concentration in the data set for this drain (31 ug/L Se).

Arsenic concentrations are very low in these groundwaters, around 1 ug/L (Figure 2.5.3). These represent some of the lowest values found in groundwater within the boundaries of the historic Swamp of the Frogs Marsh. Results from this drain study provide additional spatial coverage of selenium and arsenic concentrations in areas where no data had been available before.

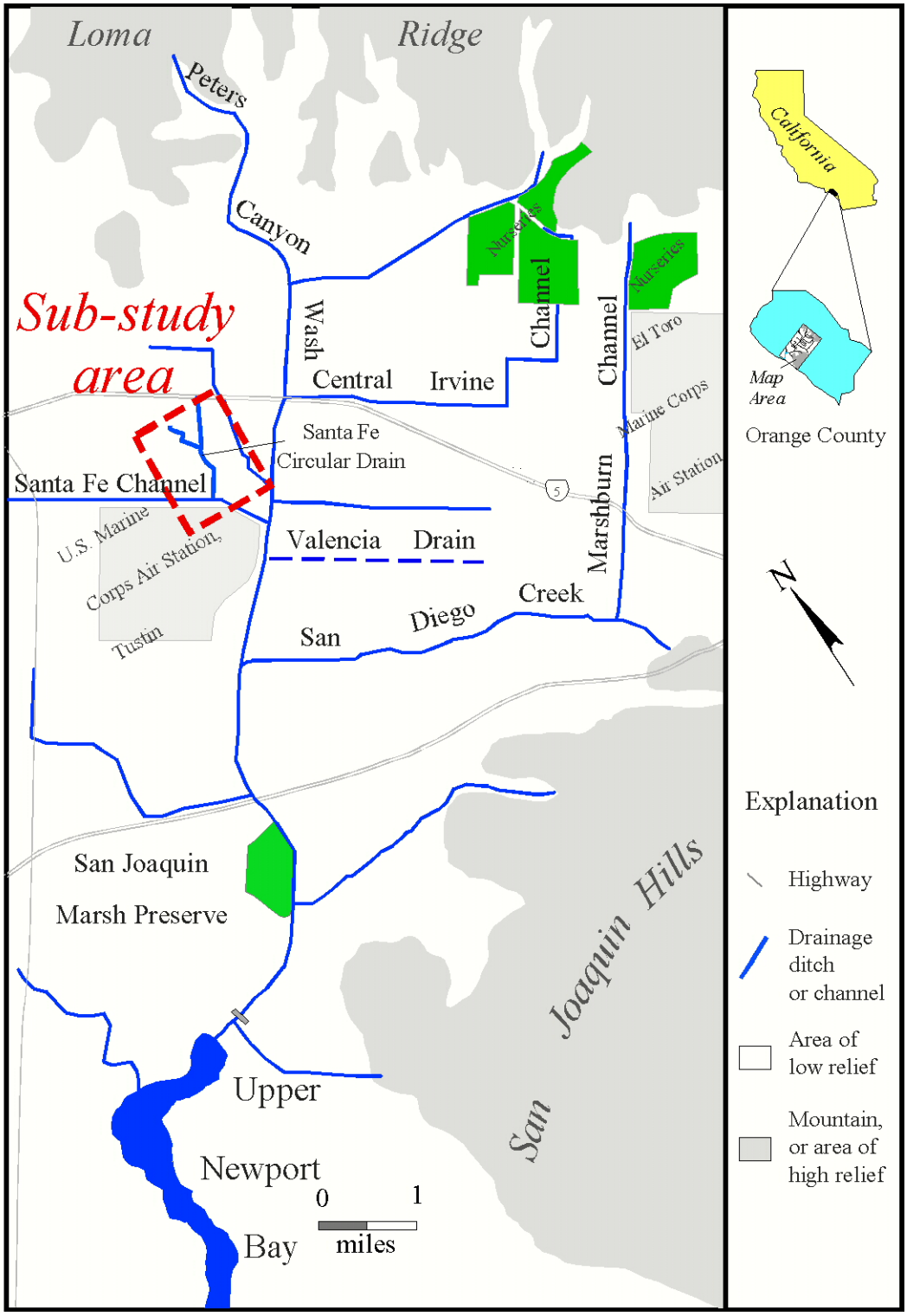


Figure 2.5.1. Location of Santa Fe Underground Circular Drain sub-study area.

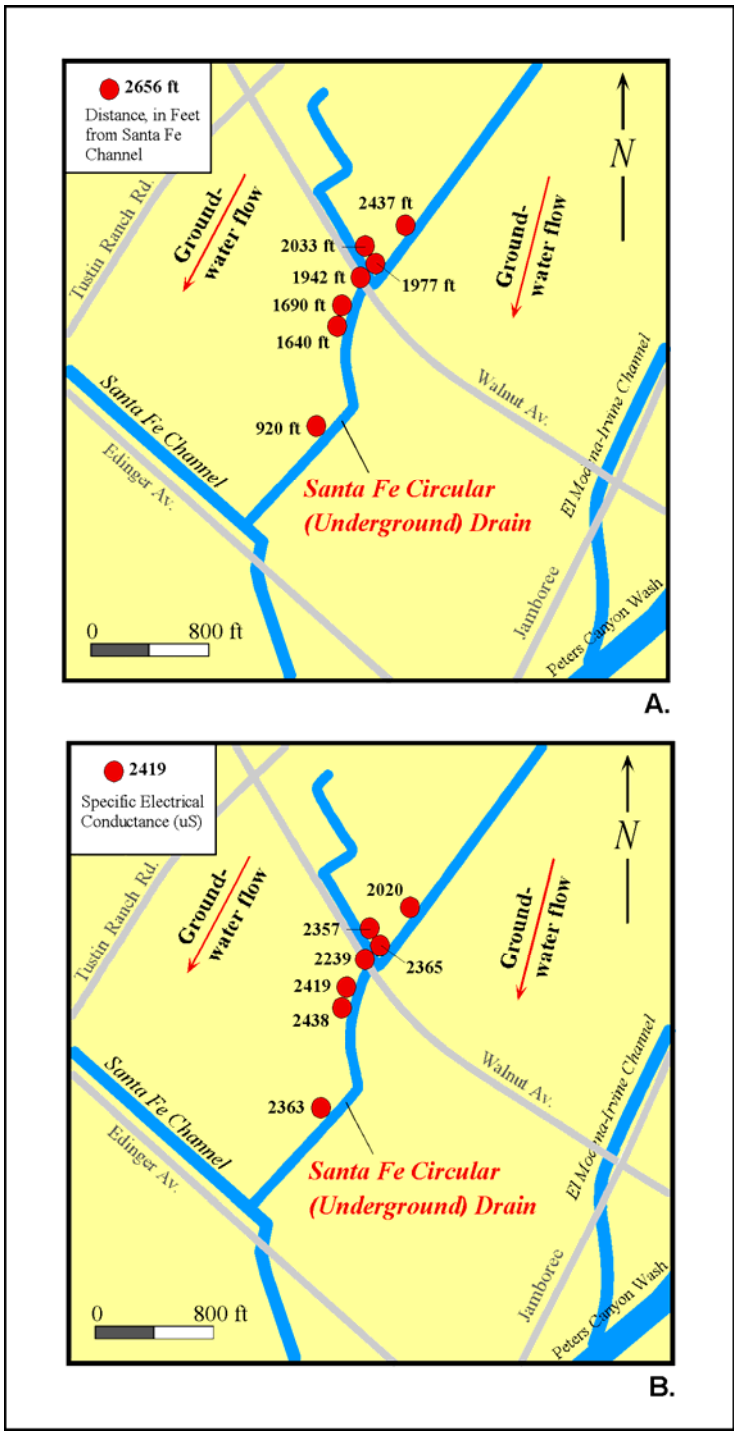


Figure 2.5.2. Salinity concentrations in groundwater in Santa Fe Underground Circular Drain, March 2005. Figure 2.5.2A shows groundwater sample locations, in feet from Santa Fe Channel. Figure 2.5.2B shows salinity (specific conductance) in groundwater at the seven groundwater sample points.

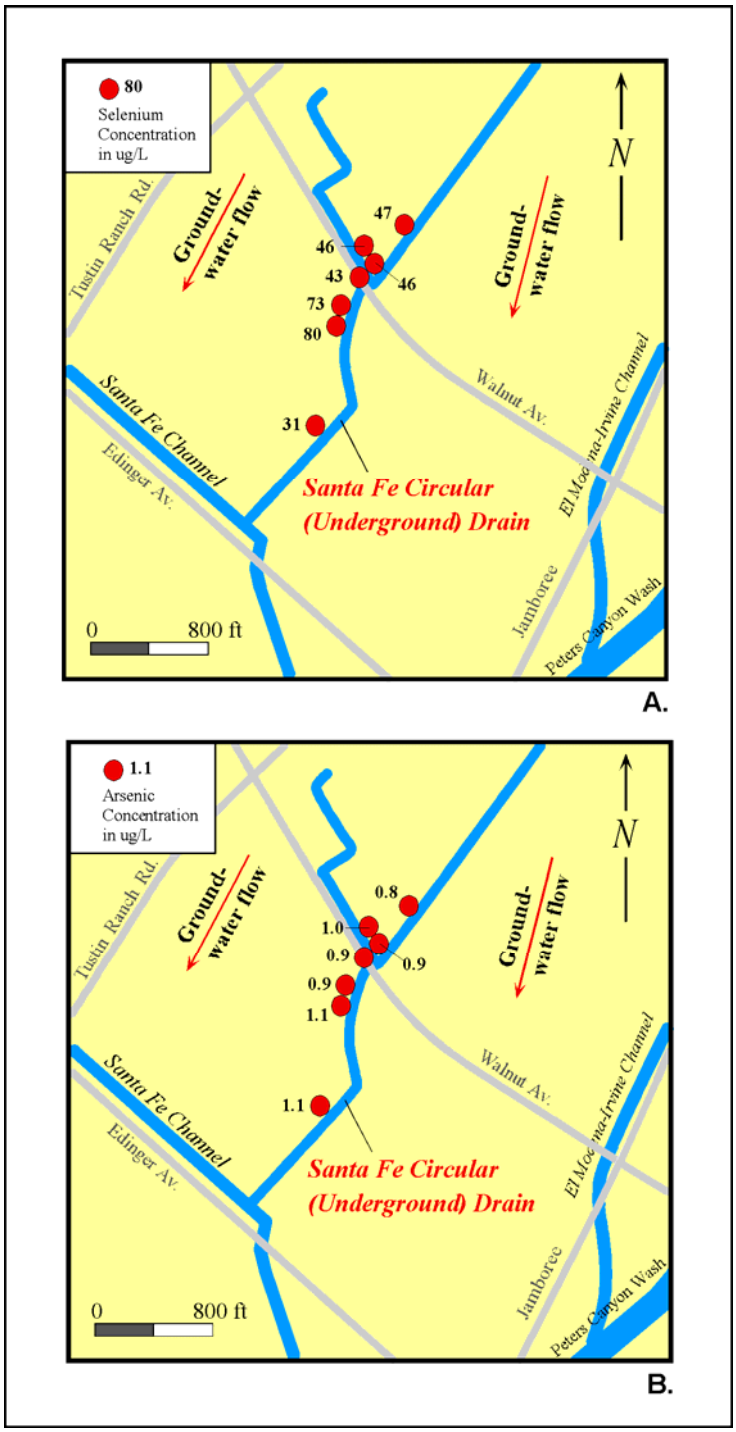


Figure 2.5.3. Selenium and arsenic concentrations in groundwater in Santa Fe Underground Circular Drain, March 2005. Figure 2.5.3A shows groundwater selenium concentrations and Figure 2.5.3B shows arsenic concentrations in groundwater at the seven groundwater sample points.

2.6 EDINGER UNDERGROUND CIRCULAR DRAIN STUDIES

The prop 13 research team performed underground reconnaissance in Edinger Circular Drain (Figures 2.6.1 and 2.6.2) to try to determine sources of extremely high selenium discharging from the drain. In previous studies of Edinger Circular Drain, Hibbs and Lee (2000) and Meixner and others (2004) detected highest concentrations of selenium of any major drain in San Diego Creek Watershed (100 to 160 ug/L total dissolved selenium in the discharge from the drain).

During channel reconnaissance, the research team discovered 14 groundwater seeps and flows where segments of concrete pipe are joined together. Most of the joints in the drain did not have groundwater flowing out of them. It appeared that certain joints had been affected by groundwater pressure resulting in a breach in the seal of the joint. In some cases groundwater issued from joints as "mini-geysers" that could be sampled very easily. Other groundwater flows occurred as sheet flows across the joint in the pipe.

The team sampled five of the flows at designated stations in Edinger Circular Drain, December 2004 (Figure 2.6.3). These stations extended above Harvard Avenue to a location just above the outlet of the drain at Peters Canyon Wash. The groundwater sample collected at the furthest upstream point (marked 1854 ft in Figure 2.6.3) contained 50 ug/L total dissolved Se and 14 ug/L total dissolved As (Figures 2.6.3 and 2.6.4). Further downstream, the selenium values increased gradually to 213 ug/L Se and 73 ug/L As. At the point closest to the outlet, the selenium value then decreased to 61 ug/L total Se while the arsenic value

continued to increase to its highest value of 168 ug/L As (compare Figures 2.6.3 and 2.6.4).

Sulfur isotope values progressively decline from 1.6 per mil $\delta^{34}S[SO_4^{2-}]$) up the hydraulic gradient to -2.4 per mil $\delta^{34}S[SO_4^{2-}]$ near Peters Canyon Wash. For reasons that were not known at the time, this particular data set shows a somewhat better correlation between dissolved arsenic concentrations and sulfur isotope signature relative to selenium (Figure 2.6.4). Other data sets in other areas have shown a stronger correlation between dissolved selenium and sulfur isotope signature. Our findings indicate that most of the dry weather flows of Edinger Circular Drain are fed by percolating groundwaters, not by urban runoff.

High selenium concentrations were observed down the hydraulic gradient, that dropped off at the sample location closer to Peters Canyon Wash. This was an interesting observation. Therefore, the project team returned to Edinger Drain to collect important selenium speciation and nitrate data in April 2005 in order to augment data collected in December 2004.

During the April 2005 sampling period, selenium concentrations had increased in groundwater in Edinger Circular Drain (compare Tables 2.6.1 and 2.6.3). The increase in selenium concentration at the sampling points in Edinger Drain was about 10% to 25%. This increase in selenium concentration after the rainy season has been noted previously (Meixner and others, 2004). The groundwater sample collected at the furthest upchannel point (marked 1854 ft in Figure 2.6.3) contained 59 ug/L total dissolved Se in April 2005 (Table 2.6.3). Further downchannel, the selenium values increased gradually to 301 ug/L Se. At

the point closest to the outlet, the selenium value then decreased to 65 ug/L total dissolved Se (Table 2.6.3). Notably, the nitrate concentration was relatively high at all points (12 to 15 mg/L NO3-N) except at the point closest to the outlet (point 324 ft), where nitrate-nitrogen was only 3.3 mg/L (2.6.3). Likewise, the specific conductance value was moderate at all upstream points (3900 to 4300 uS/cm) except further downstream (324 ft) where specific conductance was much higher (8590 uS/cm) (Table 2.6.3).

As groundwater enters the Swamp of the Frogs Marsh region, selenium concentration increased from 59 to 301 ug/L in the presence of high nitrate. However, the selenium concentration decreased to 65 ug/L at point 324 ft, where nitrate concentration is relatively low, and where salinity is high. These observations support the covariate relationships and hypotheses discussed in the section on Santa Ana Delhi Channel. Further evidence for the covariate relationships between selenium solubility, nitrate concentration and elevated salinity is provided by selenium speciation data (Table 2.6.4). All four upstream sample points contain selenate (Se-VI) primarily, with only a small amount of selenite (Se-IV). However, the downstream sampling point (324 ft), where low nitrate and high salinity were observed, contains a much greater percentage of selenite (compare Tables 2.6.3 and 2.6.4). This implies a very important solubility constraint affected by nitrate and salinity.

Additional Studies and Hypothesis Testing in Edinger Circular Drain

Due to the intriguing test results in 2004 and 2005, the prop 13 research team performed additional studies in Edinger Circular Drain during spring 2007 to try to resolve sources of extremely high selenium and arsenic discharging from the drain. Water quality parameters selected for testing were expanded substantially (Exhibit 2.6.1). In previous studies of Edinger Circular Drain, concentrations of selenium and arsenic were higher than in any major drain in San Diego Creek Watershed. Our current analysis, we believe, helps to resolve relationships between arsenic and selenium in groundwater near the drain. A new hypothesis is provided that complements previous ideas provided in Meixner and others (2004) and Hibbs and Lee (2000).

Arsenic has been investigated (Bechtel - Tustin Marine Corps Air Station studies; Meixner and others, 2004) but is not yet considered to be highly detrimental to the ecology of San Diego Creek Watershed. A few facts about arsenic processes in watersheds are mentioned. Arsenic (III) has a lower toxicity than Arsenic (V) on phytoplankton communities (Blanck and others, 1989). Unlike selenium, arsenic has a tendency to decrease with increasing trophic levels in food webs (Mason and others, 2000). The presence of relatively high concentrations of selenium *and* arsenic in shallow groundwater between Edinger Drain and Warner Drain has been discussed by Meixner and others, 2004. In other areas, such as near El Modena Channel and Santa Fe Circular Drain, selenium is very concentrated in shallow groundwater, but arsenic is very dilute. Therefore, arsenic may be related

or unrelated to selenium near Valencia Drain. To shed insights on these different relationships, arsenic and selenium in Edinger Drain area are co-investigated.

During channel reconnaissance in Edinger Drain in 2004, the research team discovered 14 groundwater seeps and flows where segments of concrete pipe are joined together. The team sampled nine of the flows at designated stations in Edinger Circular Drain during expanded studies in March 2007 (Figure 2.6.5). These stations extended above Harvard Avenue to a location just above the outlet of the drain at Peters Canyon Wash. These sampling points were oriented in-line with a groundwater flowpath, providing opportunity to assess evolution of groundwater along the flowpath. Of particular note is the orientation of the flowpath from a "Transitional Swamp of the Frogs" region to a region we have interpreted to be an evaporative salt flat that existed in the predevelopment period (Figures 2.6.6 and 2.6.7). Historical salt flats have been mapped in the Lane Channel area and Barranca Channel area (Meixner and others, 2004). The salt flats identified in the lower reaches of Edinger Drain have not been identified or cited in our earlier literature (Figures 2.6.5 and 2.6.6).

Exhibit 2.6.1: Laboratory Analysis in Edinger Drain Intensive Study

Parameters Analyzed in Edinger Drain Groundwater	Laboratory/Analysts
Anions, Nutrients	Cal-State LA Hydrochemistry Lab, Hollinger and assistants
Selenium & Selenium Speciation	UC-Riverside, Zhang
Arsenic Speciation, Iron Speciation	Applied Speciation, Staff
Manganese, Iron, Vanadium, Molybdenum	Montgomery Watson, Staff
Sulfate-Oxygen-Hydrogen Isotopes	University of Arizona Isotope Geochemistry Lab, Eastoe and Assistants

In the historic salt flats of San Diego Creek Watershed, the land surface was very flat and low lying (Figures 2.6.6 and 2.6.7). By Darcy's law, a free surface or shallow groundwater table that mimics flat land surface topography beneath a phreatic playa (i.e., salt flats) will have a very flat hydraulic gradient and very slow rate of groundwater movement. Such areas are frequently enriched in salts because sluggish groundwater evaporates, leaving behind salts and other evaporative residues (Figures 2.6.6 and 2.6.7). The shallow groundwater near the confluence of Edinger Circular Drain and Peters Canyon Wash already has been shown by Bechtel Corporation to be an area of very high total dissolved solids, very high arsenic concentrations, and relatively low selenium concentrations (Figures 2.6.8, 2.6.9, and 2.6.10). These relationships do not correlate with observations made by Meixner and others (2004) where arsenic and selenium were positively correlated. The purpose of this study is to determine why these reverse relationships develop in nearby areas.

Results of March 2007 Sampling

The groundwater sample collected at the furthest upstream point in Edinger Drain (marked 1854 ft in Figure 2.6.5) contained about 50 ug/L total Se (Table 2.6.5 and Figure 2.6.11). Further downstream, the selenium values increased gradually to 228 ug/L total Se at the boundary between the "Transitional Swamp Region" and the "Historic Salt Flats" (Figures 2.6.7 and 2.6.11). At the sample point closest to the outlet, the selenium values decrease to about 65 ug/L total Se (Table 2.6.5 and Figure 2.6.11). Almost all of the selenium is in the (+VI)

oxidation within the Transitional Swamp Region, while about 11% of the selenium is in the (+IV) oxidation state within the Historic Salt Flats Region (Table 2.6.5). Rarely are shallow groundwaters detected in San Diego Creek Watershed with more than 4% Se(IV), except beneath San Joaquin Marsh and beneath this Historic Salt Flats.

The groundwater sample collected at the furthest upstream point (1854 ft in Figure 2.6.5) contained about 13.5 ug/L total As (Table 2.6.6 and Figure 2.6.11). Arsenic increased steadily to a concentration of 90 ug/L at the boundary between the "Transitional Swamp Region" and the "Historic Salt Flats" (Figures 2.6.7 and 2.6.11). Below the boundary, arsenic continues to increase to as much as 196 ug/L (Table 2.6.6 and Figure 2.6.11). This is, as far as we know, the highest arsenic concentration ever measured in shallow groundwater in San Diego Creek Watershed. All of the arsenic is in the (+V) oxidation state (Table 2.6.6).

Sulfate is plotted alongside the arsenic and selenium data in the groundwater flowpath charts (Figure 2.6.11). Arsenic and sulfate have a correlative increase in concentration once groundwater enters the Historic Salt Flats (Figure 2.6.11). Above the boundary between the Transitional Swamp Region and the Salt Flats, the sulfate concentration does not vary much along the flowpath. Even so, selenium and arsenic increase substantially in the Transitional Swamp Region (Figure 2.6.11).

Visual comparison of parameters is obtained by creating a "reference point" that is adjusted so that the concentration scales match with respect to the parameter values at the reference point (see Figure 2.6.11 and find "reference point"). The

parameter values overlap directly with one another at the "reference point". This provides a comparison of how parameters evolve downgradient of the "reference point" (Figure 2.6.11). Correlative results are observed between sulfate, bromide, chloride, and arsenic, but *not* with selenium. All except selenium increase in a proportional manner within the Historic Salt Flats (Figures 2.6.11, 2.6.12 and 2.6.13). The concentration of selenium decreases in groundwater in the Historic Salt Flats (Figure 2.6.11). These trends are opposite of the trends documented along El Modena Channel, where selenium and sulfate show a correlative increase in concentration along a groundwater flowpath, while chloride remains virtually unchanged (Hibbs and Lee, 2000 and Section 2.2). This implies that unique hydrochemical processes operate along Edinger Drain Flowpath.

Ion correlation trends between arsenic, chloride, bromide, and sulfate are calculated with an enrichment coefficient developed at the "reference point" (Figure 2.6.11) and other points downgradient of the reference point (Table 2.6.7). For example, the concentration of sulfate at the reference point at 883 ft is 1246 mg/L. At the next sample point at 441 ft, sulfate has increased to 2354 mg/L. Thus, an enrichment factor of 1.89 (2364/1246) is calculated (Table 2.6.7). Similar enrichment factors for chloride, bromide, and arsenic are strongly correlated at the various points downgradient from the reference point (Table 2.6.7). Enrichment factors for sulfate, arsenic, chloride, and bromide increase progressively within the Historic Salt Flats. Evaporative concentration of these soluble salts and arsenic (V) in evaporative salt crusts (in predevelopment times) and subsequent leaching into shallow groundwater is the probable cause.

Other findings include the observation that concentration of selenium and nitrate decrease in a correlative manner within the Historic Salt Flats Region (Figure 2.6.14). Also, the Cl/Br and SO4/Cl ratios do not vary greatly along the Edinger Drain flowpath (Figure 2.6.15). This is because concentrations of chloride, bromide, and sulfate do not change much down the hydraulic gradient in the Transitional Swamp Region (Figures 2.6.11, 2.6.12, and 2.6.13). Therefore, associated anion ratios (Cl/Br and SO4/Cl) do not vary that much along this first part of the flowpath. The concentrations of these anions increase in the Historic Salt Flats, but in a nearly proportional manner. This is demonstrated by the similar enrichment factors for Cl, SO4, and Br (Table 2.6.7). The result is that the Cl/Br and SO4/Cl ratios are relatively (but not perfectly) uniform down the entire groundwater flowpath (Figure 2.6.15).

Discussion

Results of sampling indicate local groundwater contains a lot of selenium and arsenic, and by association, so does Edinger Circular Drain. Our findings indicate that most of the dry weather flows of Edinger Circular Drain are fed by percolating groundwaters, not by urban runoff.

The initial pattern of selenium enrichment in groundwater seeps in Edinger Circular Drain is generally consistent with results found in Valencia Drain (see Section 2.7) as selenium concentrations increases along a downstream trend toward Peters Canyon Wash (Figure 2.6.11). Further down the hydraulic gradient, close to Peters Canyon Wash, the concentration of selenium decreases once groundwater

enters the Historic Salt Flats area (Figures 2.6.5 and 2.6.6). Selenium is even lower in groundwater right by Peters Canyon Wash (see Bechtel, Figure 2.6.9). Arsenic, on the other hand, increases continuously in samples down the hydraulic gradient (Table 2.6.6). Concentrations of bromide, chloride, and sulfate do not change much in the Transitional Swamp Region (Figure 2.6.7), but increase (much like arsenic) in the Historic Salt Flats (Figures 2.6.11, 2.6.12, and 2.6.13). Nitrate does not change much in the Transitional Swamp Region but decreases (much like selenium) in the Historic Salt Flats (Figure 2.6.14).

To shed insights on these irregular data, stable isotopes of oxygen, hydrogen, and sulfur were analyzed (Figure 2.6.16 and 2.6.17). These data were collected specifically to help assess possible evaporation processes and sources of water, and to help evaluate redox processes in groundwater (Figure 2.6.18). Maps of regional arsenic distribution were prepared and soils and geologic maps were developed to compare to soil types exposed in construction trenches near Edinger Drain (Figures 2.6.19, 2.6.20, 2.6.21, and 2.0.1). These data, maps, and photos are used to refine previous conceptual hydrogeochemical models related to the time-series changes in the watershed (Figure 2.6.22). Details on the ***predevelopment*** and ***postdevelopment*** models are provided below. The conditions outlined in these models reflect only those along Edinger Drain flowpath and are distinct from models discussed for El Modena Channel and Santa Ana Delhi Channel.

Predevelopment Model

- Arsenic and selenium bearing runoff, and groundwater containing fairly dilute concentrations of selenium and moderate concentration of arsenic entered the Transitional Swamp Region. There the entrant waters encountered an intermediate redox environment. This region, along the current path of Edinger Drain, was not

highly reducing because of fluctuating water tables that were associated with dry seasons and drought years (Figure 2.6.22) (Meixner and others, 2004; Sjolin, 2005). In other parts of the historic watershed, such as in the lower El Modena Channel-middle Santa Fe Channel-upper Santa Ana Delhi Channel areas, the conditions were reducing for long periods of time. In those other areas water tables were more stable, and shallow. Evidence of intermediate oxidation conditions in the Transitional Swamp Region are shown in soil profiles near Edinger Drain and Harvard Avenue (Figure 2.6.20). These profiles contain alternating layers of phreatic caliche (stable, shallow water tables) and layers of iron-stained soils which indicate semi-oxidizing conditions during dry periods when water tables were deeper. Semi-oxidizing conditions frequently transitioned to intermediate redox to slightly reducing conditions during periods when water tables were high and when wetlands were stable (Figure 2.6.20). The overall average was an intermediate redox condition in the Transitional Swamp Region. This aspect of the model, within the Transitional Swamp Region, corresponds closely to interpretations provided by Meixner and others (2004) and Sjolin (2005).

● Intermediate oxidation states dominated in the Transitional Swamp Region during predevelopment times (Figure 2.6.22 and 2.6.23). Iron oxide coatings indicate that soils were not highly reducing and that water tables probably fluctuated (Figure 2.6.20). During dry times when water tables were deeper, arsenic probably wicked up into the more oxidizing vadose zone and was oxidized to arsenic (V). Arsenic (V) sorbed onto iron and aluminum oxide surfaces, organics, and clays. During wet times when water tables were shallow, redox conditions were more reducing and arsenic was probably reduced from arsenic (V) to arsenic (III). The reduced form of arsenic is more soluble than arsenic (V). Soluble arsenic moved with groundwater into the Historic Salt Flats region (Figures 2.6.22 and 2.6.23).

● Selenium (VI) was probably reduced to selenium (IV) in the intermediate redox zone discussed above. Selenium (IV) probably sorbed onto organic particles and clay minerals in the Transitional Swamp Region. Selenium was not reduced sufficiently in this region to produce iron selenides (-II) or elemental selenium (0). Sulfate was not reduced to a great degree because this area was not sufficiently reducing (Figure 2.6.18). This is indicated by generally positive sulfur isotope values ($\delta^{34}S[SO_4^{2-}]$) that do not vary much in the Transitional Swamp Region (Figure 2.6.17).

● Soluble ions that are not redox sensitive in intermediate redox zones (bromide, chloride, sulfate) and arsenic (III) moved with subsurface water into the Historic Salt Flats (Figures 2.6.22 and 2.6.23). Salt precipitates were not persistent in the Transitional Swamp Region because soluble ions were flushed by episodes of surface runoff and/or periodic high water tables. Instead, soluble salts accumulated in the Historic Salt Flats. Some residual selenium (IV) in groundwater and selenium (VI) in surface runoff also moved into the Salt Flats, but the supply of selenium may have been limited because much of the mass of selenium (as Se-IV)

had been sequestered in the Transitional Swamp Region. In the salt flats region where topography was low-lying, the water table was perennially shallow. There the waters evaporated strongly to produce crusts of salts consisting of sulfate, bromide, and chloride, along with considerable amounts of arsenic (V), but with little selenium. Most of the selenium had already been removed in the Transitional Swamp Region, and/or within the shallow groundwaters of the hypersaline, strongly alkaline Historic Salt Flats. These saturated environments beneath salt flats are known for their strongly anoxic conditions below the water table (Figures 2.6.22 and 2.6.23) (Boyd and Kreitler, 1986; Ryu and others, 2003). Likewise some of the sulfate was reduced beneath the Historic Salt Flats to form iron-sulfide compounds (Figure 2.6.23). This is indicated by generally negative sulfur isotope values ($\delta^{34}S[SO_4^{2-}]$) within the Salt Flats region (Figure 2.6.17). The bulk reduction is only about 4 per mil (1.8 to -2.2), not nearly as reduced as along El Modena Channel where the reduction is closer to 18 per mil $\delta^{34}S[SO_4^{2-}]$. The interpretation of the existence of and hydrochemical processes within the Salt Flats region, and corresponding relation to high arsenic and diminished selenium, is originally described in this chapter.

● Gao and others (2006) identified oxidizing conditions in the exposed salt crusts of phreatic salt flats, due to exposure of crusts to the atmosphere. Arsenic and sulfur in these salt crusts are stable as arsenic (V) and evaporite sulfate (VI) salts. Gao and others (2006) found that about 98% of arsenic in the crusts of the salt flats was arsenic (V). Beneath salt crusts, shallow groundwater is usually highly anoxic (Boyd and Kreitler, 1986; Ryu and others, 2003). In these saturated anoxic zones, sulfur is reduced to iron-sulfide while selenium is reduced to elemental selenium and iron-selenide. Thus, much of the sulfur and arsenic in the Historic Salt Flats remained in oxidized forms in the salt crusts until and after periods of swamp drainage and eventual leaching of residual salts. A smaller amount of sulfur (and probably selenium) was reduced in the anoxic groundwater zone beneath the salt flats, and became isotopically negative $\delta^{34}S[SO_4^{2-}]$. Thus, a mixture between unreduced and isotopically positive sulfur (sulfate [VI]) in salt crusts with reduced and isotopically negative sulfur (iron sulfide) that was reduced in the anoxic groundwater produces a bulk sulfur isotope signature that is only 4 per mil lighter than its original source. Furthermore, the oxidized form of arsenic (As-V) deposited in the salt crusts continues to leach out of the residuum of the crusts into shallow groundwater beneath the Historic Salt Flats (Table 2.6.6).

● This summary predevelopment model includes a strong sink for selenium (IV) and arsenic (V) via sorption onto clay minerals, Fe and Al-oxides, and organic material within the intermediate redox sites of the Transitional Swamp Region. There was little <u>persistent</u> enrichment of soluble ions (Cl, SO4, and Br) by evapoconcentration or sulfate reduction in this transitional zone. Arsenic (III) and soluble anions moved downgradient into the Historic Salt Flats region. Further, the model proposes strong concentration of large amounts of Cl, SO4, Br, and arsenic (V) in the evaporative salts crusts in the Historic Salt Flats region. In the groundwater beneath the Salt Flats, where soils were anoxic, a smaller mass of

sulfate was probably reduced to iron-sulfides. A limited pool of selenium was probably reduced to iron-selenide and elemental selenium in the anoxic groundwater beneath the Historic Salt Flats (Figures 2.6.22 and 2.6.23).

Postdevelopment Model

● After drainage of the Swamp of Frogs, the area was developed for irrigated agriculture (Figures 2.6.22 and 2.6.24). Most nitrogen fertilizer was applied to crops and orchards above the Historic Swamp of the Frogs Marsh where soils were less saline and better drained. Nitrate and dissolved oxygen began to oxidize selenium (IV) in the vadose soils and aquifer sediments within the Transitional Swamp Region, while arsenic probably desorbed from Fe and Al-oxides, clays, and organic matter. Arsenic and selenium concentrations in groundwater moving through the transitional region increase along the flowpath, while Cl, SO4, Br, NO3 and sulfate isotopes do not change very much. Iron-sulfide is not abundant in the Transitional Swamp Region and nitrate is not consumed by oxidation of metal-sulfides (i.e., as opposed to the El Modena Channel, where nitrate oxidizes sulfides and is denitrified in groundwater). Contemporary groundwater is highly oxidizing in the Transitional Swamp Region, as indicated by the absence of iron, manganese, and ammonium; and abundance of oxidized forms of arsenic (V) and selenium (VI) (Tables 2.6.5, 2.6.6, and 2.6.8).

● Residual salts remaining in unsaturated soils are now leaching into groundwater within the Historic Salt Flats. This carries large masses of Cl, SO4, Br, and arsenic (V) into shallow groundwater. The fact that the oxygen and deuterium isotopes in groundwater show no evaporative enrichment along the Edinger Drain flowpath (Figure 2.6.16) indicates that high salinities in groundwater are due to second cycle dissolution of previously precipitated salts, and not due to enrichment of solutions in groundwater, directly by evaporation.

● Nitrate in contemporary groundwater enters the Salt Flats Region in moderately low concentrations (Figures 2.6.14 and 2.6.23), probably because it has been diluted by recharge in areas that received little synthetic nitrogen fertilizer (e.g., Tustin Marine Corps Air Station personnel housing). Development of synthetic fertilizer post dated construction of the air base. Contemporary denitrification is another, but probably less important factor in nitrate reduction in the Historic Salt Flats region.

● Bound selenium is probably present in limited amounts in the soils of the Historic Salt Flats. Selenium was sequestered in the Transitional Swamp Region before masses of Se ever made it to the Historic Salt Flats. The slightly suboxic (intermediate to slightly oxidizing) redox states that exist in contemporary groundwater in the Historic Salt Flats is indicated by small amounts of manganese and relative abundance of selenium (IV) (Tables 2.6.5 and 2.6.8). Groundwaters are more oxidizing in the Transitional Swamp Region where no manganese is present and where selenium (IV) is meager. Suboxic redox state does not allow selenium to be oxidized in the same amount as in the Transitional Swamp Region.

Nitrate deficiency also diminishes oxidation potential for bound selenium. Most likely, selenium was never enriched in soils of the Historic Salt Flats to begin with.

● A pertinent set of questions remain. Are nitrate and selenium concentrations lower in the Historic Salt Flats due to contemporary suboxic conditions which might remove some of the selenium and nitrate by reduction and denitrification? Or is selenium diminished because it was never as abundant in the soils beneath the Historic Salt Flats, or because nitrate (a selenium oxidant) is diluted by nitrate-deficient recharge waters in nearby areas that had limited use of synthetic fertilizer? With only small amounts of manganese, negligible iron, and negligible amounts of ammonium in the groundwater beneath the Historic Salt Flats (Table 2.6.8) we feel that the flats are not sufficiently reducing today to remove significant amounts of nitrate and selenium. Conditions are just slightly suboxic. We are less comfortable with the former question/hypothesis and lean toward the latter. It would be useful at some future date to test these hypotheses with nitrogen isotopes to perhaps answer these questions.

Original Source of Arsenic

A model for the occurrence and evolution of high arsenic (and selenium) concentrations in the Edinger Drain area was summarized above. Sorption and desorption on Fe-Al oxides, organics, and clays and associated land use change appear to be the dominant factors controlling arsenic enrichment in shallow groundwater in the Transitional Swamp Region (Meixner and others, 2004; Sjolin, 2005) (Table 2.6.6; Figures 2.6.10 and 2.6.11). Evaporative enrichment in the salt crusts of the Historic Salt Flats and subsequent leaching seems to have concentrated arsenic in groundwater much more.

Just as is the case for selenium, determining the *original* geologic (or anthropogenic?) source of arsenic in the watershed is challenging. Preliminary insights are provided by comparing watershed-wide distribution of arsenic maps, soils maps, and geologic maps (Figures 2.6.19, 2.6.20 and 2.6.21). Of note is the moderately low concentration of arsenic of 13.5 ug/L at the upstream sampling

point in Edinger Circular Drain (Sample point 1854 ft, Figure 2.6.5 and Table 2.6.6). This value is not that much different from arsenic concentrations in shallow groundwater in most of the Upper San Diego Creek, Upper Como Channel drainage areas (Figure 2.6.19). Even above the Historic Swamp of the Frogs Marsh area, many of the arsenic concentrations near San Diego Creek and Como Channel are 10 ug/L or more. In other drainage areas the arsenic concentrations are usually less than 5 ug/L (Figure 2.6.19).

These spatial relationships seem to suggest that the important arsenic sources came from mountain terrains that drain into the Como Channel – Upper San Diego Creek region. The arsenic may very well be dissolved in-situ from mineralogical or sediment deposits sourced from the mountains that were eroded and deposited in the low lying Tustin Plain. In this possible scenario, arsenic bearing minerals in the upper San Diego Creek/Como Channel drainage area (above Swamp of the Frogs Marsh) could be releasing As directly into groundwater at concentrations up to 12 ug/L. Alternatively, the arsenic may come from solution of minerals *within* the mountains followed by drainage of arsenic bearing runoff onto the low lying plains. Other areas (e.g., Santa Ana Delhi Channel drainage, Santa Fe Channel drainage, El Modena Channel drainage) do not appear to have such a prominent source of arsenic. Once groundwater and surface water moved into the Swamp of the Frogs Marsh region, other processes enriched arsenic to the abnormally high concentrations observed in Edinger Drain (Table 2.6.6; Figure 2.6.19).

Inspection of the 1900 USDA soils map shows areas of drainage into the Swamp of the Frogs area that came from different mountains (Figure 2.6.21). Unfortunately the map does not cover the San Diego Creek drainage adequately, but the Fresno Sand deposits, which formed distributary creeks across the Tustin Plain, show different mountain drainage sources for the different creeks. The Santa Ana Delhi Channel, Santa Fe Channel, and El Modena Channel drainages were evidently sourced from mountains that were also drained by Santiago Creek (Figure 2.6.21). Como Channel and San Diego Creek drainages were connected to channels that extended into the mountains ranging from Hicks Canyon Channel to Borrego Canyon Channel. San Joaquin Channel and Sand Canyon Wash drained the San Joaquin Hills (Figure 2.0.1). We believe that the mountains bounded by Hicks Canyon Channel and Borrego Canyon Channel contain naturally higher concentrations of arsenic. Geologic literature investigations and cartography should be performed to help determine what are the geologic formations that are the most likely source of the arsenic (Figure 2.0.1).

Table 2.6.1: Selenium and Specific Conductance Data for Edinger Circular Drain - Groundwater Seeps, December 2004

Sample ID	Dissolved Selenium (ug/L)	Specific Conductance (uS/cm)
Edinger Circular Drain 324 ft	61	8410
Edinger Circular Drain 883 ft	213	3990
Edinger Circular Drain 1107 ft	113	3897
Edinger Circular Drain 1546 ft	73	3721
Edinger Circular Drain 1854 ft	50	4029

Table 2.6.2: Arsenic and Sulfur Isotope Data for Edinger Circular Drain - Groundwater Seeps, December 2004

Sample ID	Dissolved Arsenic (ug/L)	Sulfur Isotope (del 34S – SO4)
Edinger Circular Drain 324 ft	168	-2.4
Edinger Circular Drain 883 ft	73	0.5
Edinger Circular Drain 1107 ft	33	1.5
Edinger Circular Drain 1546 ft	23	1.5
Edinger Circular Drain 1854 ft	14	1.6

Table 2.6.3: Selenium, Nitrate, and Specific Conductance Data for Edinger Circular Drain - Groundwater Seeps, April 2005

Sample ID	Dissolved Selenium (ug/L)	Nitrate-Nitrogen (mg/L)	Specific Conductance (uS/cm)
Edinger Circular Drain 324 ft	65	3.3	8590
Edinger Circular Drain 883 ft	301	15.0	4241
Edinger Circular Drain 1107 ft	167	13.7	4022
Edinger Circular Drain 1546 ft	108	12.2	3930
Edinger Circular Drain 1854 ft	59	13.1	4050

Table 2.6.4: Selenium Speciation Data for Edinger Circular Drain - Groundwater Seeps, April 2005

Sample ID	Se VI (ug/L)	Se IV (ug/L)	Organic Se (ug/L)	Total Dissolved Se (ug/L)
Edinger Circular Drain 324 ft	55.0	10.1	<0.2	65.1
Edinger Circular Drain 883 ft	297.3	3.4	<0.2	300.7
Edinger Circular Drain 1107 ft	166.1	0.9	<0.2	167.0
Edinger Circular Drain 1546 ft	107.7	0.8	<0.2	108.5

Table 2.6.5: Selenium Speciation Data for Edinger Circular Drain - Groundwater Seeps, March 2007

Sample ID	Se VI (ug/L)	Se IV (ug/L)	Organic Se (ug/L)	Total soluble Se (ug/L)	% Se VI
Edinger Circular Drain 1854 ft	49.57	0.86	<0.2	50.43	98.3%
Edinger Circular Drain 1704 ft	57.55	0.89	<0.2	58.44	98.5%
Edinger Circular Drain 1546 ft	72.04	0.98	<0.2	73.02	98.6%
Edinger Circular Drain 1298 ft	91.86	1.08	<0.2	92.94	98.8%
Edinger Circular Drain 1107 ft	126.97	1.25	<0.2	128.22	99.0%
Edinger Circular Drain 883 ft	226.68	1.83	<0.2	228.51	99.2%
TRANSITION POINT					
Edinger Circular Drain 441 ft	63.19	7.70	<0.2	70.89	89.14%
Edinger Circular Drain 324 ft	61.32	7.47	<0.2	68.79	89.14%
Edinger Circular Drain 263 ft	65.31	7.32	<0.2	72.63	89.9%
PETERS CANYON WASH – 0 FT					

Table 2.6.6: Arsenic Speciation Data for Edinger Circular Drain - Groundwater Seeps, March 2007

Sample ID	As V (ug/L)	As III (ug/L)	DMAs (ug/L)	MMAs (ug/L)	% As V
Edinger Circular Drain 1854 ft	13.5	<0.08	<0.08	<0.08	~100
Edinger Circular Drain 1704 ft	20.8	<0.08	<0.08	<0.08	~100
Edinger Circular Drain 1546 ft	23.3	<0.08	<0.08	<0.08	~100
Edinger Circular Drain 1298 ft	29.2*	--	--	--	--
Edinger Circular Drain 1107 ft	33.6	<0.08	<0.08	<0.08	~100
Edinger Circular Drain 883 ft	90.3	<0.08	<0.08	<0.08	~100
TRANSITION POINT					
Edinger Circular Drain 441 ft	170.0	<0.08	<0.08	<0.08	~100
Edinger Circular Drain 324 ft	176.0	<0.08	<0.08	<0.08	~100
Edinger Circular Drain 263 ft	196.0	<0.08	<0.08	<0.08	~100
PETERS CANYON WASH – 0 FT					

DMAs – dimethylated arsenic
MMAs – monomethylated arsenic
*total soluble arsenic measured by AA

Table 2.6.7: Enrichment Data Calculations for Edinger Circular Drain - Groundwater Seeps, March 2007

Sample ID	Cl (mg/L)	Cl Enrichment. Factor* Value/Value @ 883 ft	SO4 (mg/L)	SO4 Enrichment Factor* Value/Value @ 883 ft
Edinger Circular Drain 883 ft	379	1.0	1246	1.0
TRANSITION POINT				
Edinger Circular Drain 441 ft	576	1.52	2364	1.89
Edinger Circular Drain 324 ft	638	1.68	2529	2.03
Edinger Circular Drain 263 ft	652	1.72	2591	2.08

Sample ID	Br (mg/L)	Br Enrichment. Factor* Value/Value @ 883 ft	As (mg/L)	As Enrichment Factor* Value/Value @ 883 ft
Edinger Circular Drain 883 ft	1.54	1.0	90.3	1.0
TRANSITION POINT				
Edinger Circular Drain 441 ft	2.52	1.64	170.0	1.88
Edinger Circular Drain 324 ft	2.79	1.81	176.0	1.95
Edinger Circular Drain 263 ft	2.80	1.82	196.0	2.17
PETERS CANYON WASH – 0 FT				

*Calculated by dividing chemical value at seep by value at Edinger Circular Drain @ 883 ft

Table 2.6.8: Additional Redox Sensitive Parameters for Edinger Circular Drain - Groundwater Seeps, March 2007

Sample ID	Fe (ug/L)	Mn (ug/L)	NO3-N (mg/L)	NH3-N (mg/L)
Edinger Circular Drain 1854 ft	<5	<2	14.65	<0.1
Edinger Circular Drain 1704 ft	<5	<2	14.32	<0.1
Edinger Circular Drain 1546 ft	<5	<2	13.85	<0.1
Edinger Circular Drain 1298 ft	<5	<2	13.75	<0.1
Edinger Circular Drain 1107 ft	<5	<2	13.64	<0.1
Edinger Circular Drain 883 ft	<5	<2	13.41	<0.1
TRANSITION POINT				
Edinger Circular Drain 441 ft	<5	7	2.73	<0.1
Edinger Circular Drain 324 ft	<5	30	2.71	<0.1
Edinger Circular Drain 263 ft	<5	70	2.72	<0.1
PETERS CANYON WASH – 0 FT				

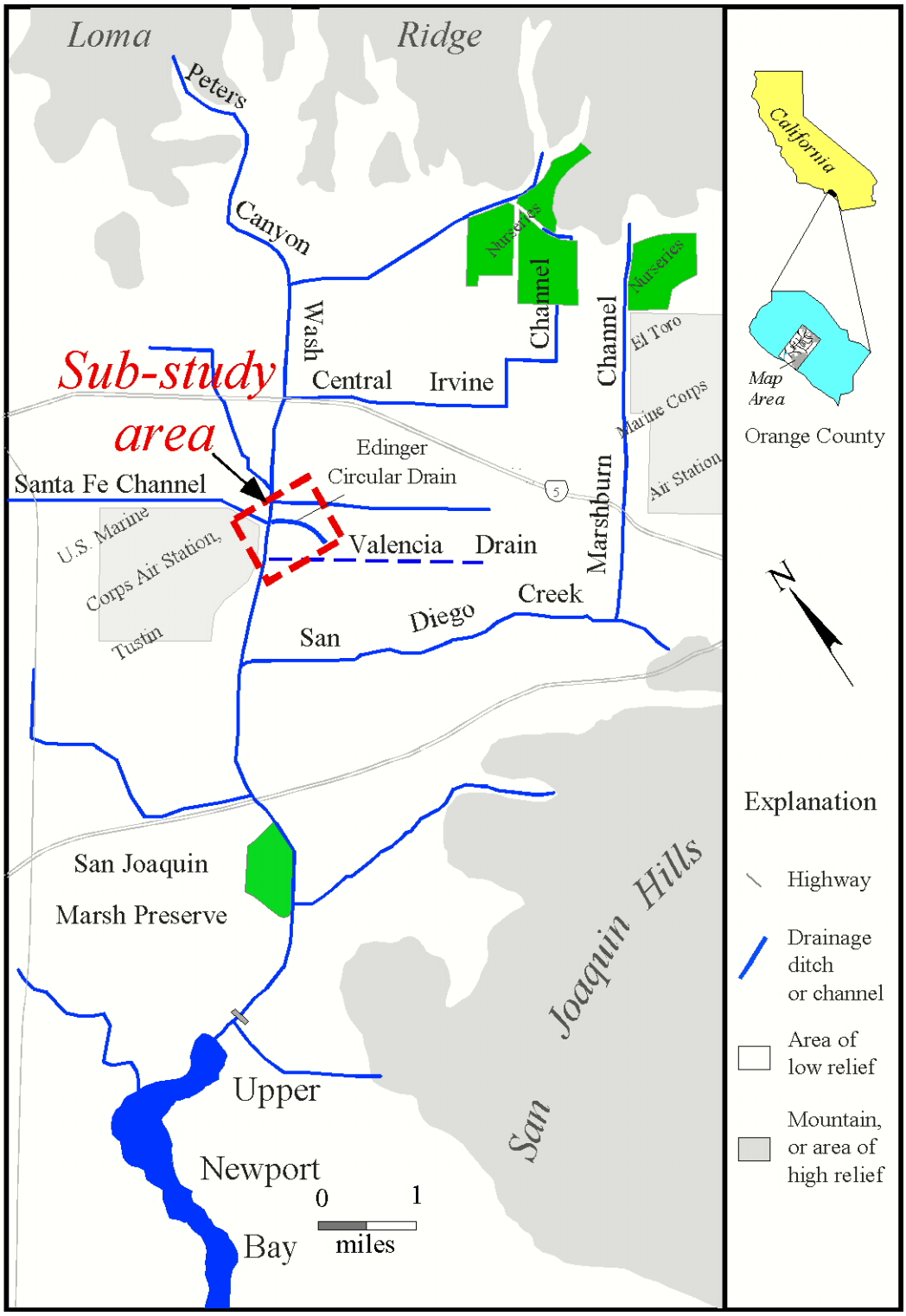


Figure 2.6.1. Location of Edinger Circular Drain sub-study area.

Figure 2.6.2. Outlet of Edinger Circular Drain.

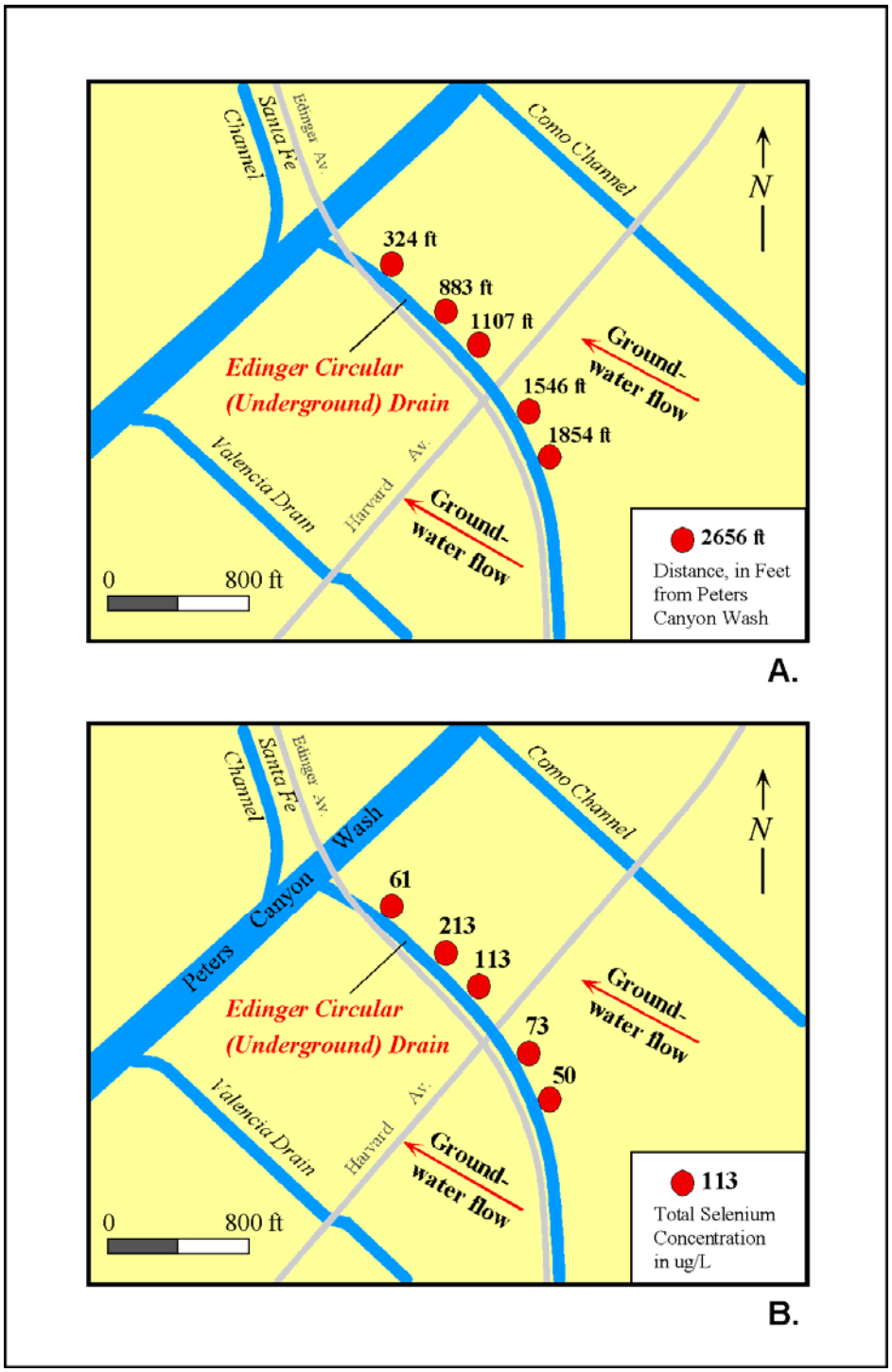


Figure 2.6.3. Selenium concentrations in groundwater in Edinger Circular Drain during December 2004 studies. Figure 2.6.3A shows groundwater sample locations, in feet from Peters Canyon Wash. Figure 2.6.3B shows total selenium values in groundwater at the five groundwater sample points.

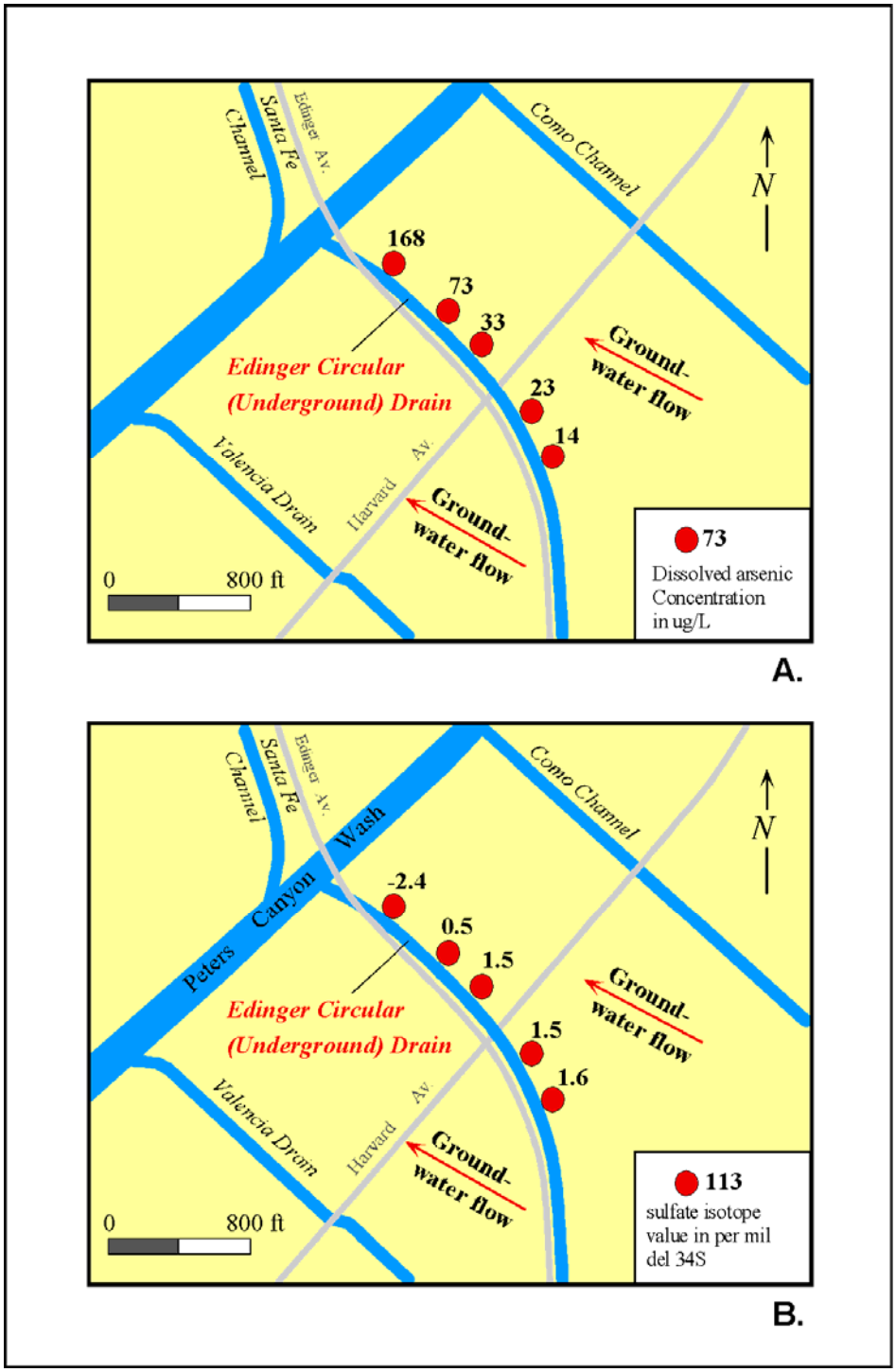


Figure 2.6.4. Arsenic and sulfur isotope values in groundwater in Edinger Circular Drain during December 2004 studies. Figure 2.6.4A shows total dissolved arsenic values and Figure 2.6.4B shows sulfur isotope values (per mil del 34S) in groundwater at the five groundwater sample points.

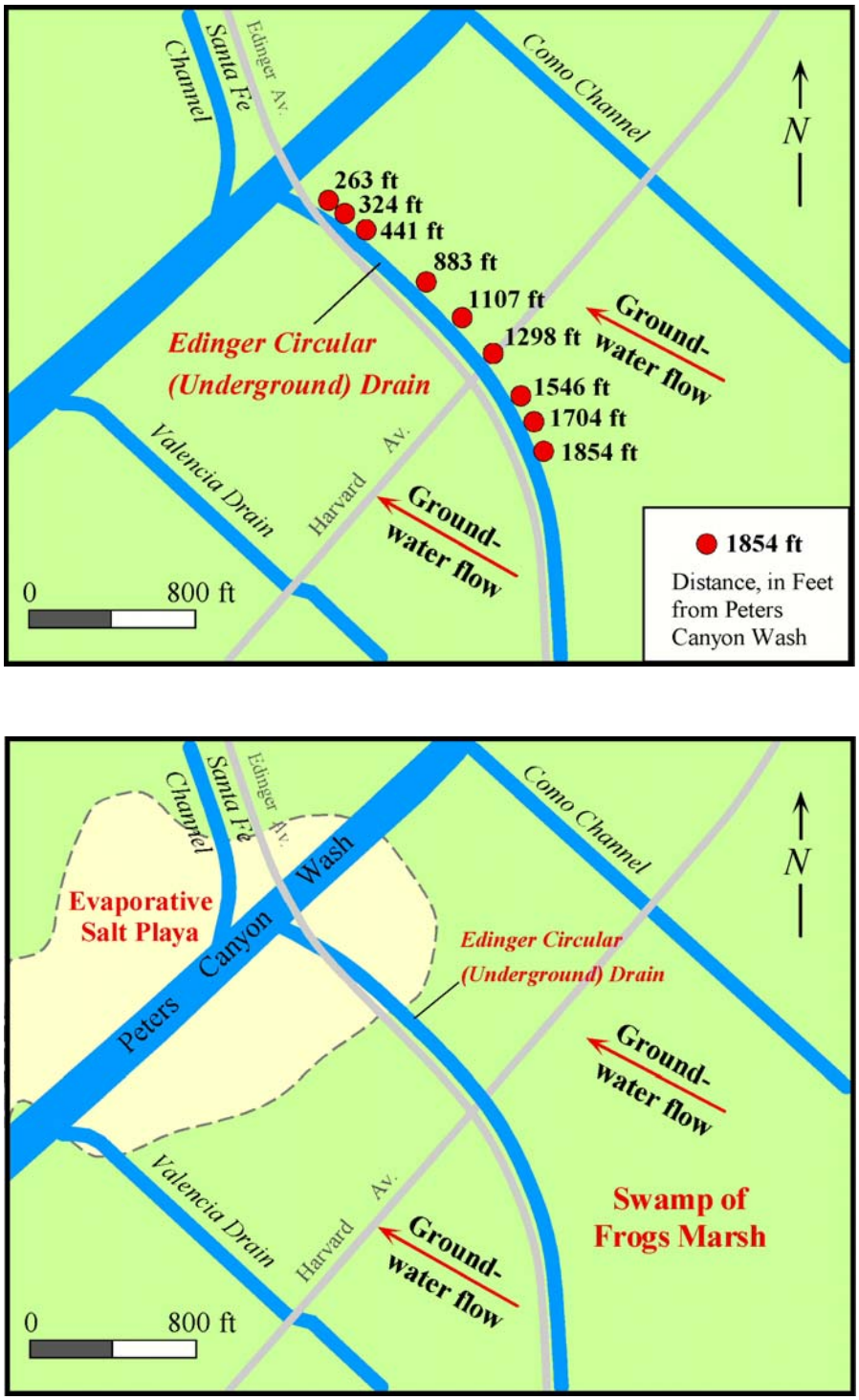


Figure 2.6.5. Groundwater sampling sites in Edinger Drain during March, 2007 sampling run. Edinger drain crosses a newly interpreted historic alkali flat (i.e., evaporative salt playa; or phreatic playa) that is thought to be an important source of high arsenic in the area.

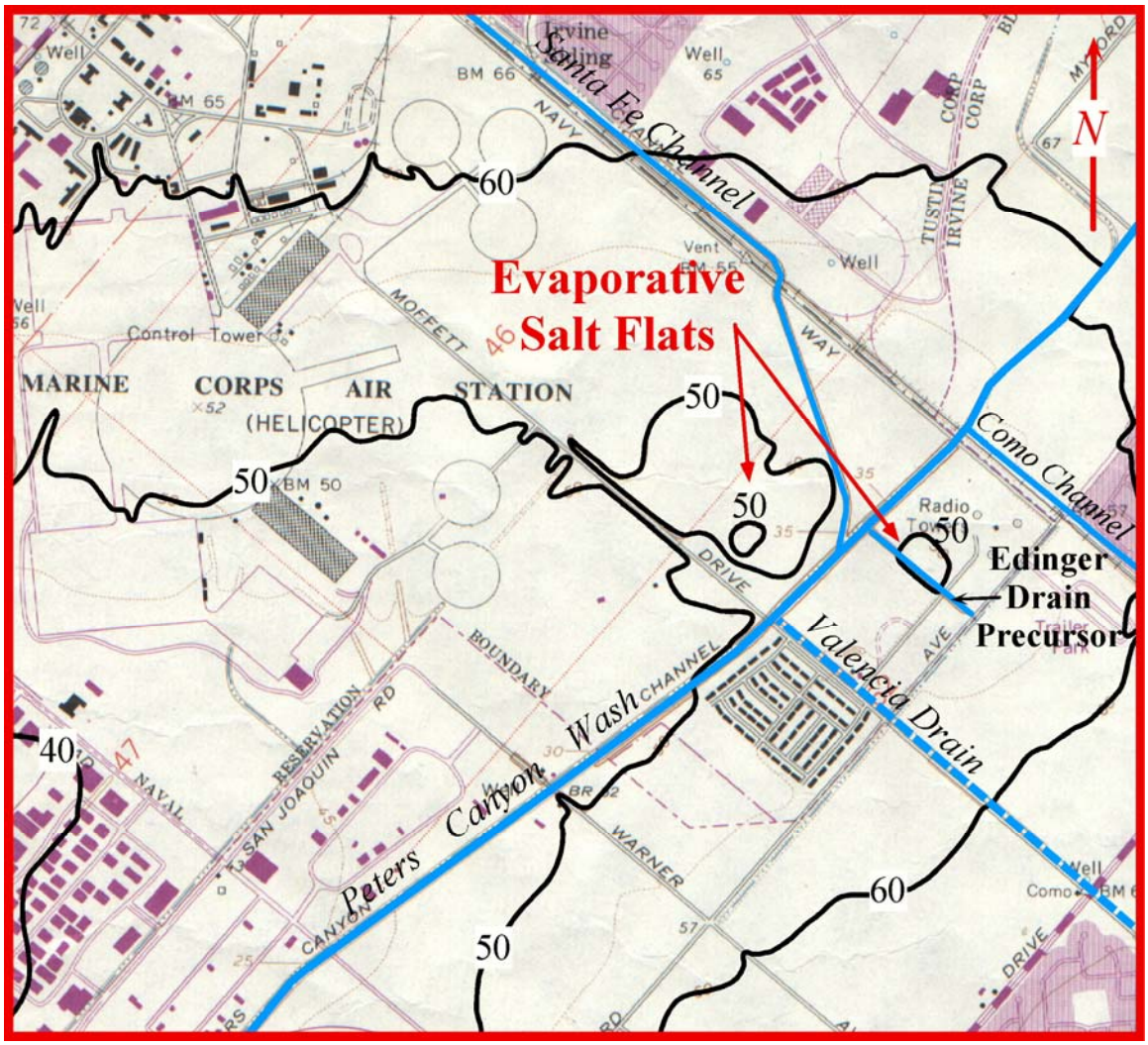


Figure 2.6.6. Topographic contours from USGS map shows areas of low lying and flat elevation near the confluence of Edinger Drain, Santa Fe Drain, and Peters Canyon Wash. Such areas had high evaporation rates and slow drainage of surface water and groundwater during predevelopment times, leading to accumulation of heavy alkali in soils. Contour elevations in feet above sea level.

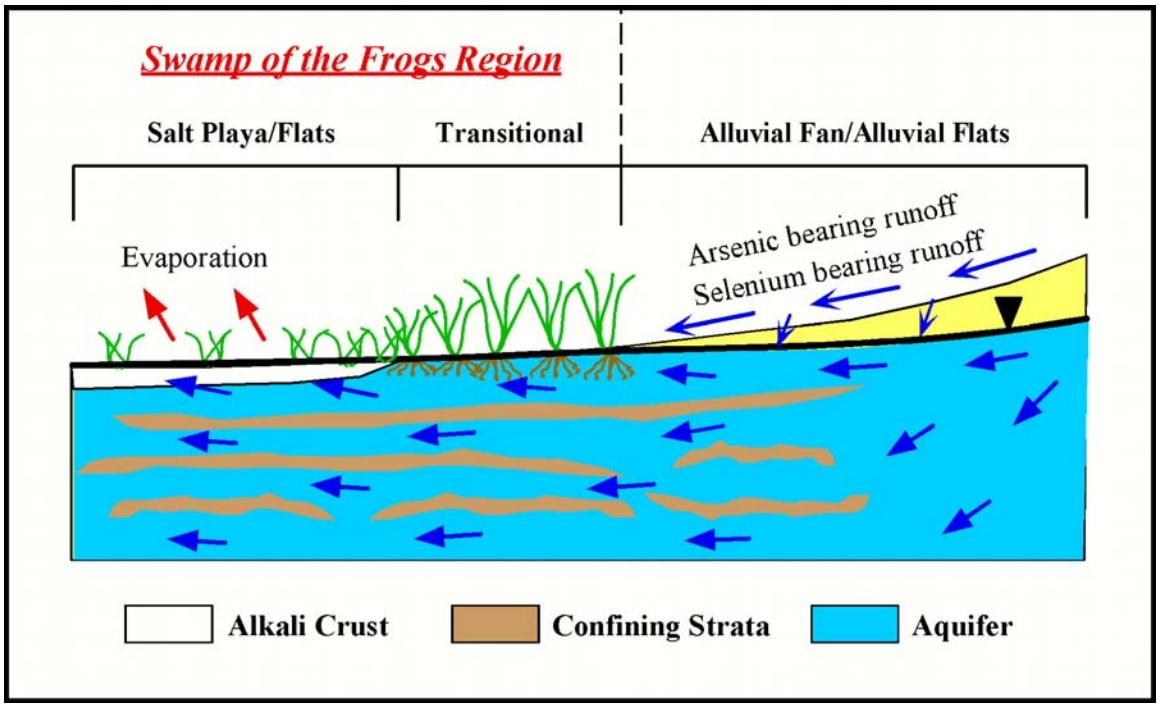


Figure 2.6.7. Conceptual figure showing how the alkali salt flats relate spatially to the Transitional (outer) Swamp of the Frogs marsh and areas above the marsh.

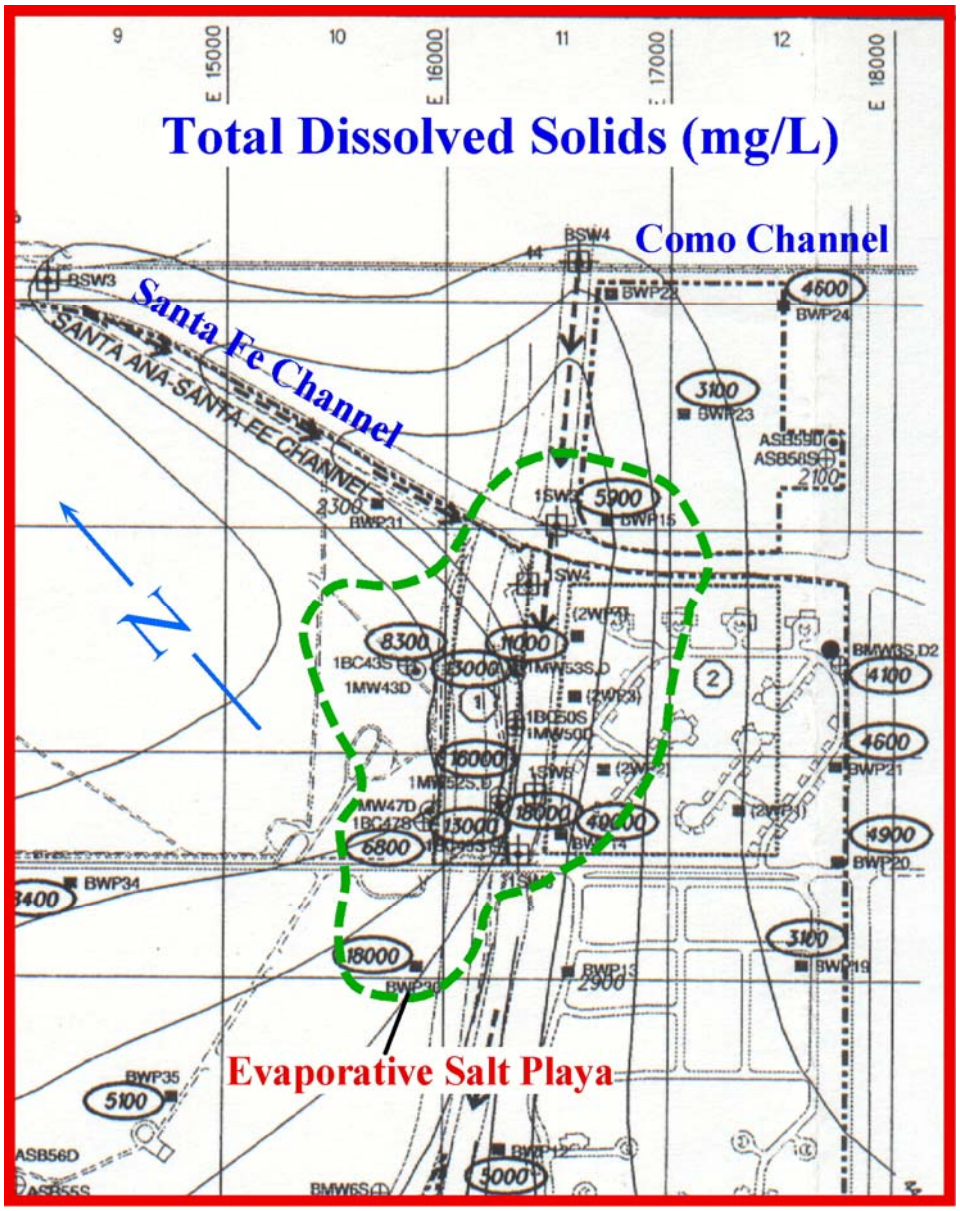


Figure 2.6.8. Bechtel map showing high total dissolved solids in groundwater (1st water bearing unit) within the area interpreted to be a historic alkali salt flat (green stipple). All values of total dissolved solids shown in mg/L. Most TDS values within the stippled boundary are greater than 10,000 mg/L, reaching values up to 40,000 mg/L.

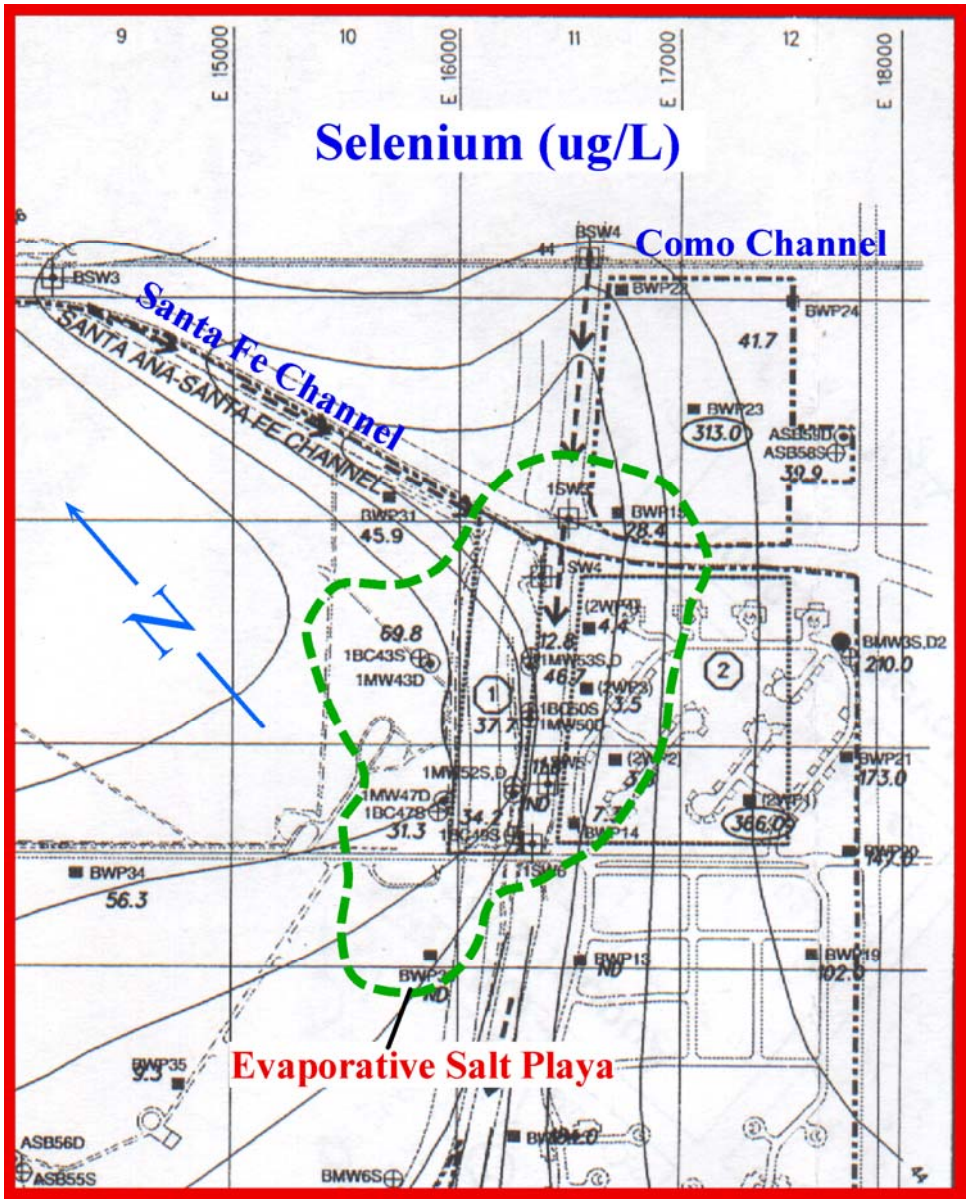


Figure 2.6.9. Bechtel map showing generally low selenium concentrations in groundwater (1st water bearing unit) within the area interpreted to be a historic alkali salt flat (green stipple). All values of selenium in ug/L. Selenium values are typically above 100 ug/L in the region to the southeast of the alkali flat. Many selenium values within the alkali flat are less than 10 ug/L.

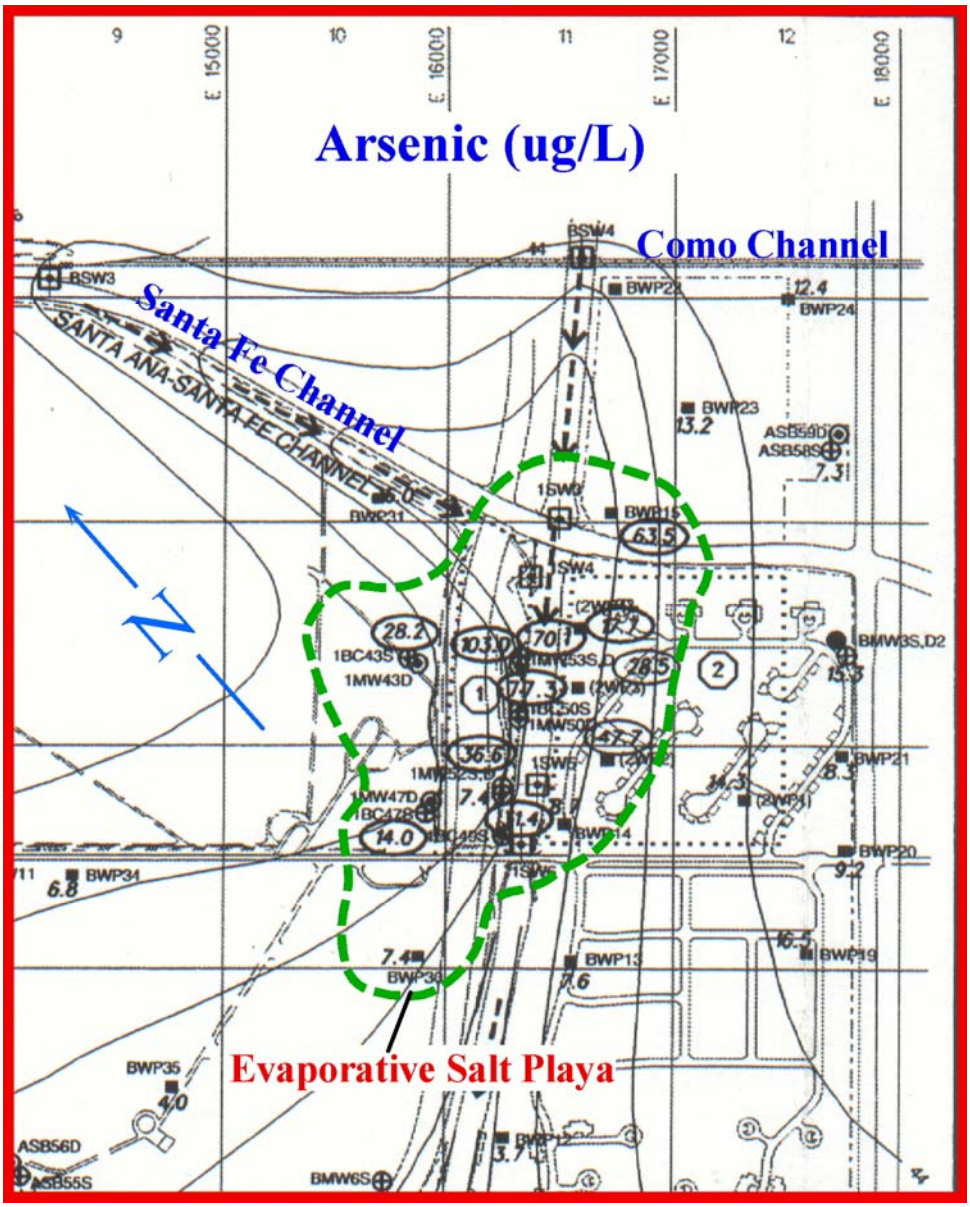
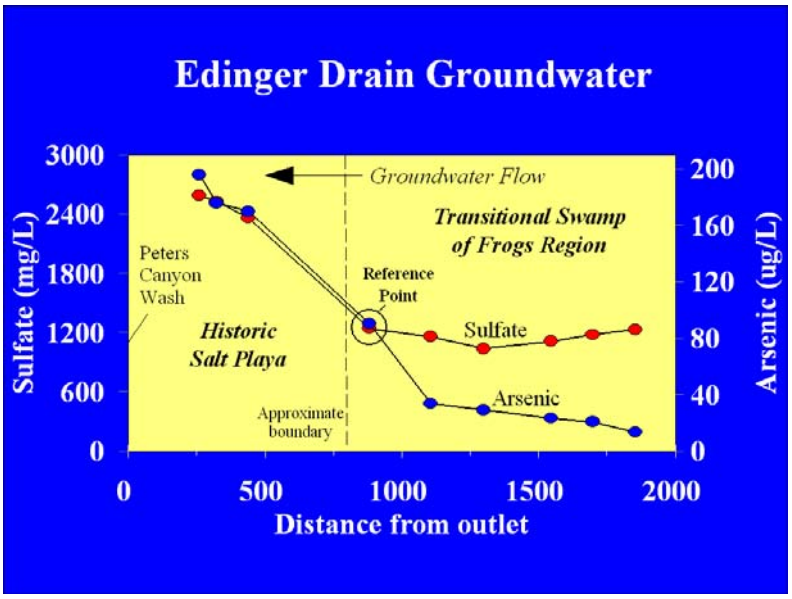


Figure 2.6.10. Bechtel map showing high arsenic concentrations in groundwater (1st water bearing unit) within the area interpreted to be a historic alkali salt flat (green stipple). All values of arsenic shown in ug/L. Many arsenic values within the stippled boundary are greater than 30 ug/L, reaching values up to 103 ug/L.



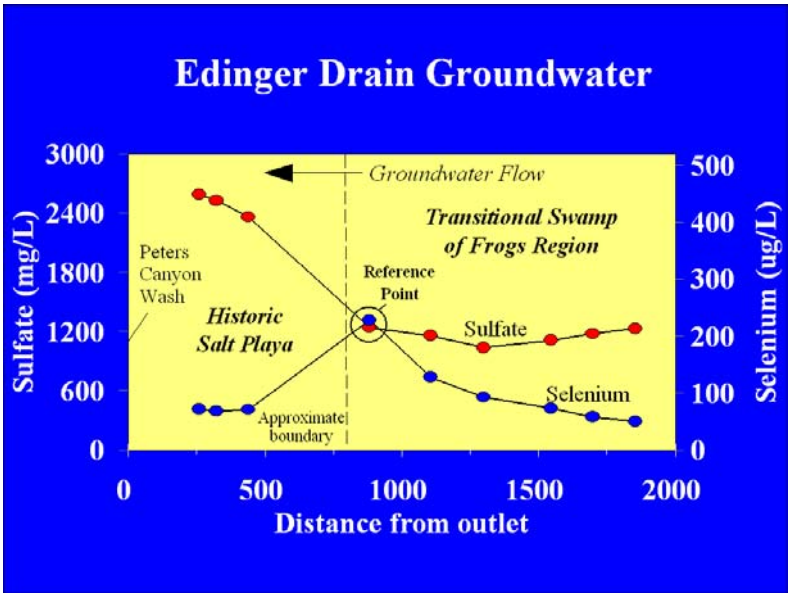
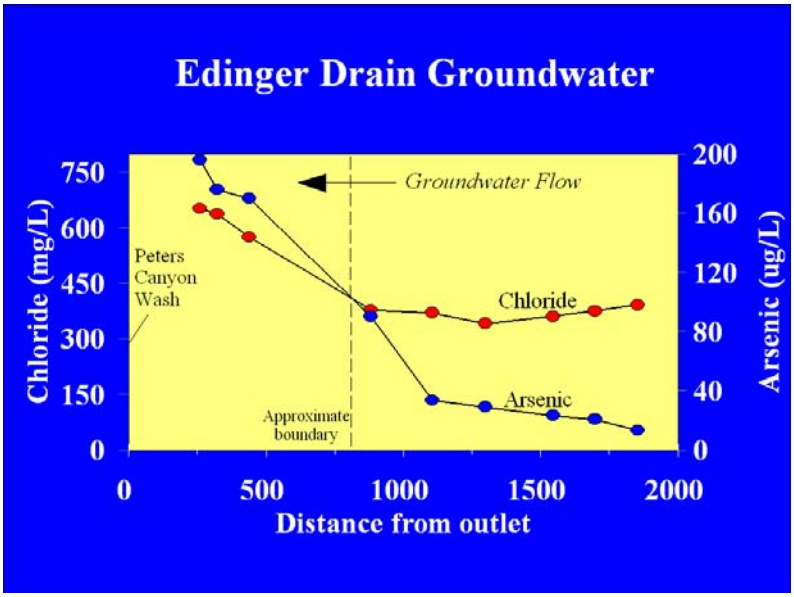


Figure 2.6.11. Graphs showing concentrations of sulfate and arsenic (upper figure) and sulfate and selenium (lower figure) in groundwater in Edinger Drain. The reference point is calibrated on the axis scale so the points overlap directly for the ions on the relative axes right above the salt flats (dashed line). Sulfate doesn't vary much in the transitional region (right of dashed line), where selenium and arsenic both increase. As groundwater moves into the alkali region (left of dashed line), sulfate and arsenic increase in concentration in a proportional manner, whereas selenium decreases sharply in concentration. Evaporative enrichment of arsenic and sulfate is implied in the alkali salt flats region.



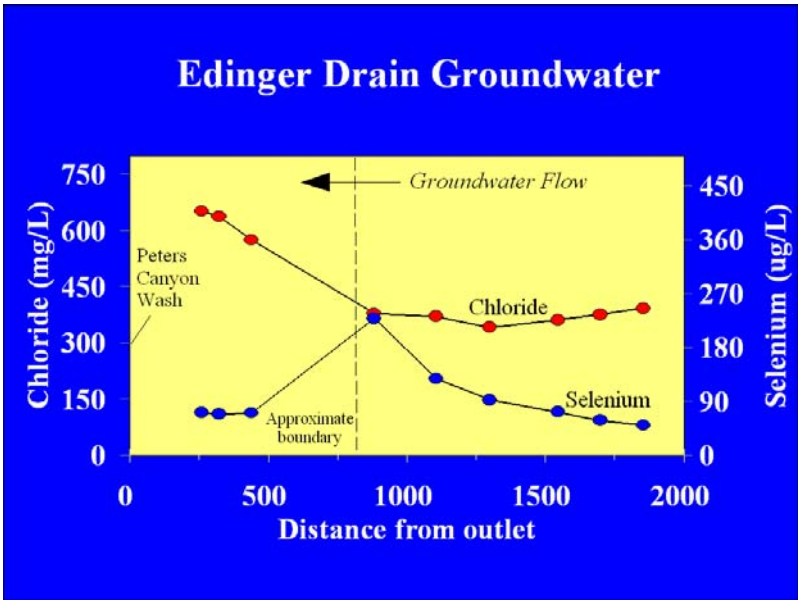
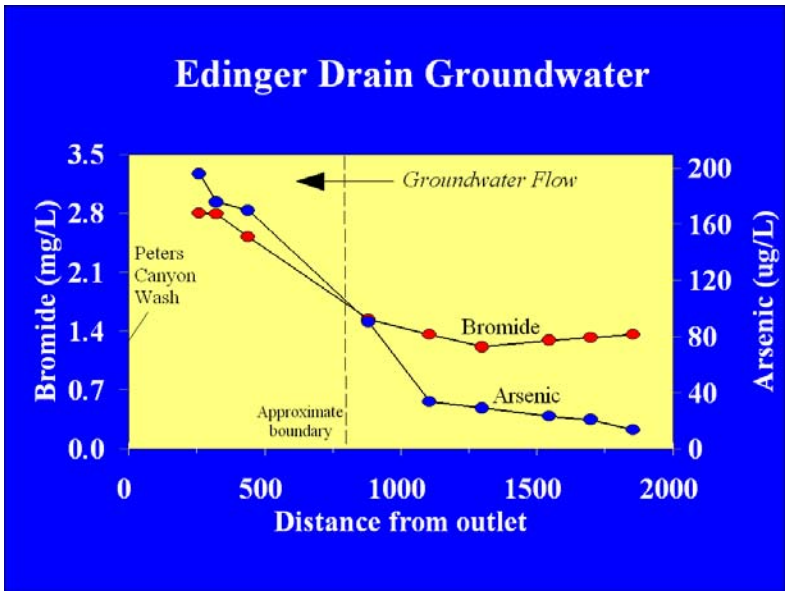


Figure 2.6.12. Graphs showing concentrations of chloride and arsenic (upper figure) and chloride and selenium (lower figure) in groundwater in Edinger Drain. The reference point is calibrated on the axis scale so the points overlap directly for the ions on the relative axes right above the salt flats (dashed line). Chloride doesn't vary much in the transitional region (right of dashed line), whereas selenium and arsenic both increase. As groundwater moves into the alkali region (left of dashed line), chloride and arsenic increase in concentration in a nearly proportional manner, whereas selenium decreases sharply in concentration. Evaporative enrichment of arsenic and chloride is implied in the alkali salt flats region.



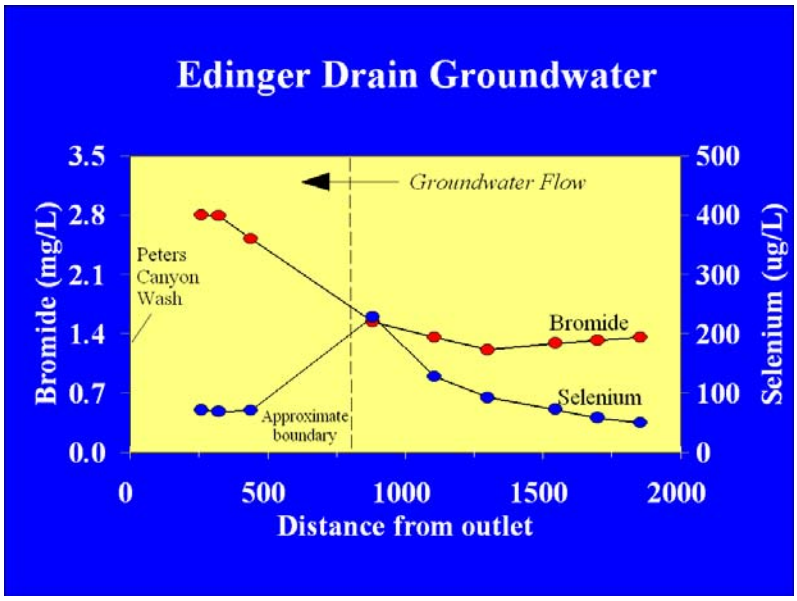
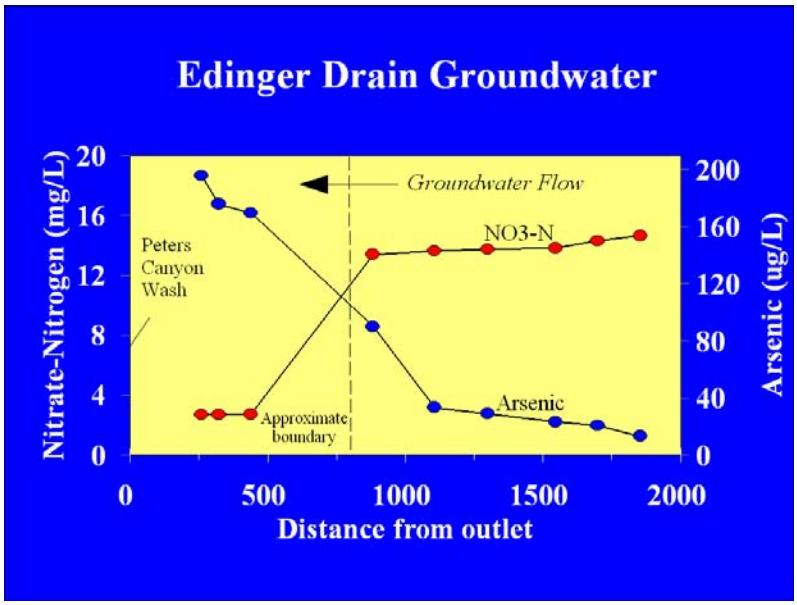


Figure 2.6.13. Graphs showing concentrations of bromide and arsenic (upper figure) and bromide and selenium (lower figure) in groundwater in Edinger Drain. The reference point is calibrated on the axis scale so the points overlap directly for the ions on the relative axes right above the salt flats (dashed line). Bromide doesn't vary much in the transitional region (right of dashed line), whereas selenium and arsenic both increase. As groundwater moves into the alkali region (left of dashed line), bromide and arsenic increase in concentration in a nearly proportional manner, whereas selenium decreases sharply in concentration. Evaporative enrichment of arsenic and bromide is implied in the alkali salt flats region.



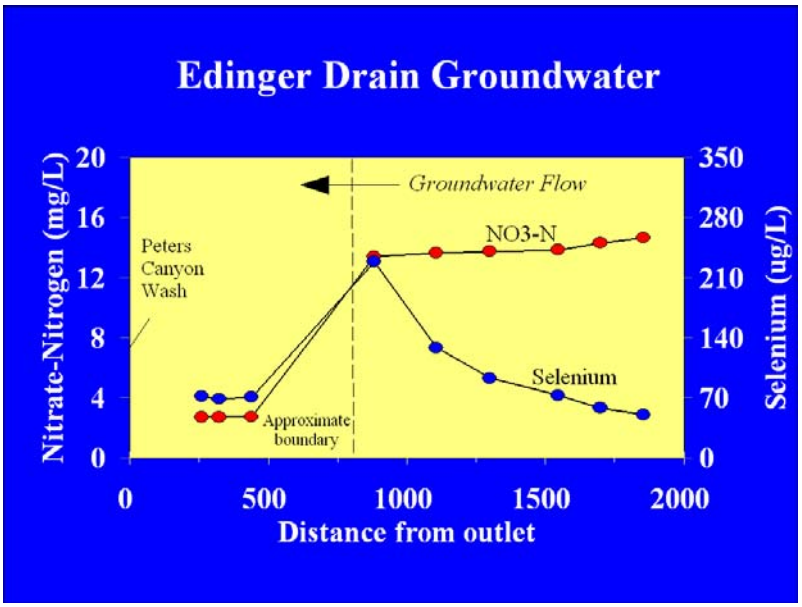


Figure 2.6.14. Graphs showing concentrations of nitrate and arsenic (upper figure) and nitrate and selenium (lower figure) in groundwater in Edinger Drain. The reference point is calibrated on the axis scale for selenium so the points overlap directly for the ions on the relative axes right above the salt flats (dashed line). Nitrate is very high but doesn't vary much in the transitional region (above dashed line), whereas selenium and arsenic both increase. As groundwater moves into the alkali region (below dashed line), arsenic continues to increase in concentration, whereas selenium and nitrate decrease sharply in concentration. Oxidation of reduced forms of selenium by nitrate may be implied in the region above the alkali salt flats.

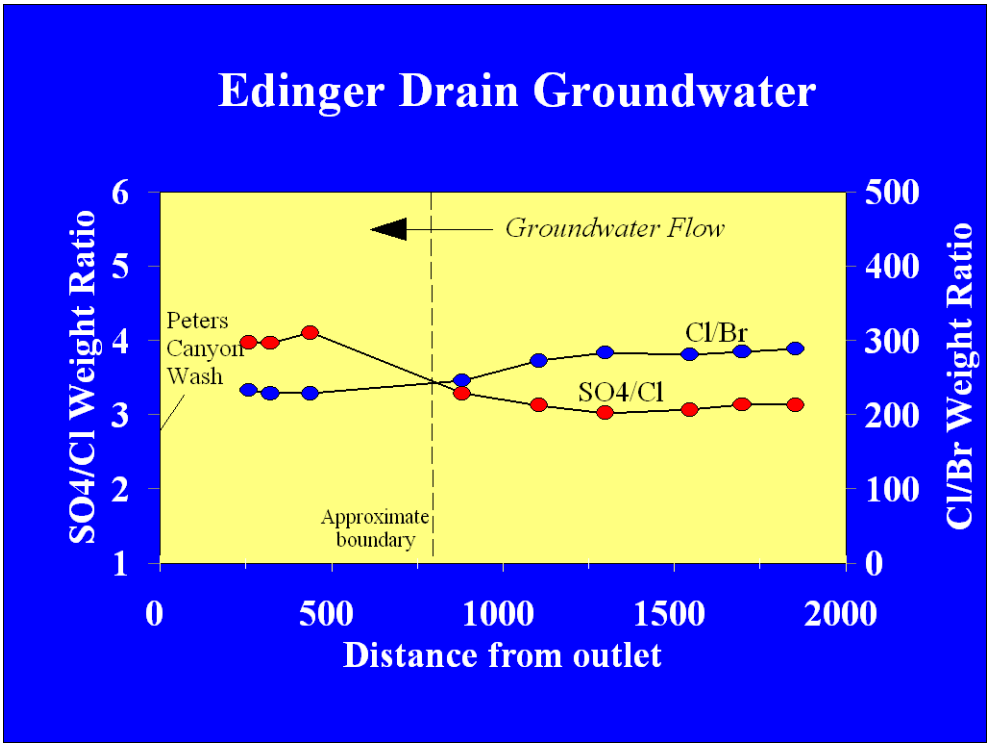
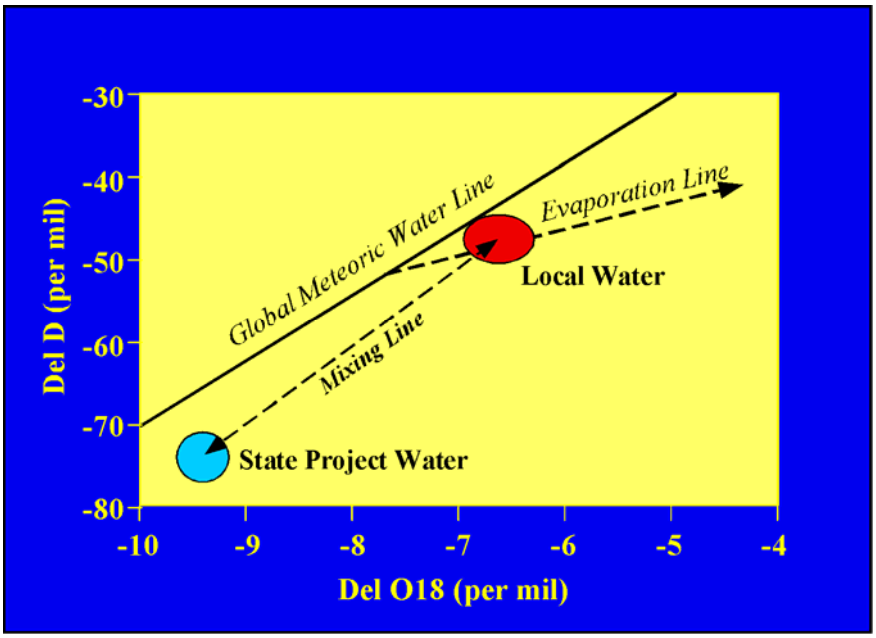
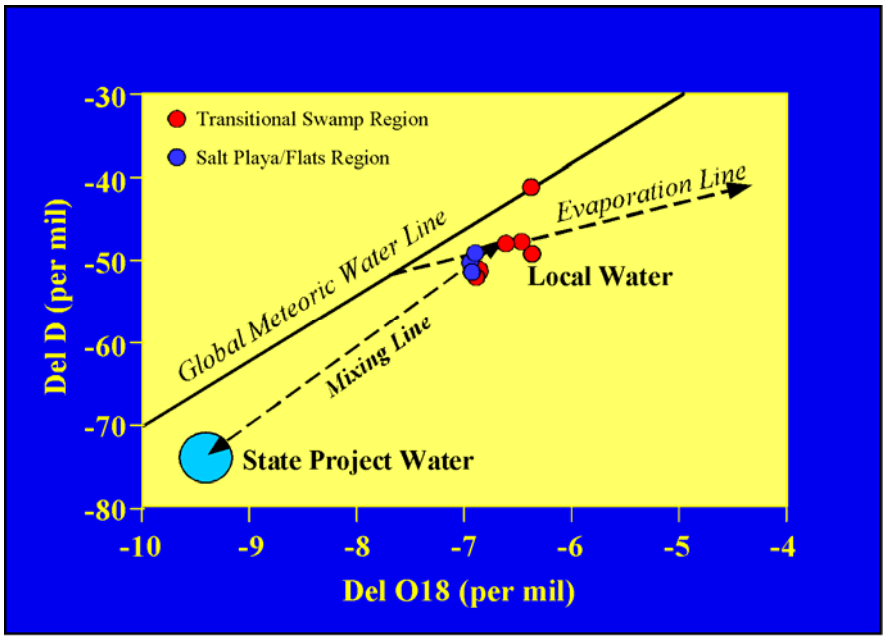


Figure 2.6.15. Graphs showing Cl/Br and SO4/Cl ratios in groundwater in the transitional (above dashed line) and alkali (below dashed line) regions in Edinger Circular Drain. Ion ratios do not vary substantially along the groundwater flowpath.



A.



B.

Figure 2.6.16. Stable isotope data for Edinger Circular Drain. Figure 2.6.16A shows the evaporation line that defines most shallow groundwater in San Diego Creek Watershed. The mixing line for State Project Water was mapped where state project water was found in the shallow aquifer of San Diego Creek Watershed. Groundwaters within the Transitional Swamp Region and Historical Salt Flats are isotopically similar (Figure 2.6.16B). This means that saline groundwater within the salt flats forms from dissolution of salts during aquifer recharge, and not due to pure evaporation of groundwater.

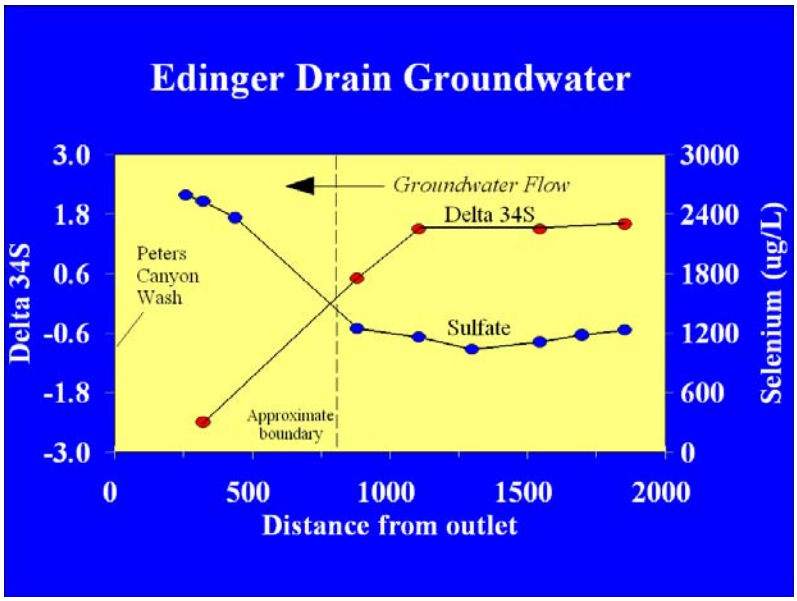


Figure 2.6.17. Sulfur isotope values and sulfate concentrations for groundwater within Edinger Circular Drain. Sulfate isotope signatures and sulfate concentrations do not vary much in the Transitional Swamp Region (above dash line). This implies that sulfides did not precipitate in this upper region during predevelopment times. Sulfur isotope signatures are negative within the Historic Salt Flats (below dash line), suggesting that sulfides formed in this lower region in the predevelopment period. Higher sulfate concentrations within the contemporary groundwaters of the Historic Salt Flats is thought to be due to dissolution of sulfate salts, but some sulfide oxidation is indicated by the negative sulfur isotope signatures. The leaching of sulfate salts from salt flats, combined with moderate or minor sulfide oxidation in soils beneath the salt flats, causes the elevated sulfate concentration and isotopically lighter sulfur isotopes in the salt flats area.

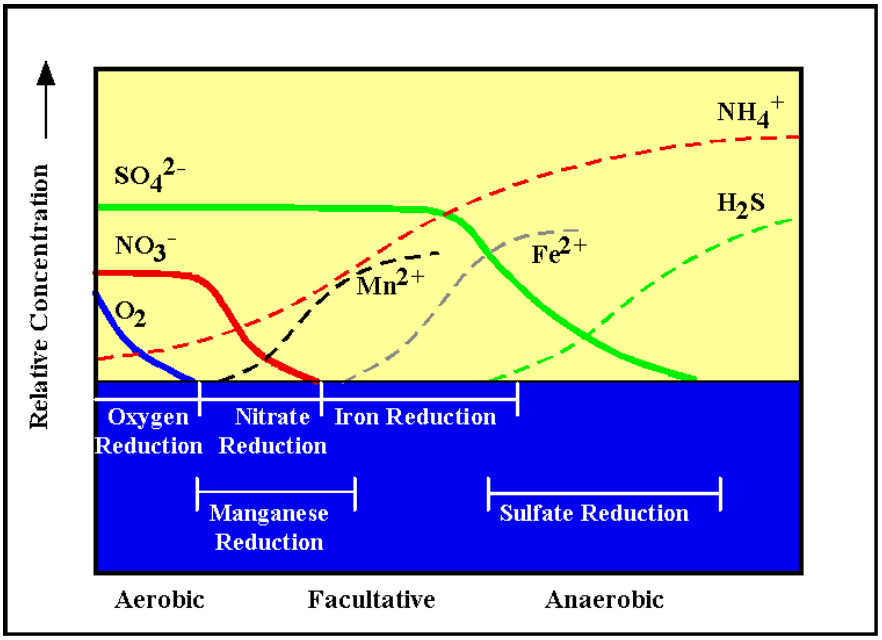


Figure 2.6.18. Stability domains for ions based on redox conditions in natural waters. This diagram is relevant to redox systematics and stability of trace elements in shallow groundwater in the Edinger Drain area (modified from Kadlec and Knight, 1996).

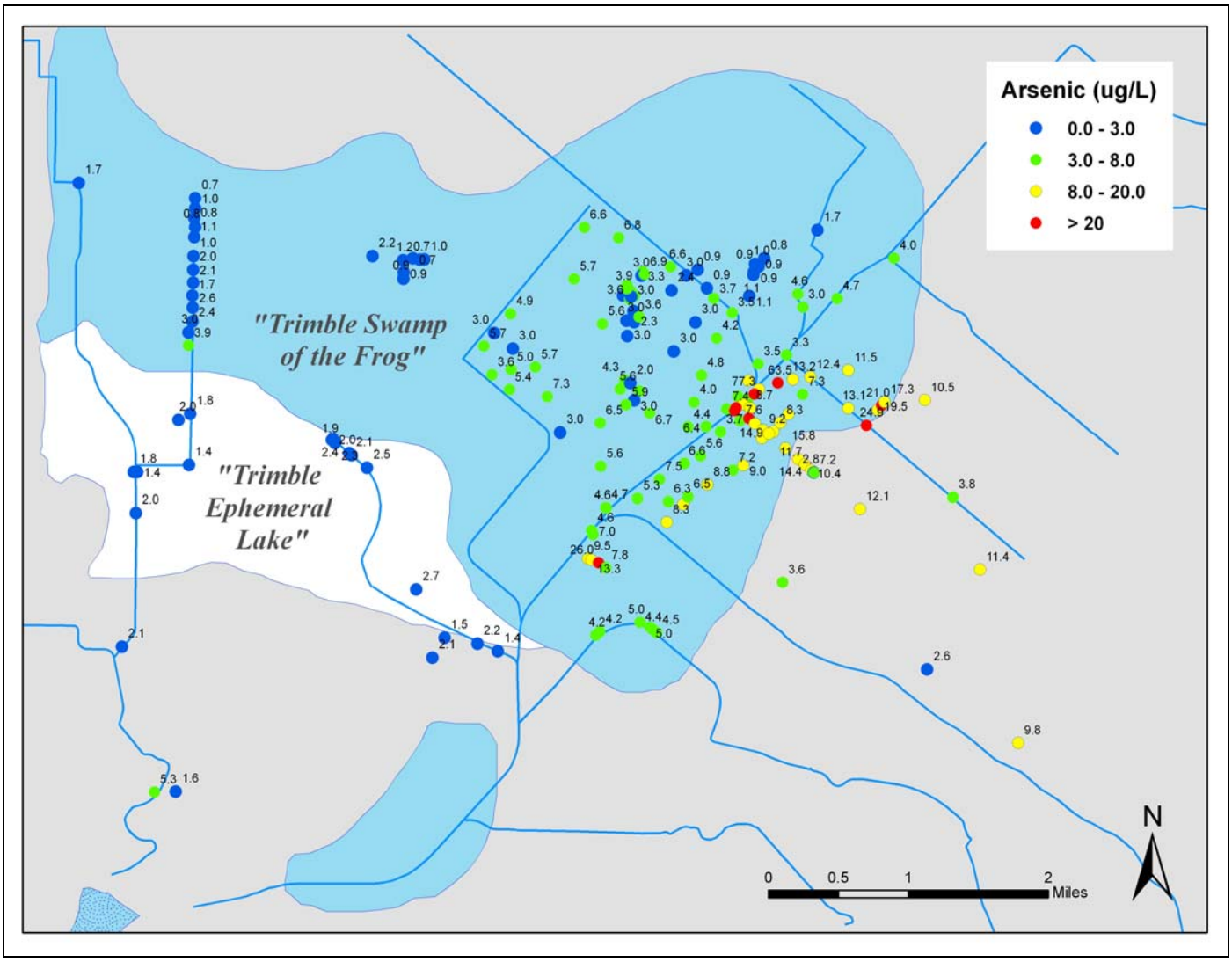


Figure 2.6.19. Provisional arsenic map for shallow groundwater in San Diego Creek Watershed. Arsenic is already relatively high in shallow groundwater above the Swamp of the Frogs Marsh in the areas west of the marsh (upper San Diego Creek/upper Como Channel area). Once the arsenic enriched groundwater (and surface water?) reached the salt flats area near the confluence of Santa Fe Channel and Peters Canyon Wash, it evaporated in predevelopment times, leaving behind alkali salts enriched in arsenic, sulfate, chloride, bromide, and other salts. The salts and arsenic contained in the historic salt crusts are now leaching into groundwater in the lower Edinger Drain area.

Figure 2.6.20. Soil profiles in trenches near Edinger Drain and Harvard Avenue show soil zones that are oxidized (red iron staining) along with layers of phreatic caliche (white layers). This area is well inside of the Transitional Swamp Region of the Historic Swamp of the Frogs Marsh (see Figure 2.6.7). Soil profiles suggest that the transitional swamp zone was not highly reducing in predevelopment times, supporting the interpretation of arsenic sorption to iron and aluminum oxides, organics, and clays and intermediate selenium reduction to selenite (selenium IV). Conditions were not sufficiently reducing in the Transitional Swamp Region to form selenide or sulfides.

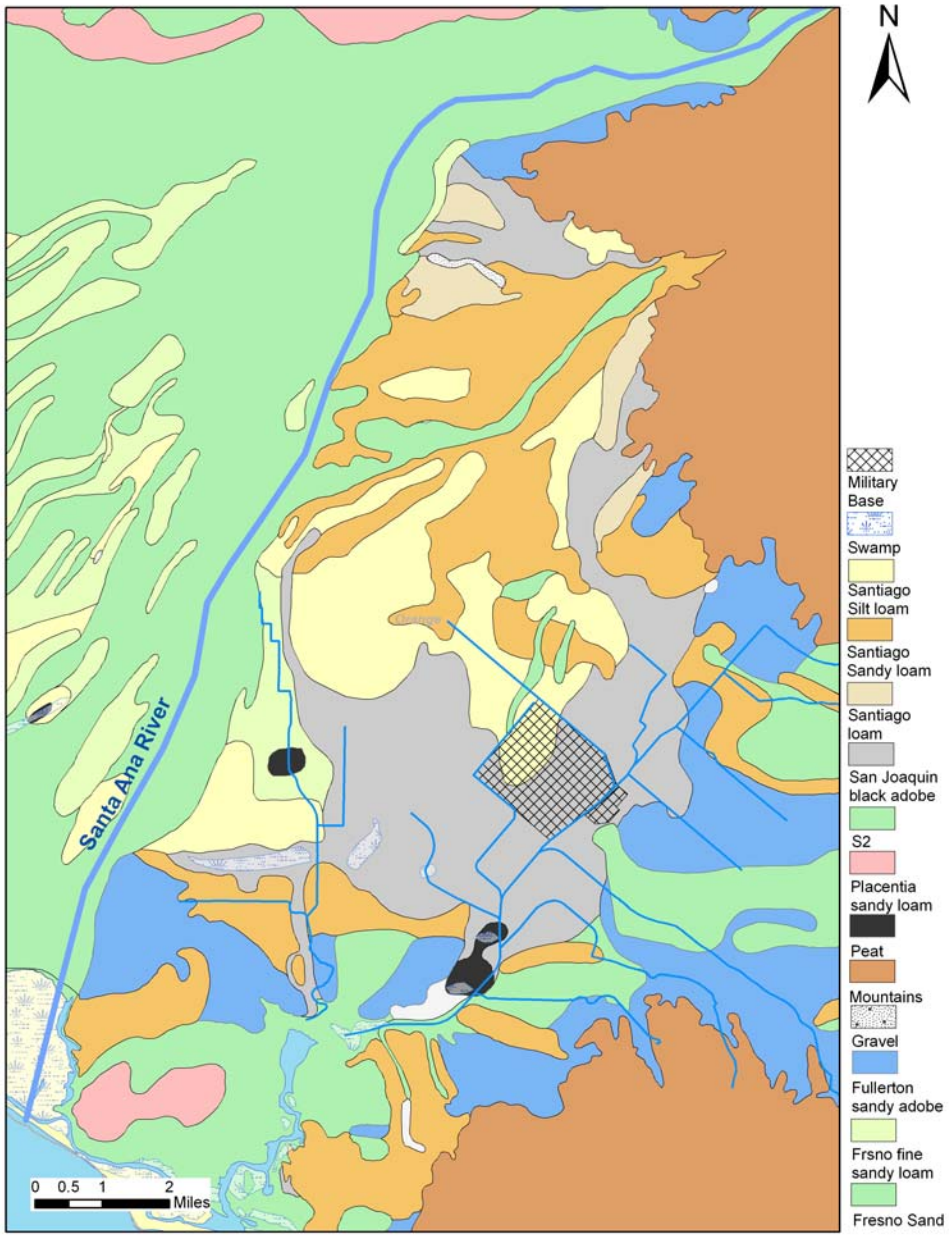


Figure 2.6.21. Modification of USDA soil map published in 1900 (from Holmes, 1901). Using Tustin Air Base and mountains as a reference, the green Fresno Sand and orange Santiago Sandy Loam areas represent antecedent drainages that flowed into the Swamp of the Frogs Marsh (Frog Marsh roughly delineated by San Joaquin Black Adobe). El Modena Channel, Santa Ana Delhi Channel, and Santa Fe Channel areas are sourced from the same mountains as Santiago Creek (upper middle, linear deposit of Fresno Sand). Como Channel and San Diego Creek drainage areas are sourced from mountain areas not shown in the soil map. San Joaquin Channel and Sand Canyon Channel sourced from the San Joaquin Hills (bottom right).

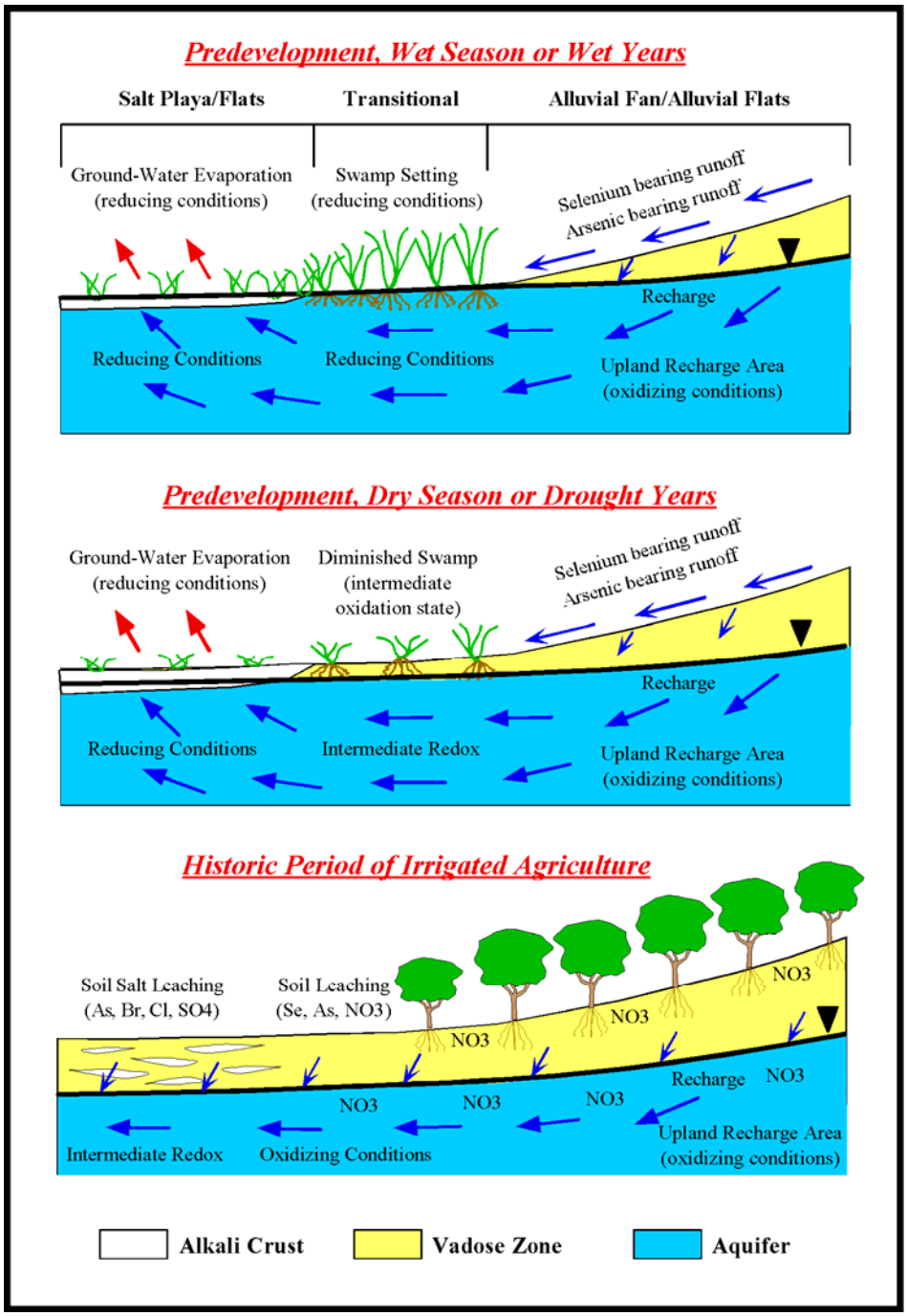


Figure 2.6.22. Time series conceptual models for water table and land surface conditions along a transect extending approximately from Peters Canyon Wash to Jeffrey Avenue, along and above Edinger Drain.

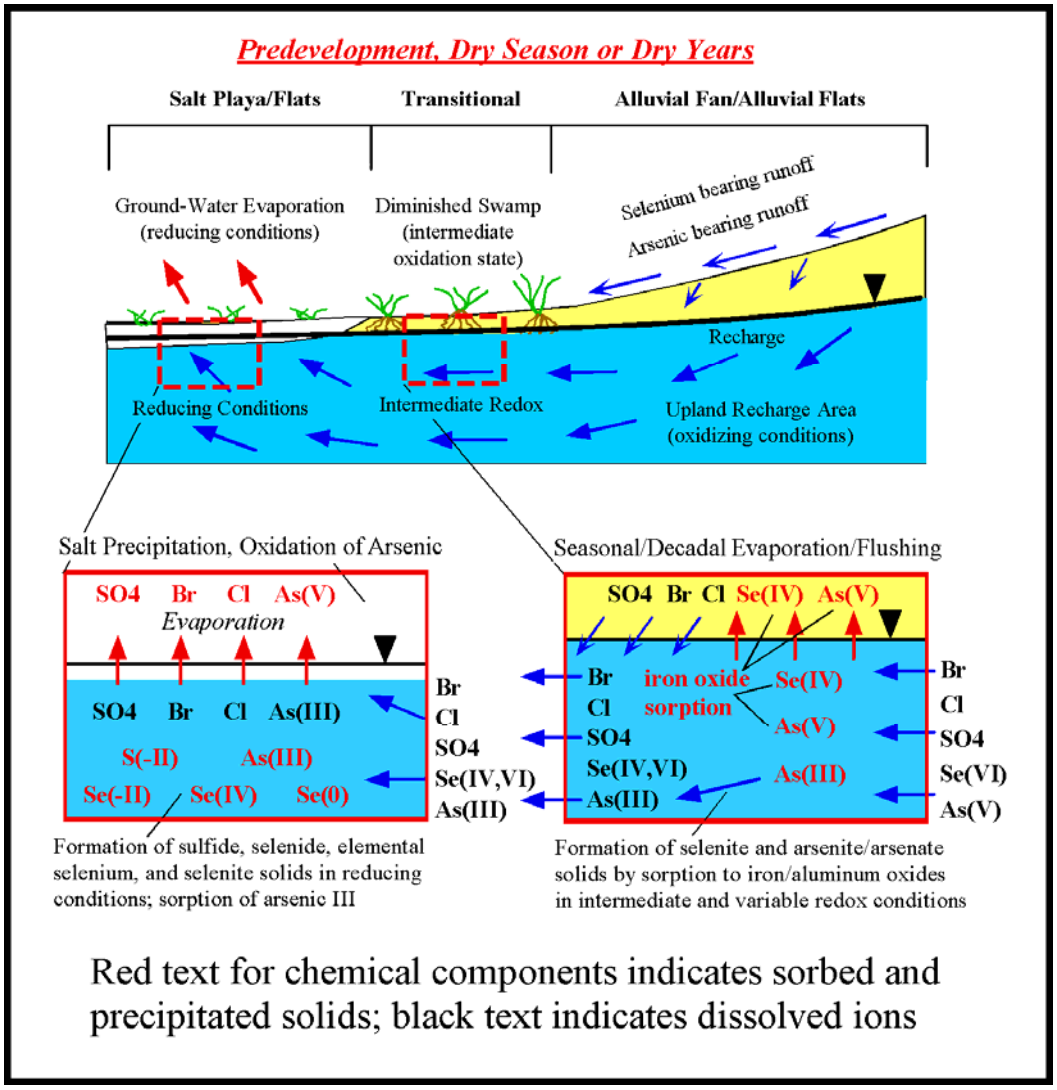


Figure 2.6.23. Predevelopment conceptual models for water table and land surface conditions along a transect extending approximately from Peters Canyon Wash to Jeffrey Avenue, along and above Edinger Drain. Inset regions show hypothesized and interpreted details for hydrochemical processes, and migration and attenuation of solutes in the Transitional Swamp Region and Historic Alkali Salt Flats Region.

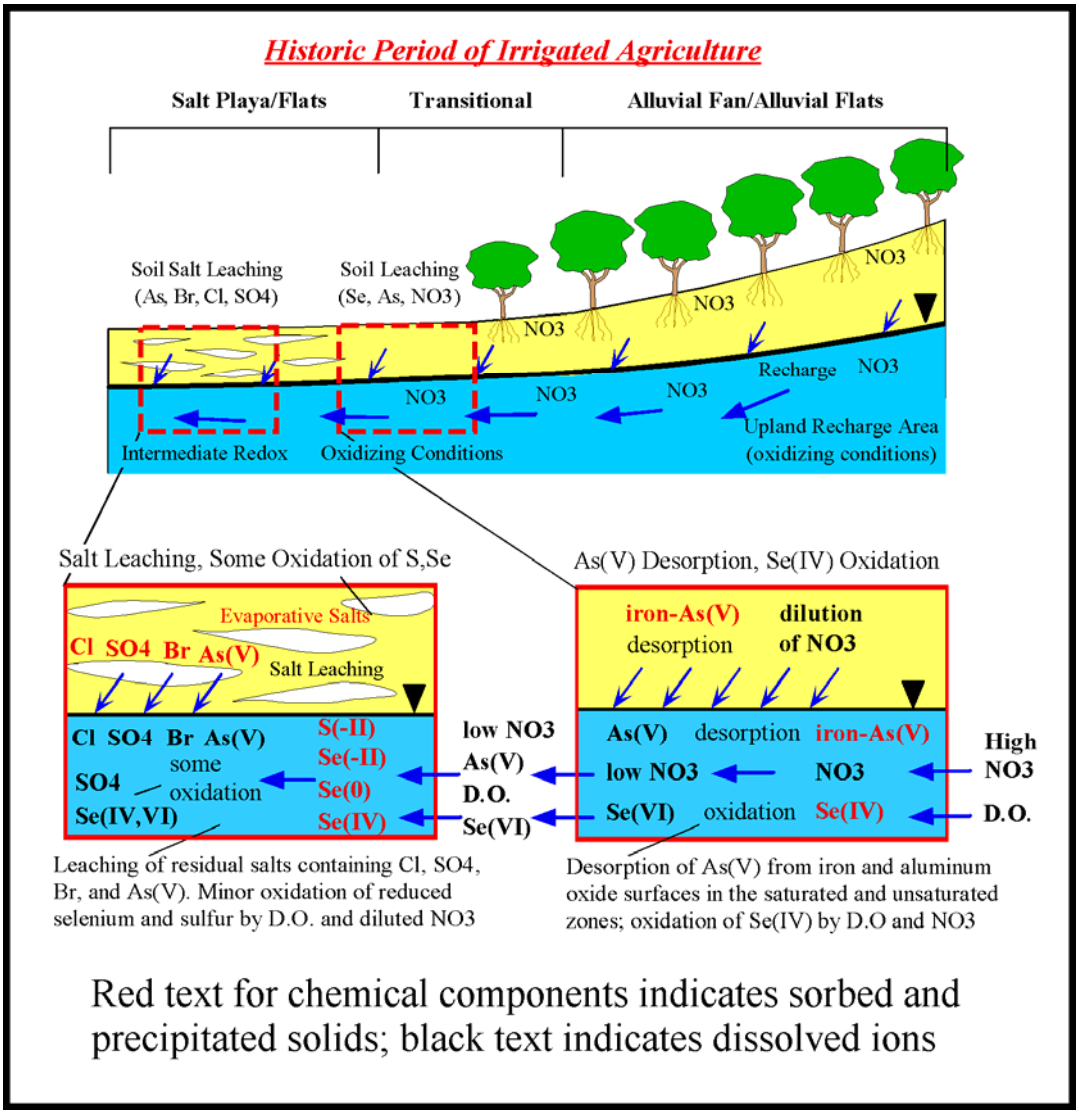


Figure 2.6.24. Postdevelopment conceptual models for water table and land surface conditions along a transect extending approximately from Peters Canyon Wash to Jeffrey Avenue, along and above Edinger Drain. Inset regions show hypothesized and interpreted details for hydrochemical processes, and migration and attenuation of solutes in the Transitional Swamp Region and Historic Alkali Salt Flats Region.

2.7. VALENCIA UNDERGROUND DRAIN STUDIES

Previous investigations by Hibbs and Lee (2000) and previous sections in this chapter indicated that many of the subsurface drain laterals in San Diego Creek Watershed receive a significant amount of dry weather flows from groundwater seepage. Examples of baseflow-fed drains cited by Hibbs and Lee (2000) included Valencia Drain at Peters Canyon Wash and Moffett Drive. Baseflow was confirmed by analysis of concentrations of hydrochemical constituents (e.g., selenium, nitrate) emitted by the drains, and by underground inspection of drains which indicated flowing weepholes and flowing seams where groundwater was identified by sampling and analysis of hydrochemistry. Valencia Drain, one of the largest underground drains in San Diego Creek Watershed was investigated internally in May 2004 to evaluate the kind of flows of the drain. In particular, the results of water sampling in Valencia Drain are compared in this section to results of sampling in Edinger Drain (Section 2.6), with useful comparisons done between selenium, arsenic, and sulfur isotopes in the two drains.

Samples were collected in Valencia Drain for measurement of index parameters (pH, temperature, conductivity, dissolved oxygen); general minerals analysis (Ca, Mg, K, Na, Cl, SO4, HCO3); nitrate, selenium, and arsenic analysis; and stable isotope analysis (O, D, S). Underground inspection of Valencia Drain indicated a large number of flows from seams and weepholes that were sampled for these constituents (Figures 2.7.1 and 2.7.2). Sample points in Figure 2.7.2 are labeled by distance from Peters Canyon Wash to the point in the drain where the sample was collected, in feet. The data proved to be a fortuitous information set

because Valencia Drain is oriented almost perfectly in-line with groundwater flowpaths in the shallow aquifer. This provided an opportunity to assess how hydrochemistry changes along a groundwater flowpath that moves downgradient through the historic Swamp of the Frogs Marsh region into Peters Canyon Wash (Figure 2.7.2). IRWD well 86N is very close to Valencia Drain and was included in the analysis. This well is the upgradient point in flowpath analysis.

Results

Selenium and arsenic concentrations decrease between IRWD Well 86N and the first sample point (3533 ft) in Valencia Drain. Concentrations then increase within the historic marsh region (Figures 2.7.2 and 2.7.3). Selenium and arsenic concentrations become substantially higher very close to Peters Canyon Wash (Figure 2.7.3). This could be due to: (1) gradation of reducing conditions that may have existed historically within the interior of the Swamp of the Frogs Marsh, or (2) a soil facies change along the flowpath (Meixner and others, 2004). It is postulated that the data collected at the terminus (outlet) of Valencia Drain is consistent with the location of the "reference point" in Edinger Drain, at the boundary between the transitional swamp region and the Salt Playa/Salt Flats area discussed in Section 2.6 on Edinger Drain. Examination of Figures 2.6.5, 2.6.6, and 2.6.8 seem to confirm this observation. Discussion in this section ties together land regions traversed by Valencia Drain and Edinger Drain.

Further upgradient, selenium and arsenic concentrations decrease at sample points 3544 ft and 3534 ft (Figures 2.7.2 and 2.7.3). An explanation for the

decrease in selenium and arsenic concentrations at these sample points (3544 ft and 3534 ft) is provided by an analysis of stable isotopes of oxygen and hydrogen (Figure 2.7.4). Previous samples collected from springs, weepholes, and water wells near Peters Canyon Wash and San Diego Creek plot along an evaporation water line of locally derived water (Figure 2.7.4A). Most groundwater depths in the Peters Canyon Wash and San Diego Creek area are shallow, sometimes only 6 to 8 feet beneath land surface. In these areas, groundwater may evaporate partially by a wicking effect as atmospheric winds cause venting of moisture vapor from the unsaturated zone, allowing physical evaporation of groundwater. Fine textured soils allow capillary rise up to a few feet above the water table, which can accelerate evaporative effects. Evaporation of soil moisture or irrigation water is also possible prior to recharge, and may explain some of the evaporative effects shown in Peters Canyon Wash and San Diego Creek samples (Figure 2.7.4A).

Most of the data collected from Valencia Drain plot very close to the evaporation line developed for shallow groundwaters in the Peters Canyon Wash/San Diego Creek area, clustering within the region identified as "Local Water" (compare Figures 2.7.4A and 2.7.4B). Other points plot along a mixing line between the region identified as "Local Water" and "State Project Water." In recent studies by the U.S. Geological Survey (USGS), State Project waters were identified in recharge waters in the Los Angeles Basin. These waters ranged narrowly about a mean of about -9.5 per mil del 18O and -75 per mil del D (USGS, 2003). Sample point 3534 ft in Valencia Drain is also in this range, identifying this sample as State Project Water.

The reason for recharge of State Project Water near the intersection of Irvine Center Drive and Culver Drive (Figure 2.7.2) was due to a leaky subsurface water main pipe. This fact was established after our findings were reported to IRWD (Norris Brandt, personal communication, 2006). The leaky pipe was subsequently repaired (Norris Brandt, personal communication, 2006). Other samples have mixed proportions of State Project Water and Local Water (Figure 2.7.4B).

Concentrations of selenium, arsenic, and total dissolved solids (TDS) are lowest in the Valencia Drain sample that plots within the region identified as State Project Water. Selenium, arsenic, and TDS concentrations increase in samples that contain greater amounts of Local Water (Figures 2.7.4B and 2.7.4C). This is logical because State Project Water is potable, and Local Water contains higher concentrations of selenium, arsenic, and salinity, even when located outside of the Swamp of the Frogs Marsh. These data explain the dip in selenium and arsenic concentrations in Figure 2.7.3, where dilute State Project Water is recharged along the hydrogeologic flowpath just above the historic marsh region (compare Figures 2.7.3, 2.7.4C, and 2.7.5). The points marked "delete data" in Figure 2.7.5 correspond to the points marked "delete data points" in Figure 2.7.4C.

In order to evaluate natural evolution of hydrochemistry along Valencia Drain flowpath, especially with respect to sulfur isotopes, it is necessary to delete samples containing excessive State Project Water (Figures 2.7.4C and 2.7.5). Imported waters contain sulfur that was imported from another basin, increasing the complexity of analysis of natural evolution of hydrochemistry along the groundwater flowpath. It is appropriate to delete data points containing excessive

State Project Water, retaining those waters along the flowpath that are locally derived, as indicated by oxygen and hydrogen isotopes (Figure 2.7.4C). It should also be noted that flowing weepholes containing State Project Water were not flowing in 1999 when Valencia Drain was internally investigated by the research team (Hibbs and Lee, 2000). Apparently, recharge of State Project Water near Valencia Drain was a temporary phenomena.

Comparing Sulfur Isotopes Along Valencia Drain and Edinger Drain Flowpaths

After deleting samples with excessive State Project Water, sulfur isotope values in Valencia Drain are plotted (Figure 2.7.6). Except for two sample points near the historic marsh boundary, where about 5% State Project Water of 1.4 per mil δ34S[$SO4^{2-}$] is mixed with Local Water (2.8 and 2.9 per mil δ34S[$SO4^{2-}$]), most data are about 3.0 to 3.2 per mil δ34S[$SO4^{2-}$] except near Peters Canyon Wash (Figure 2.7.6). One point with 5% State Project Water plots just outside of the "Local Water" region in the stable oxygen and hydrogen isotope plot, but was not deleted because it is mixed with only a small amount of extrabasinal State Project Water (Figure 2.7.4C). Near Peters Canyon Wash the samples decrease from 2.9 to 2.1 per mil δ34S[$SO4^{2-}$] (Figure 2.7.6). Decreasing values of sulfur isotopes correlate to points with increasing values of selenium and arsenic (compare Figures 2.7.3 and 2.7.6).

A two endmember mixing illustration explains why sulfur isotope values are always positive in Valencia Drain, especially near Peters Canyon Wash (Figure 2.7.7). The two endmember points include the upgradient sample point (IRWD

Well 86) and the downgradient sample point (0 ft) near Peters Canyon Wash. The upgradient point has a relatively high sulfate concentration of 1430 mg/L. The sulfur isotope signature of this water is 3.2 per mil δ34S[$SO4^{2-}$]. Down the hydraulic gradient, sample point "0 ft" has a sulfate concentration of 1931 mg/L and a 2.1 per mil δ34S[$SO4^{2-}$]value. This is just over a 23% increase in the sulfate concentration between the two mixing endmembers. With a relatively small addition of sulfate in the historic marsh area, it is necessary to mix -1.2 δ34S[$SO4^{2-}$] in order for the bulk sulfate isotope signature to decrease from 3.2 to 2.1 δ34S[$SO4^{2-}$]. This means that the sulfate isotope signature within the marsh sediments must be negative when sulfate is dissolved out of these sediments (Figure 2.7.7B).

The reason the bulk sulfate isotope signature in samples within the marsh region of Valencia Drain is positive is because so much sulfate (about 77%) with a positive sulfate isotope signature (3.2 per mil δ34S[$SO4^{2-}$]) originates in upgradient areas, and the relatively small amount of sulfate dissolving out of the historic marsh sediments (about 23% with a signature of ~ -1.2 per mil δ34S[$SO4^{2-}$]) mixes down the hydraulic gradient to produce a overall bulk sulfate isotope signature of 2.1 δ34S[$SO4^{2-}$]. This means that ~77% sulfate with a 3.2 per mil δ34S[$SO4^{2-}$] signature mixes with ~23% sulfate with a -1.2 per mil δ34S[$SO4^{2-}$] signature to produce a final bulk value of 2.1 per mil δ34S[$SO4^{2-}$]. This does not happen in other areas of the marsh where most of the waters have a negative δ34S[$SO4^{2-}$] value (Meixner and others, 2004). These negative δ34S[$SO4^{2-}$] waters derive most of their sulfate concentration internally in the historic marsh sediments.

The best explanation for these data is that the terminus of Valencia Drain and the samples collected at weepholes and springs at the terminus is consistent with the location of the "reference point" in Edinger Drain, at the boundary between the Transitional Swamp Region and the Salt Playa/Salt Flats area discussed in Section 2.6 (Edinger Drain). Figures 2.6.5, 2.6.6, and 2.6.8 show that the transitional interface with the Historic Salt Flats region is in this area and indicates that the terminus of Valencia Drain is very near to the interface between these two regions. The terminus of Valencia Drain occupies only a very small part of the outer fringe of the Salt Playa Region.

Near the "reference point" in Edinger Drain, it was observed that selenium and arsenic concentrations increased substantially below the upgradient sample points (Figure 2.6.11), while sulfate concentrations increased only a moderate amount (Figure 2.6.11). Along this same portion of Edinger Drain flowpath, sulfur isotope signatures decreased slightly (Figure 2.6.17). Despite lower concentrations of arsenic at the terminus of Valencia Drain (41 ug/L As) compared to the "reference point" at Edinger Drain (90 ug/L As), the results are strikingly similar for the two drains, at the transect just before Edinger Drain enters the Alkali Salt Flats region. Spatial boundaries between the Transitional Swamp Region and the Salt Playa/Salt Flats shown in Figures 2.6.5, 2.6.6, and 2.6.8 appear to be correct.

To further illustrate the correlation between selenium, sulfate, arsenic, and sulfate isotope concentrations in Valencia Drain, especially near its terminus, a series of correlation line graphs are presented (Figure 2.7.8). Parameter values are normalized along the y axis because the parameter concentrations do not increase in

a 1:1 ratio. For example, sulfate is 1350 mg/L at its minimum point along the y axis. Also note that the reciprocal of the sulfur isotope value is used because of the inverse correlation between sulfur isotope and sulfate values. These data indicate a very good correlation between the four parameters. Especially good correlations are shown for sulfate and sulfate isotopes values (Figure 2.7.8A) and for selenium and arsenic values (Figure 2.7.8B).

There are many known and suspected selenium and arsenic mobilization processes occurring in the historic marsh sediments, such as oxidation of metal selenides, selenium and arsenic adsorption/desorption, leaching of selenium and arsenic out of organic material, and dissolution of iron and aluminum oxyhydroxides containing arsenic. Even so, the correlations between parameters in Valencia Drain (Figure 2.7.8) suggests that processes explained for Edinger Drain in the "Transitional Swamp Region" are probably the most likely sets of processes to occur along the Valencia Drain flowpath. The processes explained for the Historic Salt Flats in Edinger Drain are not as operative however, because Valencia Drain does not traverse much of the region once occupied by these salt flats, even at its terminus (see Figure 2.6.5).

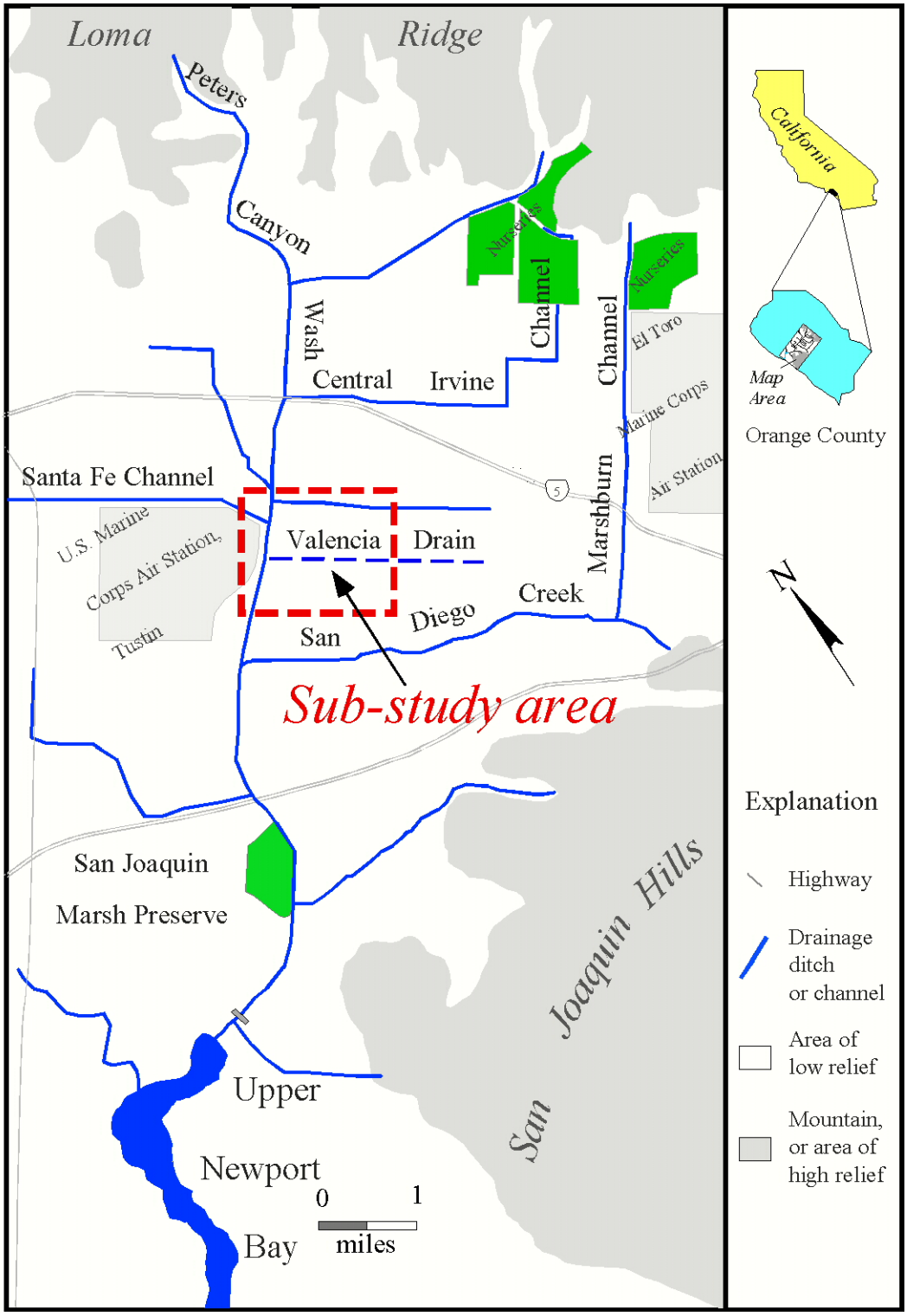


Figure 2.7.1. Location of Valencia Underground Drain sub-study area.

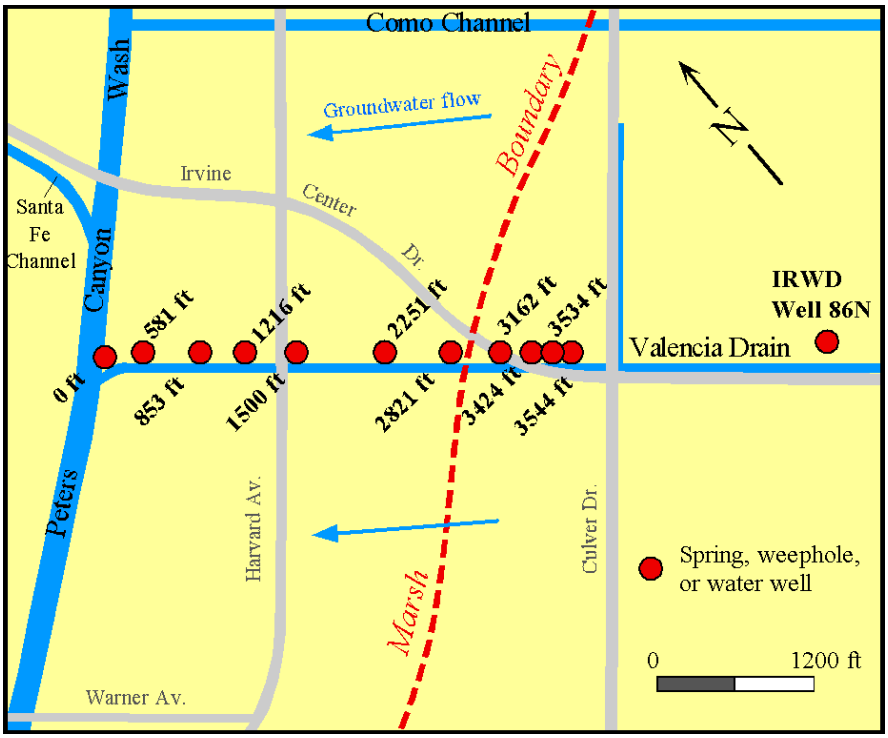


Figure 2.7.2. Weepholes and seams where groundwater was sampled within Valencia Drain in April 2004. Samples are identified by distance from Peters Canyon Wash.

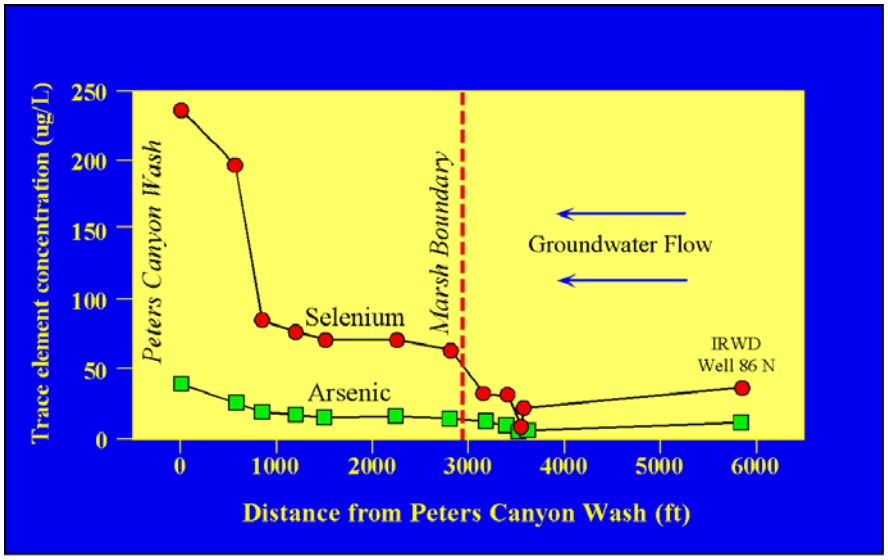
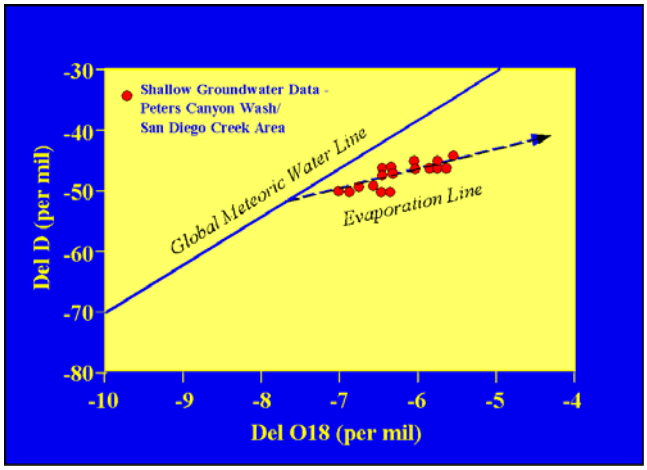
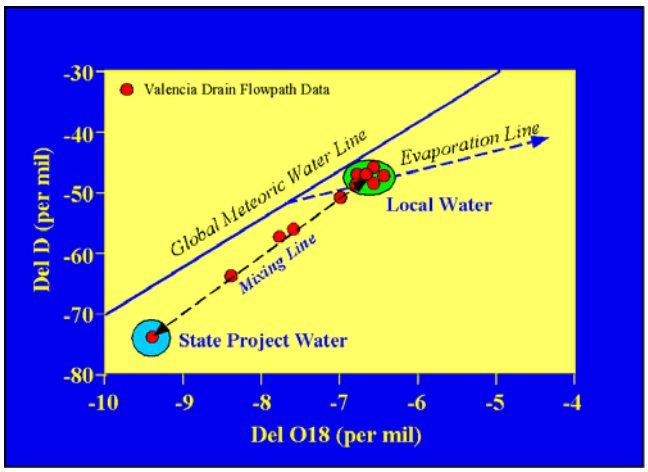


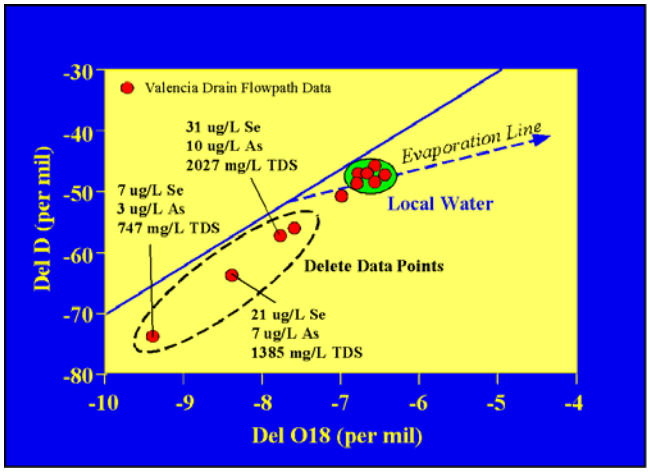
Figure 2.7.3. Concentrations of selenium and arsenic in weepholes and seams flowing into Valencia Drain, April 2004.



A.



B.



C.

Figure 2.7.4. Oxygen and hydrogen isotopes in shallow groundwater in the study area. Figure 2.7.4A shows samples collected from springs, weepholes, and shallow water wells in the vicinity of Peters Canyon Wash and San Diego Creek. Figures 2.7.4B and 2.7.4C show Valencia Drain data, including waters that are derived from local precipitation and waters containing mixtures of imported State Project Water.

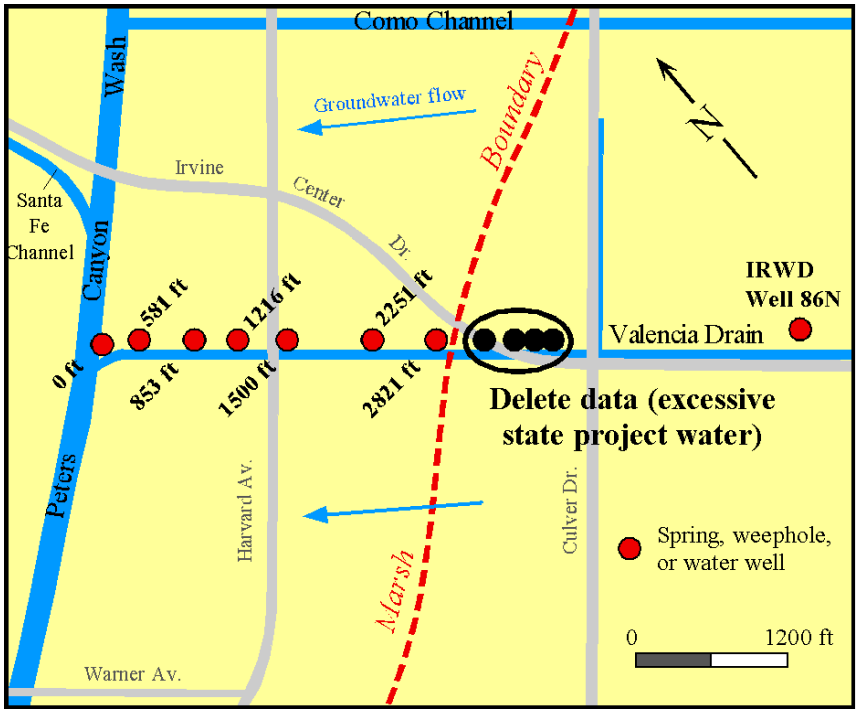


Figure 2.7.5. Samples containing excessive State Project Water must be deleted to permit analysis of hydrochemical evolution along a groundwater flowpath.

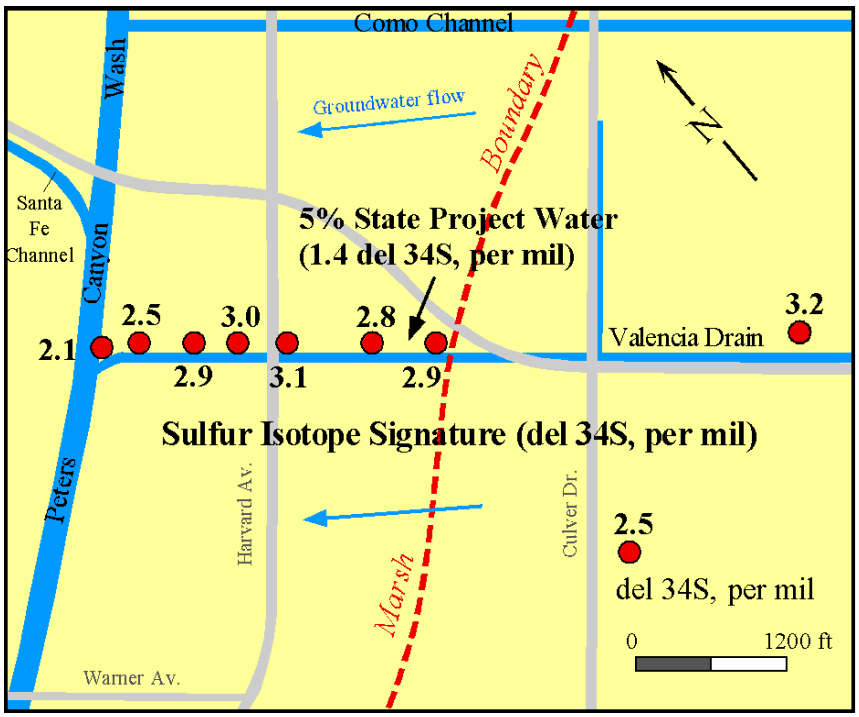
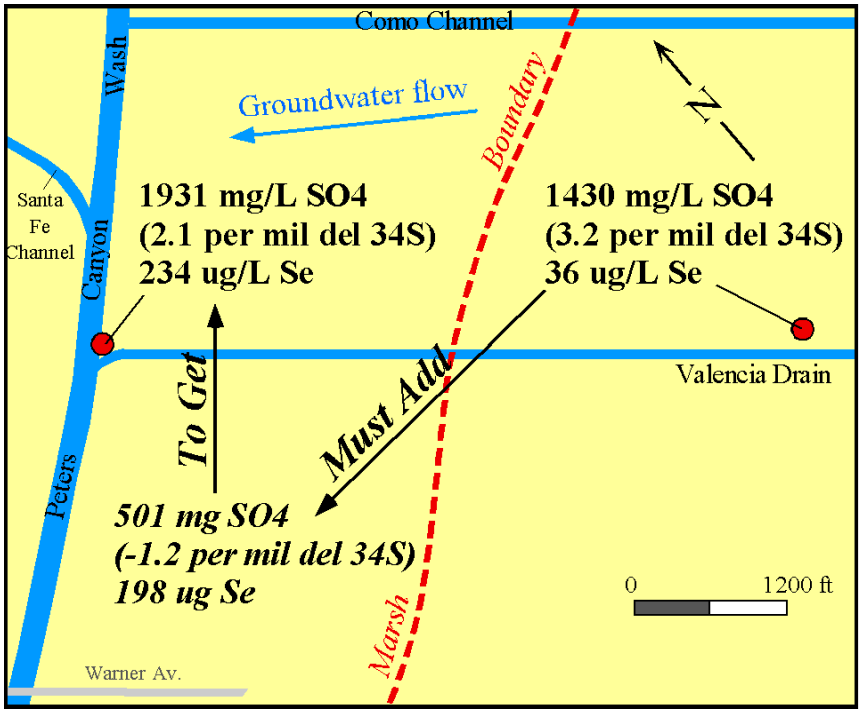
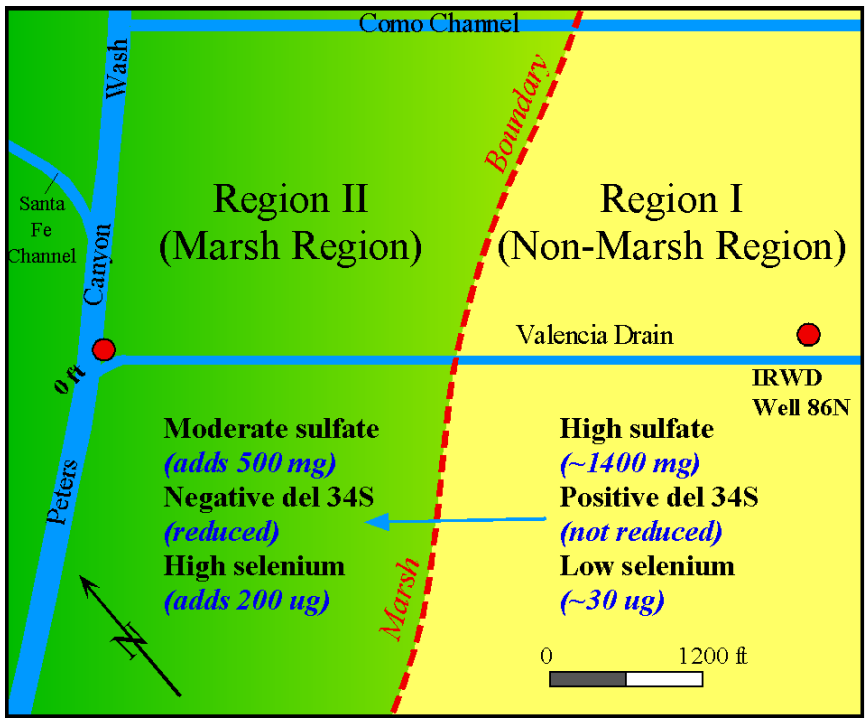


Figure 2.7.6. Sulfur isotope values (per mil) in groundwater samples from Valencia Drain are relatively consistent, except close to Peters Canyon Wash.

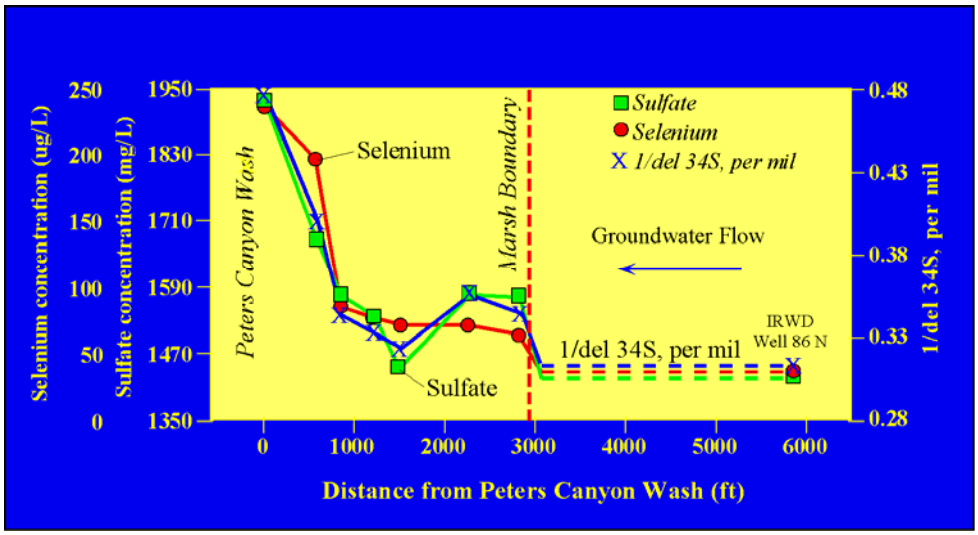


A.

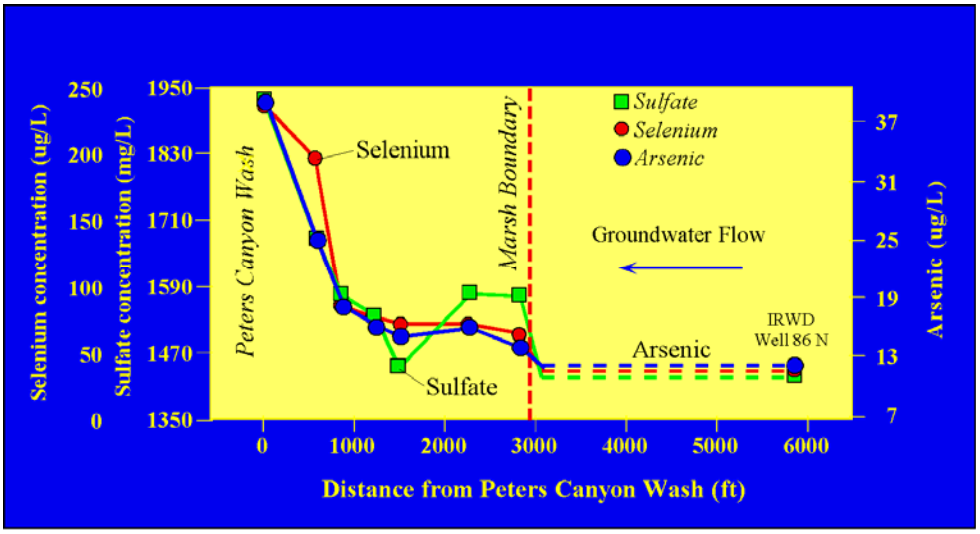


B.

Figure 2.7.7. Two endmember mixing analysis between the upstream and downstream points in Peters Canyon Wash (A). Mass balance analysis indicates that sulfur isotope signatures must be negative in the marsh sediments to produce the observed value at Peters Canyon Wash (B).



A.



B.

Figure 2.7.8. Correlation line graphs showing the correlation between selenium, sulfate, arsenic, and sulfate isotope values in Valencia Drain. Parameter values are normalized along the y axis because the parameter concentrations do not increase in a 1:1 (mass) ratio. Especially good correlations are shown for sulfate and sulfate isotope values (A) and for selenium and arsenic values (B).

2.8. LANE CHANNEL STUDIES

Lane Channel is lined above the 55 freeway and is mostly unlined from the 55 freeway down to its confluence with San Diego Creek (Figure 2.8.1). As described in the section on Santa Ana Delhi Channel, the 1900 USDA alkali map of the Santa Ana-Irvine-Tustin area shows a distinctive alkali pattern, mimicking the spatial limits of the historic Swamp of the Frogs Marsh (Figure 2.0.2 and 2.8.2). Heaviest alkali concentrations correspond to areas of shallow groundwater, where water evaporated in predevelopment times to produce sodium-sulfate salts at land surface. Our investigations have shown that the areas of high groundwater selenium concentrations match up well with the regions of moderate alkali (0.2 to 0.6 percent) in the 1900 USDA alkali map.

The regions in the 1900 alkali map with orange pattern had the lowest alkali concentrations in 1900 (Figure 2.0.2 and 2.8.2). Today, these areas have the lowest selenium concentrations in groundwater in San Diego Creek Watershed, and match up quite well with the regions above the "Swamp Fringe" described in Section 2.1. The areas near the Tustin Marine Corps Air Station and near Harvard Avenue and Irvine Center Drive (Figure 2.8.2) contained moderate alkali concentrations in the 1900 map (green patterns). These same regions of moderate alkali have the highest selenium concentrations in groundwater today (frequently 50 to 350 ug/L selenium) (Bechtel basewide groundwater geochemistry data, 1996 to 2000; Hibbs and Lee, 2000; Meixner and others, 2004). There is a generally good, but not perfect relationship between areas of moderate alkali (0.2 to 0.6 percent) and the "Swamp Fringe" discussed in section 2.1. This section uses Lane Channel groundwater data

to provide further comparisons between the alkali map and the Swamp Fringe between the 50 to 70 ft land surface elevations.

The areas of highest selenium concentration are located where moderate alkali concentrations are found at the outer edges of the historic Swamp of the Frogs Marsh. Along the margins of the marsh, prolific vegetation and wetland plant growth may have hastened selenium removal from the water column in a frequently wetted environment. Within the interior of the marsh, where alkali and salinity concentrations were higher, much of the selenium may have already been removed from percolating groundwater before it reached the interior regions of the marsh, where alkali concentrations were higher (Figure 2.8.2). It is also likely that the interior saline regions of the marsh supported varieties of sparsely thicketed vegetation that did not sequester the larger amounts of selenium seen along the outer margins of the marsh. There also appears to have been little historic use of synthetic fertilizer in the saline areas near the lower limits of Lane Channel. Nitrate is demonstrably lower in shallow groundwater in saline areas.

On the basis of the correlation between moderate alkali in 1900, and high selenium concentrations today, the research team elected to perform groundwater investigations in the underground feeder drains to Lane Channel in the region above Dyer Road and 55 Freeway (Figure 2.8.3). Studies were conducted during April 2003 and July 2004. Follow-up studies were also carried out in the more saline areas downstream during August, 2004. Thus, the study is divided into three areas; an upper area above Dyer Rd, a middle area between Dyer Road and Red Hill Avenue, and a lower area below Red Hill Avenue (Figures 2.8.1 and 2.8.3).

In the upper reach, there was no existing groundwater data available. This area is located where moderate alkali concentrations are shown in the outer margins of the Swamp of the Frogs Marsh region (just above the I-55 in Figure 2.8.2, adjacent to Lane Channel). The upper region is also located between the 70 ft and 50 ft land surface contours (see Figure 2.1.2). We made apriori predictions of high selenium concentrations in the upper area. Several weepholes were discovered and sampled in the underground feeder drains in the upper reach of Lane Channel. Selenium was present in moderate to very high concentrations in the groundwater (20 to 107 ug/L Se, Figure 2.8.3). Sampling also indicated moderately-low salinity and very high nitrate concentrations, usually greater than 10 mg/L NO3-N (Table 2.8.1). Apriori predictions of relatively high selenium concentrations in this area were correct. Nitrate is sufficiently concentrated to help oxidize reduced forms of selenium from soils.

Downstream of the underground feeder drains in the middle reach of Lane Channel (Figures 2.8.1 and 2.8.3), selenium values decrease to 20 to 38 ug/L, even while nitrate is greater than 15 mg/L NO3-N (Table 2.8.1). Lane Channel begins to enter regions of higher salinity and higher alkali concentrations, shown by increasing Cl and SO4 (Table 2.8.1 and Figure 2.8.3). Further downstream, in the lower reach of Lane Channel, the selenium concentrations in groundwater decrease to 2 to 13 ug/L Se, while salinity increases substantially (Table 2.8.1 and Figure 2.8.4). In this lower region, nitrate-nitrogen concentrations are much lower, only 0.3 to 2.7 mg/L NO3-N.

Previous analysis by Hibbs and Lee (2000) and Meixner and others (2004) showed high concentrations of dissolved solids in the lower reach of Lane Channel. Meixner and others (2004) suggested elevated salinity in this area is due to leaching of evaporite (thernardite) salts from vadose zone profiles. Thenardite salts containing selenium are present in the historic "ephemeral lake" area identified by Trimble (1997). Meixner and others (2004) suggested that the evaporite salts probably accumulated in predevelopment times due to evaporation of shallow groundwater from areas where groundwater is very shallow and where land surface is flat (Figure 2.1.4). The lower reach of Lane Channel meets these criteria.

To summarize the important findings in this section, Lane Channel traverses three hydrochemically distinct terrains. The upper terrain, located above Dyer Rd, contains moderate to high selenium concentrations (20 to 107 ug/L Se) and moderately-low salinity. Nitrate, a known oxidant of selenium, is very concentrated there, usually greater than 10 mg/L NO3-N (Table 2.8.1). The upper region is located between the 50 to 70 ft contour elevations (Swamp Fringe). The middle terrain, located between Dyer Rd and Red Hill Ave, is an intermediate zone where selenium values decrease to 20 to 38 ug/L, even while nitrate is still very high (greater than 15 mg/L NO3-N, Table 2.8.1). This is where Lane Channel begins to enter a region of moderate salinity and increasing alkali concentrations. Further downstream, below Red Hill Ave, the selenium concentrations in groundwater decrease to only 2 to 13 ug/L Se, and salinity increases substantially (Table 2.8.1 and Figure 2.8.4). In the lower region, nitrate concentrations are much lower, only 0.3 to 2.7 mg/L NO3-N. Selenium is probably not concentrated in soils in the lower

terrain. Even if reduced forms of selenium are present in soils in the third terrain, the nitrate concentration is probably too low to oxidize much selenium. Thus, the Lane Channel data fits the Swamp Fringe - Salt Flats conceptual model shown in Figure 2.1.4 presented earlier in this chapter.

Two of the groundwater samples in Lane Channel area (Figure 2.8.3) were analyzed for selenium species (Table 2.8.2). These were located in the upper and middle reaches of Lane Channel. Results are typical of those presented in Meixner and others (2004); namely, that selenium is in its most oxidized state (Se-VI) with little organic selenium in solution.

Stable Isotope Data in the Lower Reach of Lane Channel - Salinity Ramifications

The high concentrations of dissolved solids detected in the lower reach of Lane Channel (up to 8600 mg/L TDS) are rarely seen in terrestrial parts of San Diego Creek Watershed (Figure 2.8.4). Most striking is the salinity variation shown in weepholes in close proximity to one another. The values range from less than 2000 mg/L to over 8000 mg/L TDS (Figure 2.8.4). Stable isotope analysis provides insights on these differences.

A quick review of stable isotope findings in San Diego Creek Watershed is provided in order to develop context for understanding isotope signatures in the lower reach of Lane Channel. Previous samples collected from springs, weepholes, and water wells in San Diego Creek Watershed plot along an evaporation water line of locally derived water (Figure 2.8.5). Groundwater depths in many parts of the watershed are shallow, sometimes only 6 to 8 feet beneath land surface. In these

areas, groundwater may evaporate partially by a wicking effect as atmospheric winds cause venting of moisture vapor from the unsaturated zone, allowing physical evaporation of groundwater. Fine textured soils can allow capillary rise up to a few feet above the water table, which can accelerate evaporative effects. Evaporation of soil moisture or irrigation water is also possible prior to recharge, and may explain some of the evaporative effects shown in local groundwater (Figure 2.8.5).

Most of the data collected from San Diego Creek Watershed plot very close to the local groundwater evaporation line (Figure 2.8.5). A few points described in Section 2.7 on Valencia Drain report plot along a mixing line between the region identified as "Local Water" and "State Project Water." State Project Water is imported from Northern California to satisfy the thirst of Southern California. In recent studies by the U.S. Geological Survey (USGS), State Project waters were identified in recharge waters in the Los Angeles Basin. These waters ranged narrowly about a mean of about -9.5 per mil del ^{18}O and -75 per mil del D (USGS, 2003) (Figure 2.8.5).

State Project Water has been detected in the shallow aquifer in San Diego Creek Watershed, as described in the section on Valencia Drain. State Project Water is used seasonally in the Irvine area, and can recharge the shallow aquifer where irrigation waters are applied to local landscapes, or where water pipes leak. State Project Water has been detected in only a few locations in the shallow aquifer. Where recharge by State Project Water occurs, the imported water may mix with local water along numerous hypothetical mixing lines (Figure 2.8.5). Mixtures of local water with State Project Water will plot somewhere in the zone bracketed by

these mixing lines (Figure 2.8.5). Using isotope plots with known endmember waters, it is therefore possible to identify waters containing no State Project Water, small to moderate amounts of State Project Water, or mostly State Project Water (and vice-versa for water derived from infiltration of local precipitation).

From the mixing curves, groundwater collected in the lower reach of Lane Channel (Figure 2.8.4) plot in two distinct clusters. The first cluster is demonstrably a locally derived water (Figure 2.8.6). The second cluster identifies the groundwater as a mixture between State Project Water and Local Water (Figure 2.8.6). The mixed water (second cluster) includes three points with salinity values of 1997, 4238, and 5961 mg/L TDS. This is substantial variation of salinity for isotopically identical waters that were collected so close together (Figures 2.8.4 and 2.8.6).

State Project Waters detected in the shallow aquifer were very dilute with respect to salinity and selenium near Valencia Channel (Section 2.7) but this is in an area located above the historic Swamp of the Frogs Marsh. Lane Channel results are different. One of the mixed waters containing State Project Water is only slightly saline (1997 mg/L TDS) whereas others are moderately saline (4238 and 5961 mg/L TDS).

Paradoxically, the isotopic signatures of these mixed waters are virtually identical (Figure 2.8.6). A likely interpretation is that State Project Waters are leaching salts from the vadose zone in some local areas near Lane Channel, and not in other nearby areas (Figure 2.8.7). Where waters are locally derived, salinities appear to be not only more concentrated but also more uniform (7014 and 8645

mg/L TDS). This is probably because soil water percolation, salt leaching, and solute mixing is more regionally extensive during rainfall. Where State Project Water is applied locally, the salinities are lower and more variable in the Lane Channel groundwaters.

A mass balance analysis helps to clarify the interpretations of different salinities observed in this area. The isotopic mixing curve shown in Figure 2.8.6 implies that the "mixed water" clusters are about 60% State Project Water and about 40% Local Water. Assuming State Project Water is about 400 mg/L and Local Water is about 6000 mg/L TDS, the 60/40 mixture would produce a salinity of 2640 mg/L TDS. This value is reasonably close to the 1997 mg/L sample in the data set (Figure 2.8.6). Where the mixed water contains 5961 mg/L TDS, the "Local Water" component would require 14,302 mg/L TDS to get a 60/40 mixture of State Project Water and Local Water; not an especially likely scenario.

It is not impossible that local groundwater salinity exceeds 14,000 mg/L TDS in isolated areas near Lane Channel. However, it is more likely that local application of State Project Water leaches salts in some areas and not in others, depending on the local geology, salt variability in the vadose zone, and mode of recharge (i.e., via surface irrigation or leaky pipes) (Figure 2.8.7 and 2.8.8). This is a logical explanation for the salinity variations in the mixed waters (Figure 2.8.6). Rainwater percolation is spatially extensive and would probably tend to mix salinity more evenly in the aquifer.

At this time we conclude that local rain water is not the only source of recharge to the shallow aquifer; State Project Water applied to local landscapes (or

from leaky pipes) also contributes some limited recharge. Furthermore, these data provide the *first indication* that local application of State Project Water is probably leaching moderate to high concentrations of solutes (i.e., salt; possibly selenium and nitrate) into the saturated zone in some areas, and is bypassing or not mobilizing solutes in other areas.

Table 2.8.1: Hydrochemical Data for Lane Channel Groundwater Upper, Middle, and Lower Reach

Sample ID	Se (ug/L)	NO3-N (mg/L)	As (ug/L)	Cl (mg/L)	SO4 (mg/L)
ABOVE DYER RD (Upper Reach – July 2004)					
Lane Weephole 12	56.5	23.09	0.7	102	1658
Lane Weephole 11	73.5	27.50	0.7	103	1833
Lane Weephole 9	106.3	30.27	1.0	116	1875
Lane Weephole 6	20.1	16.43	2.2	86	1517
Lane Weephole 5	79.1	27.24	1.2	94	1123
Lane Weephole 3	34.3	9.17	0.9	106	1000
Lane Weephole 2	40.6	10.05	0.9	100	1325
BELOW DYER RD AND ABOVE RED HILL AVE (Middle Reach – April 2003)					
Dewatering Unit @ Atel	35.0	33.34	3.0	365	1940
Well 5/6 (shallow)	37.4	16.38	2.4	383	1996
Well 2	27.9	30.76	2.1	522	2952
Lane Weephole @ Redhill	25.0	40.53	2.5	208	2036
BELOW RED HILL AVE (Lower Reach – August 2004)					
Drain 1 (groundwater-fed drain)	8.7	2.02	2.7	2044	5375
Bat 1 (weephole)	3.2	0.30	1.5	264	1178
Bat 2 (weephole)	2.6	2.70	2.1	1481	3877
Jamb 1 (weephole)	8.5	0.64	2.3	1454	4153
Jamb 2 (weephole)	13.2	2.16	1.4	886	2648

Table 2.8.2: Selenium Speciation Data in Lane Channel Area

Sample ID	Se VI (ug/L)	Se IV (ug/L)	Organic Se	Total soluble Se (ug/L)
Lane Weephole @ Redhill	23.85	0.86	<0.2	24.71
Lane Weephole 7.5 (new)	59.55	0.65	<0.2	60.20

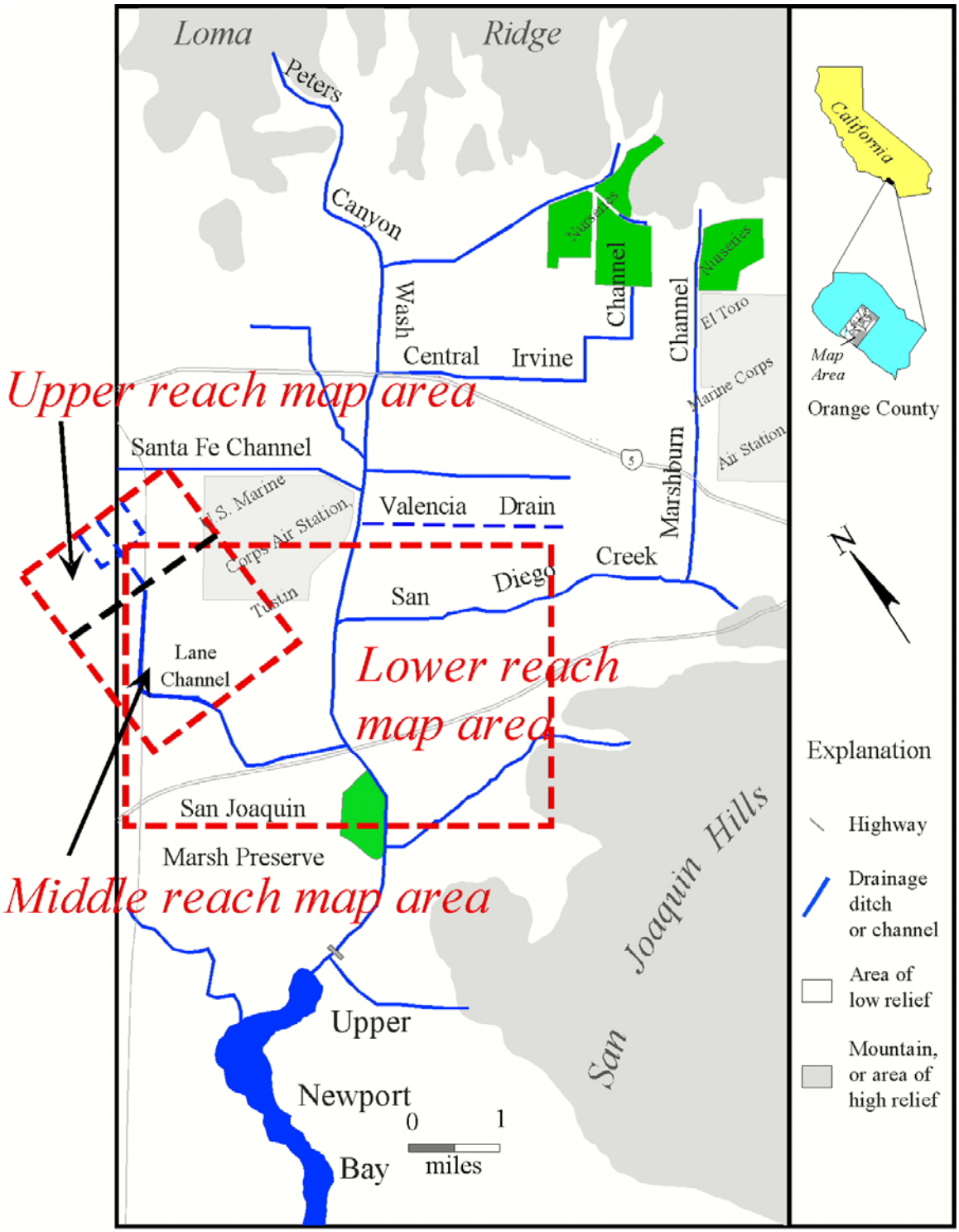


Figure 2.8.1. Location of Lane Channel sub-study areas: Upper Reach, Middle Reach, and Lower Reach.

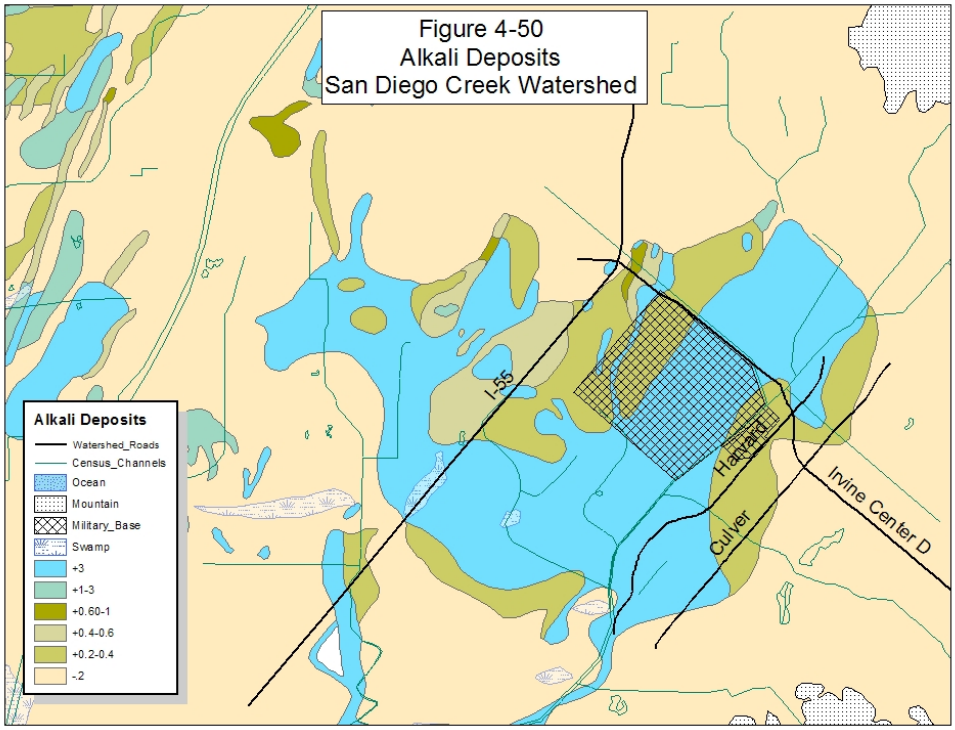


Figure 2.8.2. 1900 Alkali map superimposed on contemporary channels in San Diego Creek Watershed. Also shown is the Tustin Marine Corps air station (hatched area). Areas with green patterns, along the margins of the historic Swamp of the Frogs Marsh, generally contain the highest selenium concentrations in shallow groundwater. Upper and middle reaches of Lane Channel are located near “I-55” in the map.

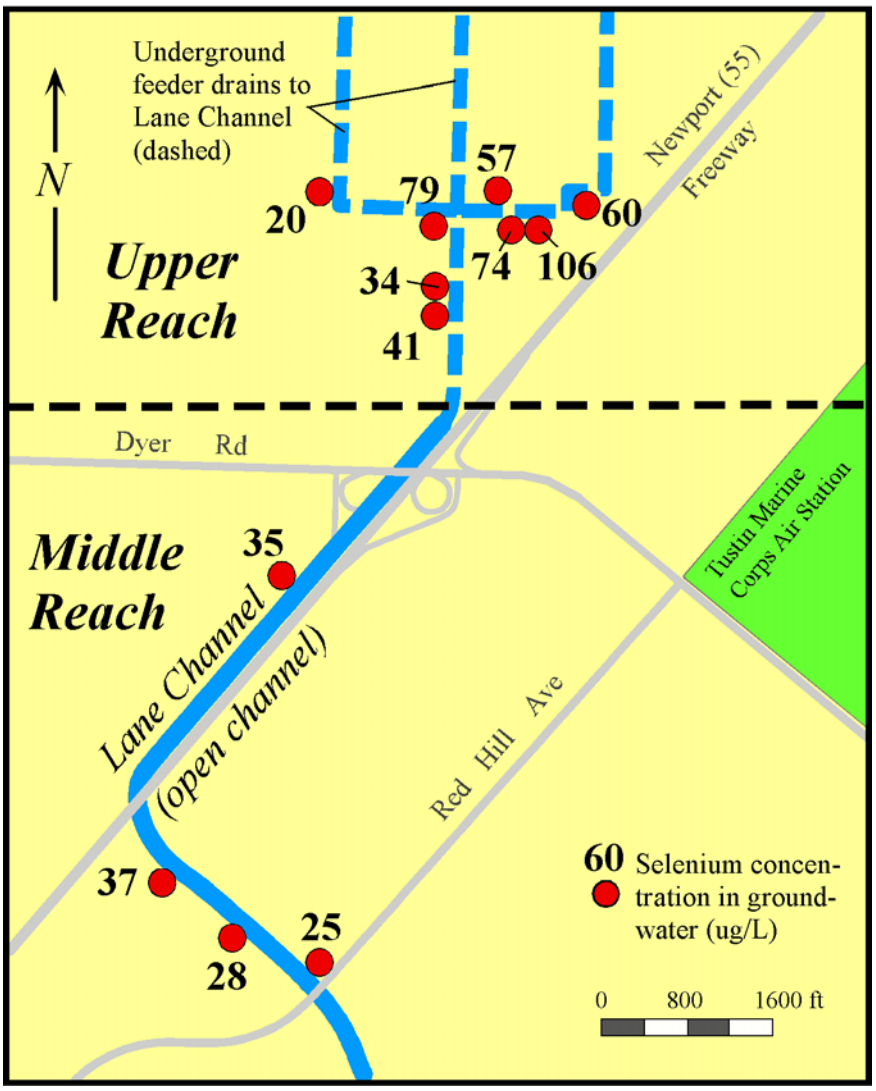


Figure 2.8.3. Selenium concentrations in groundwater at weepholes and springs in the Lane Channel area, upper and middle reaches. The underground feeder drains are located near the outer margins of the Swamp of the Frogs Marsh where alkali concentrations were moderate in 1900. Selenium concentrations in groundwater are presently highest in this region.

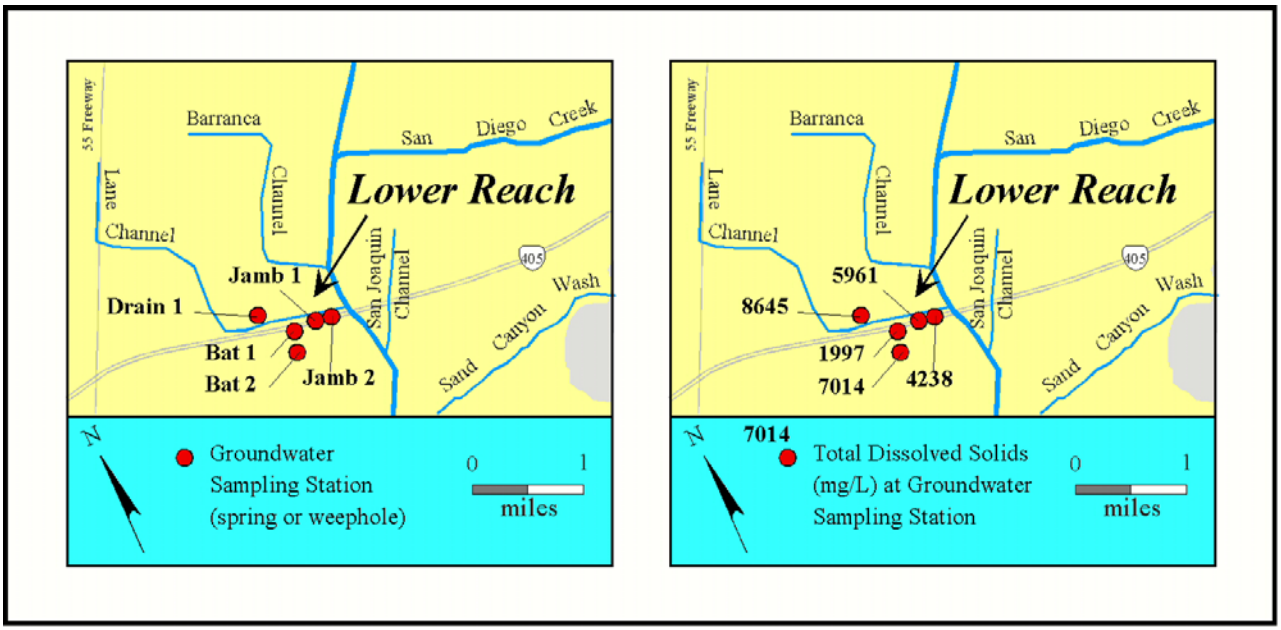


Figure 2.8.4. Locations of weepholes and springs sampled in the lower reach of Lane Channel, and their salinity values in total dissolved solids (TDS – estimated by conductivity x 0.65).

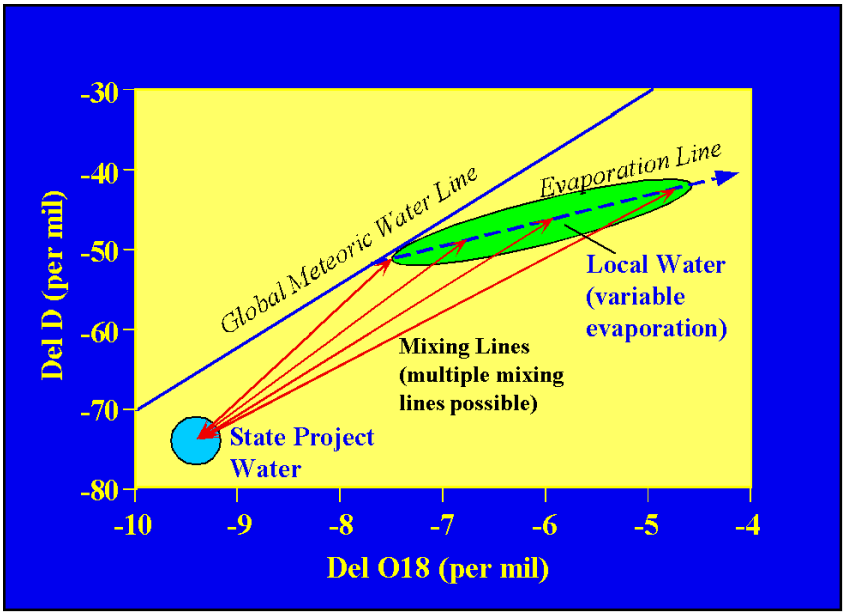


Figure 2.8.5. Two types of water have been identified in the shallow aquifer of San Diego Creek Watershed. These include Local Water derived from local precipitation and imported "State Project Water." Mixing lines bracket possible zones of mixing between the two endmember waters.

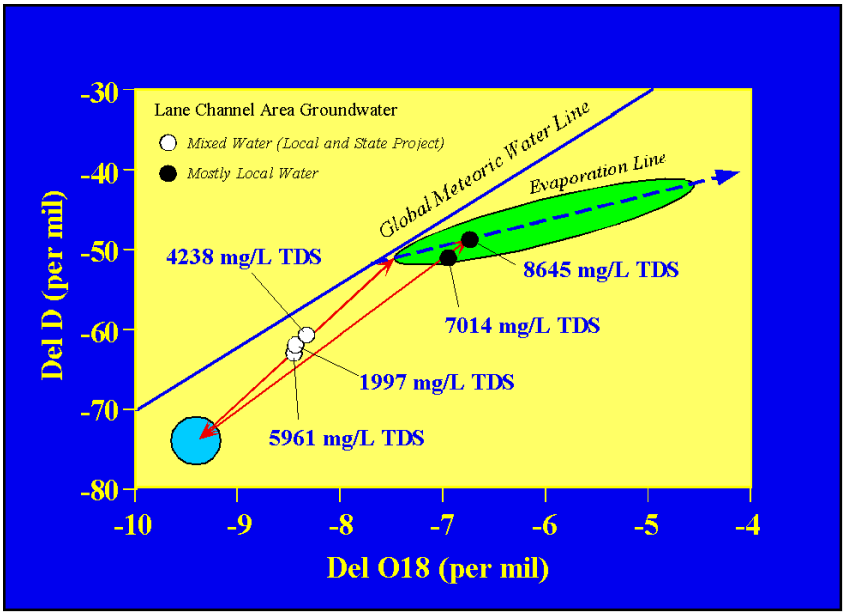


Figure 2.8.6. Isotopic plots of groundwater samples collected in Lower Lane Channel. Also shown are total dissolved solids for the plots. Two distinct clusters are identified, a mostly local water and a water that includes mixtures between local and imported State Project Water.

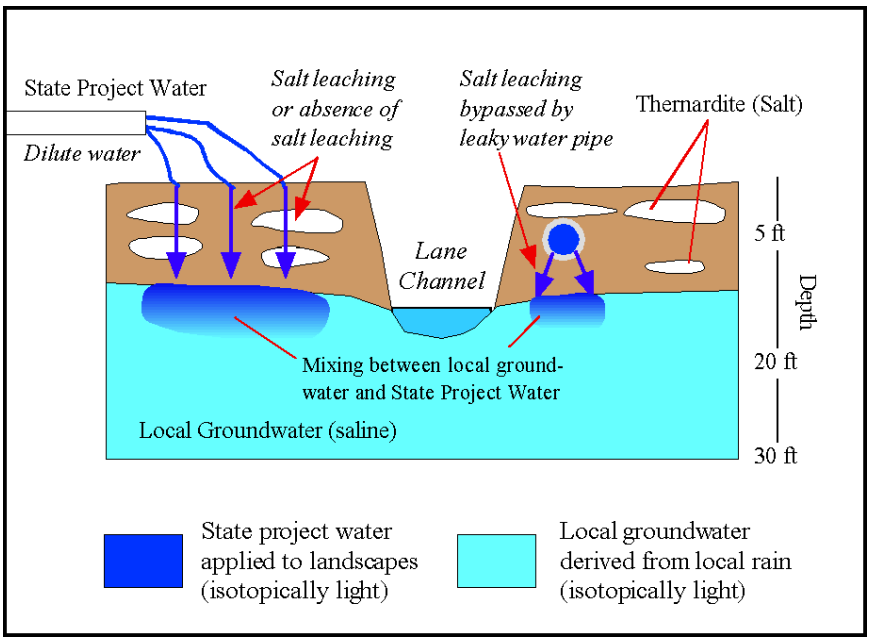


Figure 2.8.7. Conceptual model for mixing between imported State Project Water and locally derived water. State Project Water recharges the aquifer locally by surface irrigation or by leaky water main pipes. State Project Water may leach salts or bypass salts in the vadose zone due to spatially restricted recharge. Recharge by precipitation is much more extensive spatially.

Figure 2.8.8. Photographs of leachable evaporite salts in the lower reach of Lane Channel. X-ray diffraction analysis at Cal-State Los Angeles indicates this material is Thernardite, a sodium sulfate salt.

2.9. BARRANCA UNDERGROUND CIRCULAR DRAIN STUDIES

Barranca Underground Circular Drain runs parallel to Barranca Parkway and is tributary to Peters Canyon Wash (Figures 2.9.1 and 2.9.2). During previous investigations, this drain was noted for its high salinity (5000 to 7000 uS/cm) and high selenium concentrations (~100 ug//L Se) (Hibbs and Lee, 2000; Meixner and others, 2004). Such values are enigmatic, because high selenium concentrations are not usually correlated with high salinity values in drains and groundwaters in San Diego Creek Watershed (see Section 2.8, lower Lane Channel). Accordingly, the research group investigated Barranca Circular Drain in January 2005 in order to determine the reason for these anomalous values of high salinity and high selenium.

During underground reconnaissance of Barranca Underground Circular Drain, the research team discovered that the drain opened at its terminus into an unlined channel at the intersection of Barranca Parkway and Jamboree Road (Figure 2.9.2). This unlined channel was observed to drain part of the Tustin Marine Corps Air Station before flowing into Barranca Circular Drain (Figure 2.9.2). Further investigation indicated that the unlined channel flowing into Barranca Circular Drain was the "San Joaquin Ditch," also referred to as the San Joaquin Channel (not to be confused with the San Joaquin Channel near the San Joaquin Marsh). San Joaquin Ditch was, in turn, fed by the IRP-5 Ditch at the heart of the former military base (Figure 2.9.2). The drainage regime has changed since a new commercial development was constructed at the intersection of Barranca Parkway and Jamboree Road. Sampling of Barranca Circular Drain was done before

construction of the commercial development began. All discussion in this section describes conditions before construction of the commercial development.

The San Joaquin Ditch is a U.S. Army Corps of Engineers Certified Jurisdictional Wetland. Before Tustin Marine Corps Air Station was developed in the 1940s, the existing drainage ditches were deepened and new ditches were constructed to drain shallow groundwater more effectively. The San Joaquin Ditch and other extensive drainage systems, such as Barranca Channel, Santa Ana-Santa Fe Channel, and Peters Canyon Wash were installed or reconfigured for better drainage of the base. All of these channels penetrate the water table, and groundwater drains into them year round.

During our studies, heavy flows were observed to drain into Barranca Circular Drain from San Joaquin Ditch. This was partly due to the large amount of precipitation that fell in the late 2004, early 2005 rainy season, which increased recharge rates to the shallow aquifer beneath the air station. A few groundwater seeps and flows were also discovered in the underground part of Barranca Channel (Figure 2.9.2). These groundwater flows contained very high salinity concentrations (7000 to 23,000 uS/cm) and moderately-low selenium concentrations (<14 ug/L Se) (Figures 2.9.2 and 2.9.3). Such values are consistent with the hypotheses developed in previous sections; that is, it was noted that very high salinity values are correlated with rather low selenium concentrations. Groundwater seeps in Barranca Circular Drain were sampled within the area mapped near the boundary between the Swamp of the Frogs Marsh and the ephemeral saline lake of Trimble (1998). It was later suggested by Meixner and

others (2004) that this ephemeral lake might have been an area of shallow groundwater evaporation during predevelopment times (i.e., alkali flats).

Barranca Circular Drain produces high selenium concentrations and high salinity concentrations (Hibbs and Lee, 2000) because Barranca Circular Drain and San Joaquin Ditch drained two different source terrains. The first terrain is the very high selenium, moderate salinity region within the Swamp of the Frogs Marsh, near the heart of the Tustin Marine Corps Air Station. The second terrain is the upper part of the ephemeral lake/alkali flats region located south of the Swamp of the Frogs Marsh. Historical water quality data at the Marine Corps Air Station indicate that groundwater near the southeastern quadrant of the base is very saline, similar to salinity observed in Barranca Circular Drain (~10,000 to 25,000 uS/cm). This region is also drained by the lower part of San Joaquin Ditch. IRP-5 ditch drains the interior of the Tustin Marine Corps Air Station, where historical water quality data have indicated high selenium (up to 300 ug/L Se) and moderate salinity (2500 to 4000 uS/cm). IRP-5 ditch flows into San Joaquin Ditch, which eventually flows into Barranca Circular Drain.

The groundwater seeps and flows within Barranca Circular Drain are sourced from the historic alkali flats region. These flats have very high salinity and moderately low selenium concentrations (Figures 2.9.2 and 2.9.3). Accordingly, the combination of flows at Barranca Circular Drain were sourced from the two major land regions; one containing moderate salinity/very high selenium concentrations (Swamp of the Frogs Marsh) and one containing very high salinity and moderately low selenium concentrations (ephemeral lake/alkali flats region).

The result was a composite flow from Barranca Circular Drain into Peters Canyon Wash containing moderately high salinity and high selenium concentrations overall. The research team did not undertake additional studies after completion of the development at Barranca Parkway and Jamboree Road. Further sampling is recommended to determine what are the effects of the new development on flows from Barranca Underground Circular Drain.

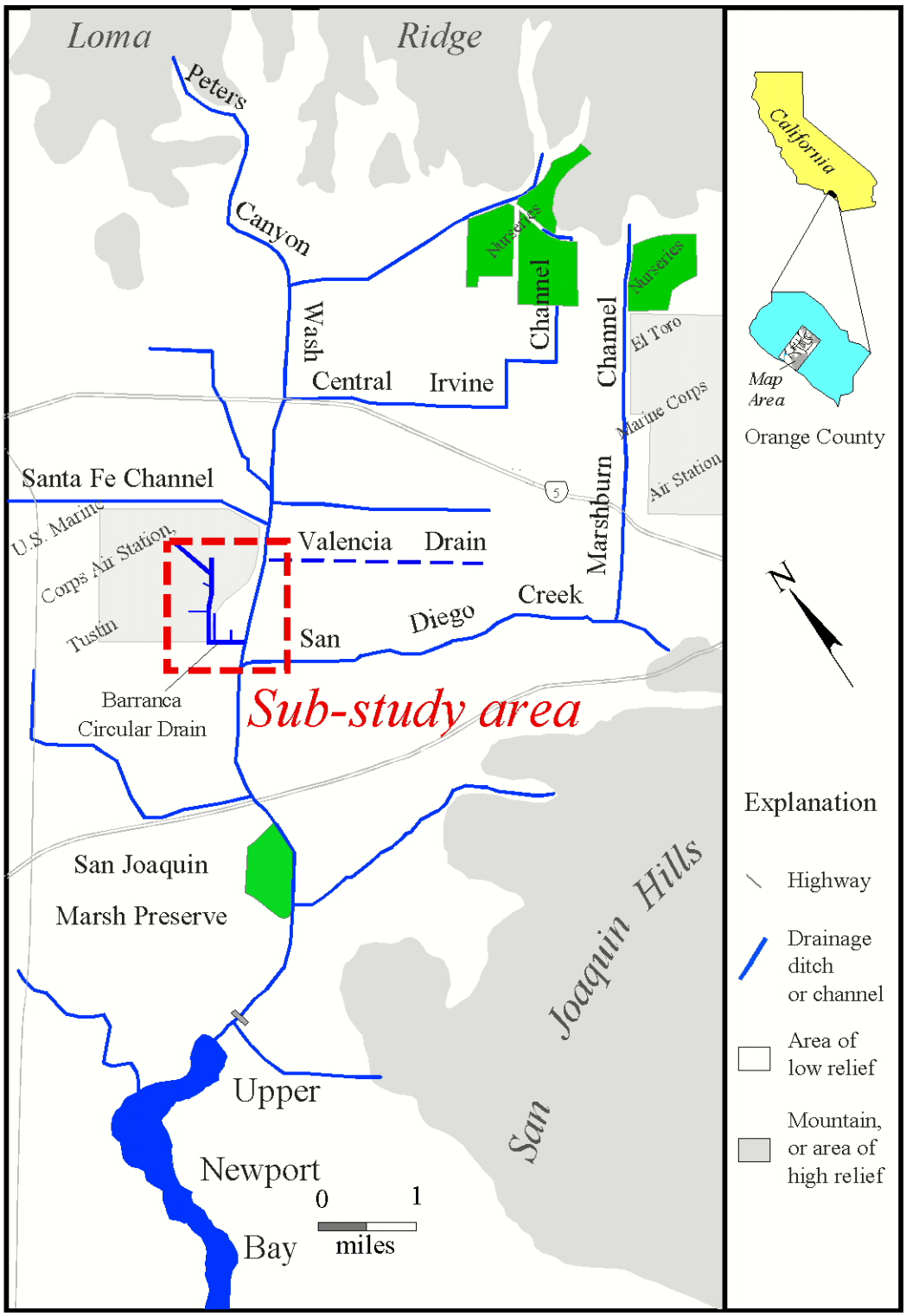


Figure 2.9.1. Location of Barranca Underground Circular Drain sub-study area.

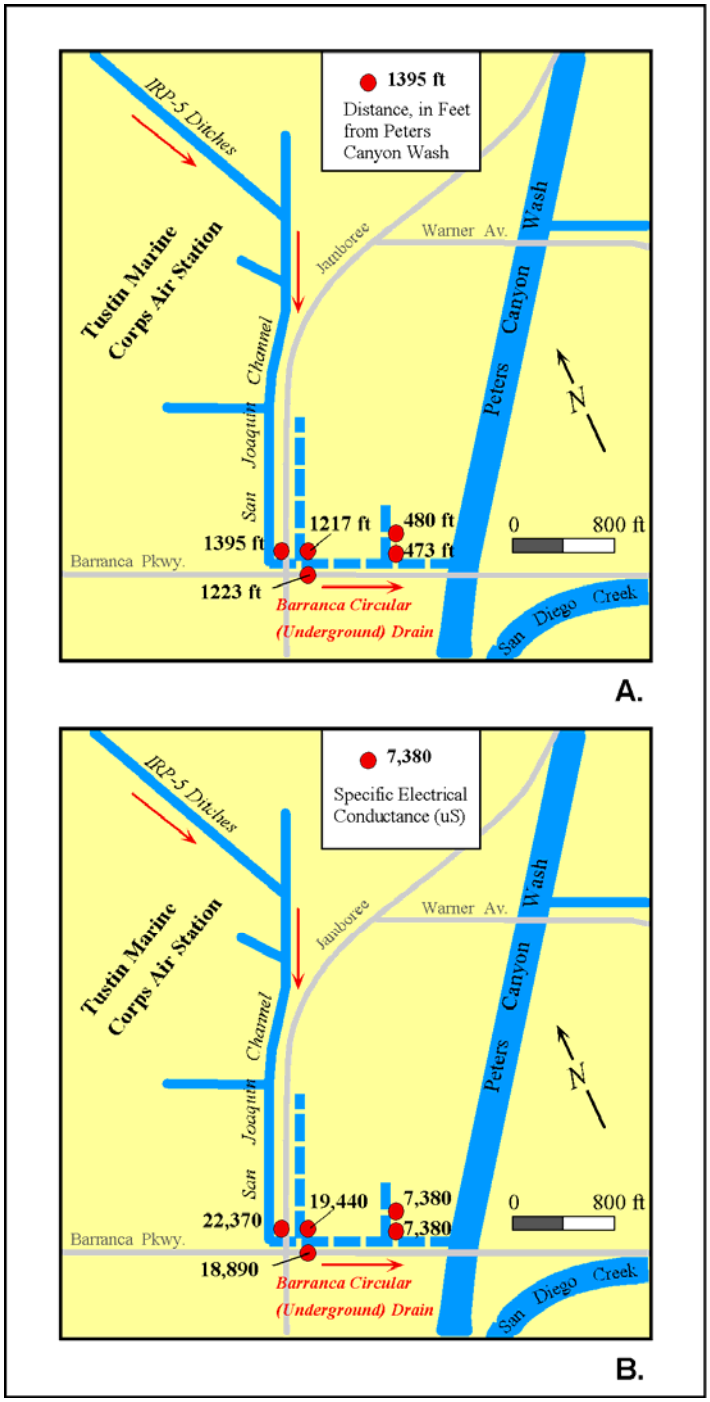


Figure 2.9.2. Salinity concentrations in groundwater in Barranca Underground Circular Drain. Figure 2.9.2A shows groundwater sample locations, in feet from Peters Canyon Wash. Figure 2.9.2B shows salinity values (specific conductance) in groundwater at the five groundwater sample points, January 2005. Note that IRP-5 Ditch flows into San Joaquin Channel and that San Joaquin Channel flows into Barranca Circular Drain. In turn, Barranca Circular Drain discharges into Peters Canyon Wash.

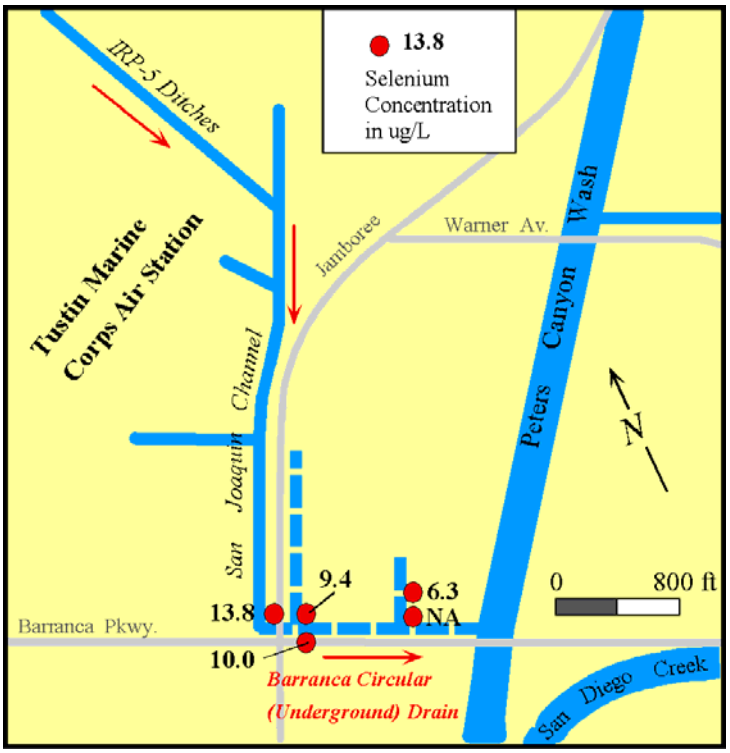


Figure 2.9.3. Selenium concentrations in groundwater in Barranca Underground Circular Drain, January 2005. Note that the IRP-5 Ditch flows into San Joaquin Channel and that San Joaquin Channel flows into Barranca Circular Drain. In turn, Barranca Circular Drain discharges into Peters Canyon Wash.

2.10. SAN JOAQUIN CHANNEL STUDIES

During the late 1990's and early 2000's, members of the research team completed selenium and nutrient studies in San Diego Creek Watershed (Hibbs and Lee, 2000; Hibbs, 2001). As part of these studies, a very limited amount of water quality information was collected in San Joaquin Channel (Figures 2.10.1 and 2.10.2) and Sand Canyon Channel (Tables 2.10.1 and 2.10.2). These data are somewhat contradictory. San Joaquin Channel had specific conductance values that are characteristic of urban runoff (~1550 uS/cm EC); nitrate-nitrogen values that are characteristic of groundwater baseflows (5 to 13 mg/L NO3-N); and selenium values that are usually a combination of urban runoff and groundwater baseflows (~10 ug/L Se). Sand Canyon Channel had parameter values that implied mostly urban runoff (~1500 uS/cm EC; ~2.0 mg/L NO3-N; ~5 ug/L Se).

A soil δ34S[$SO4^{2-}$] value of -10.0 per mil collected by the research team at San Joaquin Channel at Michelson Drive suggests that the soil at this location was deposited in a marshy, reducing environment (Figure 2.10.2). The strongly negative isotope value was identified near the edge of the marsh boundary mapped by Hibbs and Lee (2000). Where negative soil values of δ34S[$SO4^{2-}$] are found, we usually find moderate to abundant amounts of dissolved selenium in the underlying groundwater. Yet the selenium values in San Joaquin Channel are not high (Table 2.10.2). The water quality data at San Joaquin Channel have been inconsistent and difficult to interpret. Accordingly, the research team investigated San Joaquin Channel in August, 2004.

San Joaquin Channel is mostly unlined above its confluence with San Diego Creek to the location where it becomes an underground, concrete-lined channel just a few hundred feet downstream of Main Street (marked Channel Boundary in Figure 2.10.2). The historic marsh boundary mapped by Hibbs and Lee (1999) is almost coincident with the northeast orientation of the unlined part of San Joaquin Channel. Where San Joaquin channel goes underground, the channel veers to the east and southeast away from the historic Swamp of the Frogs Marsh (Figure 2.10.2).

No springs or weepholes have been observed to flow along the unlined reach of San Joaquin Channel. The research team performed channel reconnaissance in the underground, concrete lined part of San Joaquin Channel in an attempt to find locations where groundwater could be sampled. Several weepholes were discovered during underground reconnaissance. The weepholes are identified according to their walking distance from the connecting point between the open and underground reaches of San Joaquin Channel (Figure 2.10.2). The weepholes flowed in several locations. There were long stretches of lined channel where weepholes did not flow however.

The specific electrical conductance values at the weepholes varied narrowly from 2250 to 2500 uS/cm (Figure 2.10.3). These conductivity values fall toward the lower end of the values expected for the salinity of groundwaters in the shallow aquifer beneath San Diego Creek Watershed. Most surprisingly, the selenium values in groundwater varied from only 2.9 to 4.3 ug/L Se. Furthermore, selenium did not increase near the mapped location of the historic Swamp of the Frogs Marsh

(Figure 2.10.4). These data represent about the lowest concentrations of selenium found in shallow groundwater in San Diego Creek Watershed.

Arsenic did not show any representative patterns either, varying from 4.2 to 5.0 ug/L As (Figure 2.10.5). Arsenic concentrations are higher than selenium concentrations in the weepholes (Figures 2.10.4 and 2.10.5). In other parts of the watershed, arsenic rarely exceeds selenium concentrations in shallow groundwater.

A set of puzzling questions arises from the San Joaquin Channel data set. First, why is selenium so low and invariable, even at the historic marsh boundary (Figure 2.10.4)? Second, why is arsenic present in higher concentrations than selenium? Third, why is the sulfur isotope value in soil so strongly negative (-10 per mil) a few thousand feet below groundwater sampling locations? Hypotheses that may answer these questions are as follows:

● San Joaquin Channel historically did not drain selenium laden geological provinces in Loma Ridge and Santa Ana Mountains. Topographic maps from 1901 and 1948 indicate that the precursor to present-day San Joaquin Channel drained the San Joaquin Hills (Figure 2.10.6). We speculate that the geologic formations drained by San Joaquin Channel are not as enriched in selenium as are the highlands to the north.

● A topographic map from 1901 indicates that present day San Joaquin Channel passes through regions formerly occupied by local inland marshes (Figure 2.10.7). We do not know if these were part of the earlier Swamp of the Frogs Marsh or part of another local marsh complex. These local marshes provide a plausible explanation for the strongly negative $\delta 34S[SO4^{2-}]$ soil value of -10.0 per mil in San Joaquin Channel.

● Runoff waters and percolating groundwaters from the San Joaquin Hills probably created wetting conditions for these local marshes. These flows did not commingle much with runoff waters from Loma Ridge and the Santa Ana Mountains, where selenium is abundant in Miocene age rocks. The flows coming from the San Joaquin Hills are assumed not to have provided sufficient selenium to accumulate in this part of the marsh (Figure 2.10.7).

Many explanations for the occurrence of selenium, arsenic, and salinity in groundwater in San Diego Creek Watershed are geological. The anomalously low values at San Joaquin Channel are probably no exception. Even so, our explanations are preliminary. It would be useful to collect more data to confirm or revise these hypotheses. For example, it would be important to sample soils and surface water along the unlined part of San Joaquin Channel for selenium and other hydrochemical parameters. Access to the San Joaquin Hills would provide geological samples which could be tested chemically for selenium content.

It was noted earlier that surface water samples at the confluence of San Joaquin Channel and San Diego Creek had higher concentrations of selenium than the groundwater weepholes tested in this study (compare Table 2.10.2 and Figure 2.10.4). It is possible that groundwater with higher selenium concentrations is seeping into San Joaquin Channel along the unlined reach. This should be investigated further. Finally, the San Joaquin Channel study provided key groundwater data in an area where groundwater data was lacking.

Table 2.10.1. Results of Nitrate Monitoring at San Joaquin and Sand Canyon Channels (samples collected by B. Hibbs, analyzed by Orange County PFRD)

San Joaquin Channel at Michelson Ave.		
Date	**Specific Conductance (uS/cm)**	**Nitrate-Nitrogen (mg/L)**
9/14/1999	1550	5.3
9/15/1999	1510	6.7
9/16/1999	1580	10.5
9/17/1999	1530	9.0
9/18/1999	1460	9.1
9/19/1999	1540	13.1
9/20/1999	1560	9.3
Sand Canyon Channel at San Diego Creek		
Date	**Specific Conductance (uS/cm)**	**Nitrate-Nitrogen (mg/L)**
9/14/1999	1590	0.8
9/15/1999	1620	1.3
9/16/1999	1840	2.3
9/17/1999	1520	2.2
9/18/1999	1450	2.0
9/19/1999	1500	2.4
9/20/1999	1560	2.5

Table 2.10.2. Results of Selenium Monitoring at San Joaquin and Sand Canyon Channels (samples collected by B. Hibbs)

Channel	**Date**	**Selenium (ug/L)**
San Joaquin Channel at Michelson Ave	7/5/1999	11
San Joaquin Channel at Michelson Ave	10/31/1999	9
Sand Canyon Channel at San Diego Creek	10/31/1999	5

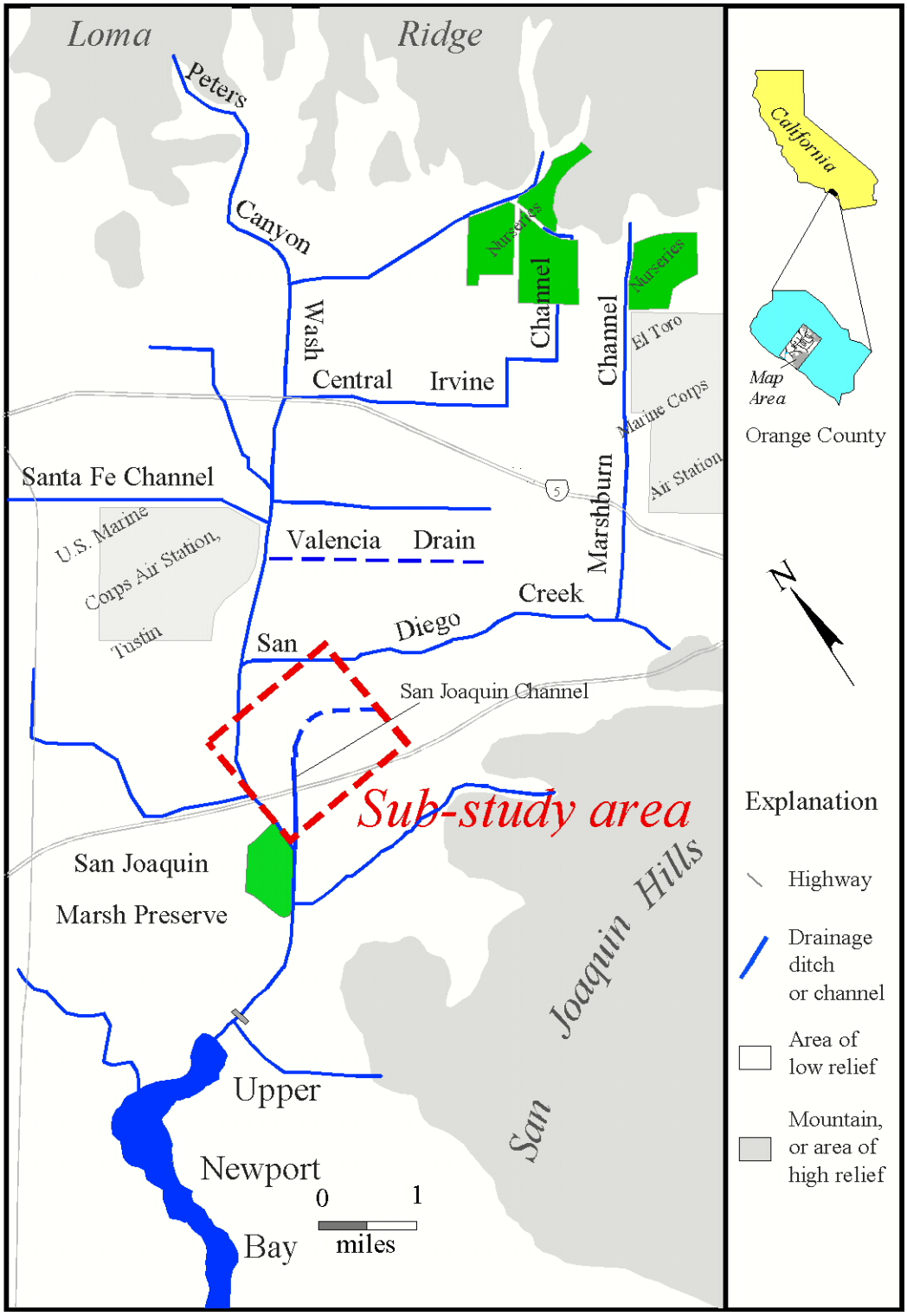


Figure 2.10.1. Location of San Joaquin Channel sub-study area.

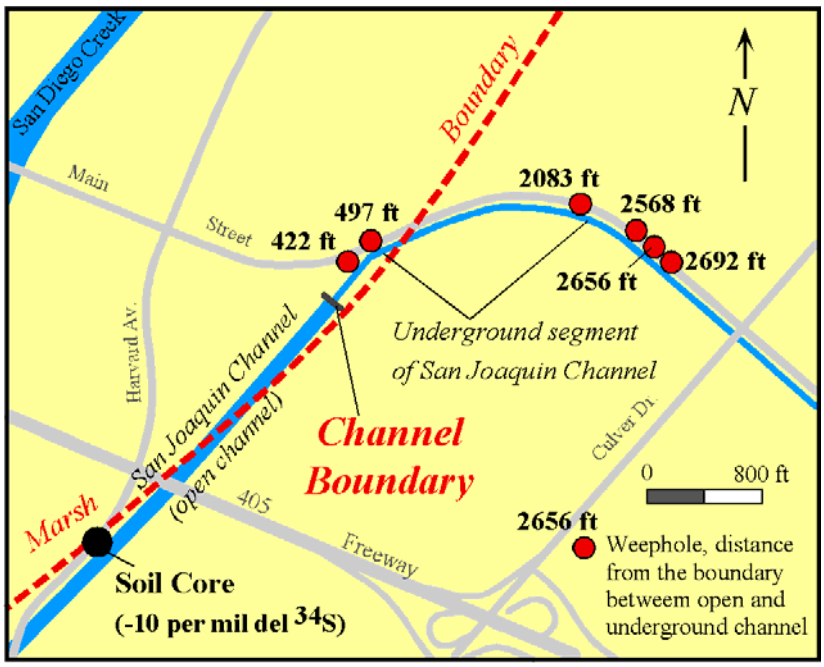


Figure 2.10.2. Location of groundwater weepholes and soil core in San Joaquin Channel. Channel Boundary indicates the location where San Joaquin Channel transitions from unlined, open channel to underground, concrete lined channel.

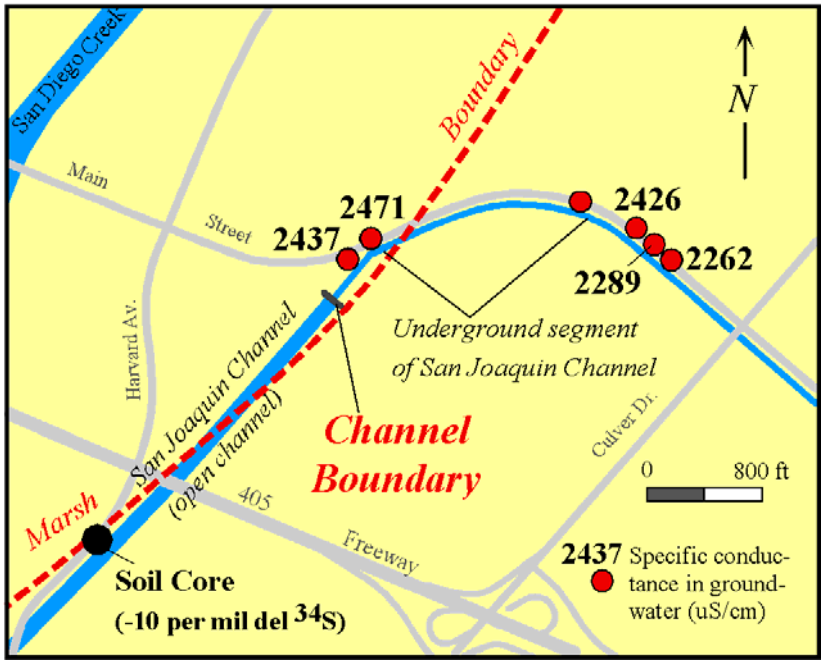


Figure 2.10.3. Specific conductance values in weepholes in San Joaquin Channel, data collected August 2004. Values are in uS/cm.

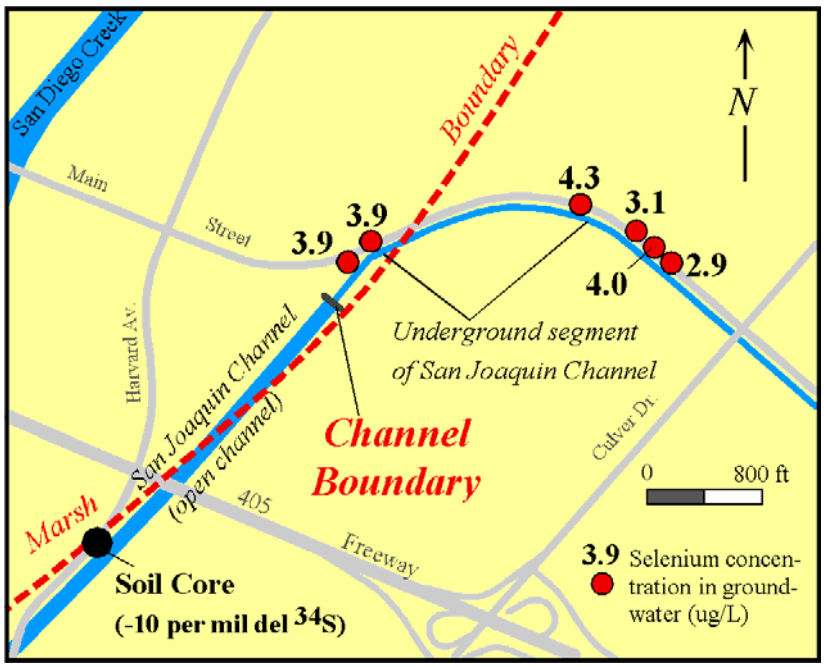


Figure 2.10.4. Selenium values in weepholes in San Joaquin Channel, data collected August 2004. Values are in ug/L.

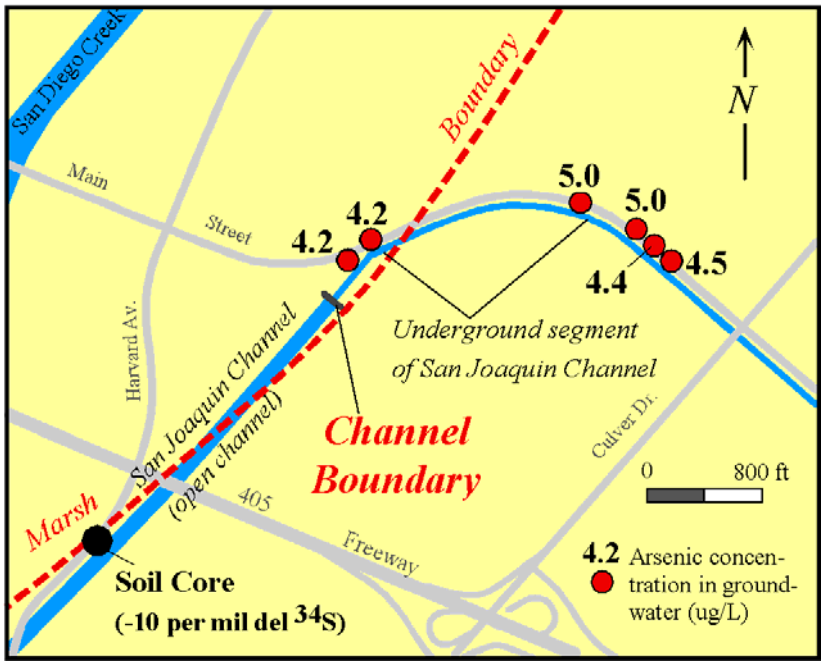


Figure 2.10.5. Arsenic values in weepholes in San Joaquin Channel, data collected August 2004. Values are in ug/L.

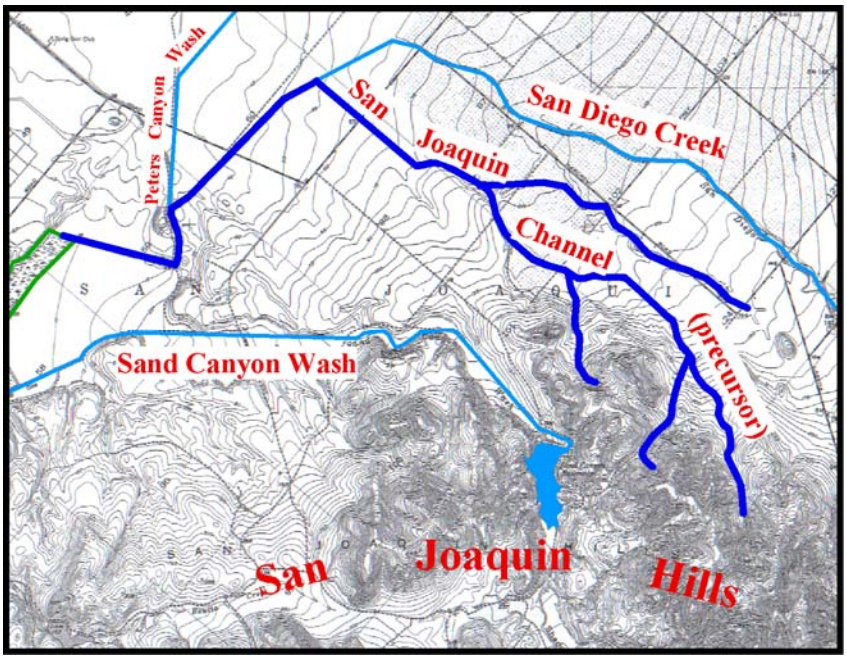


Figure 2.10.6. USGS Topographic map from 1948, indexing the precursor drainage system to present day San Joaquin Channel. San Joaquin Channel drained part of the San Joaquin Hills which may not contain as much selenium as geologic formations in Loma Ridge and Santa Ana Mountains.

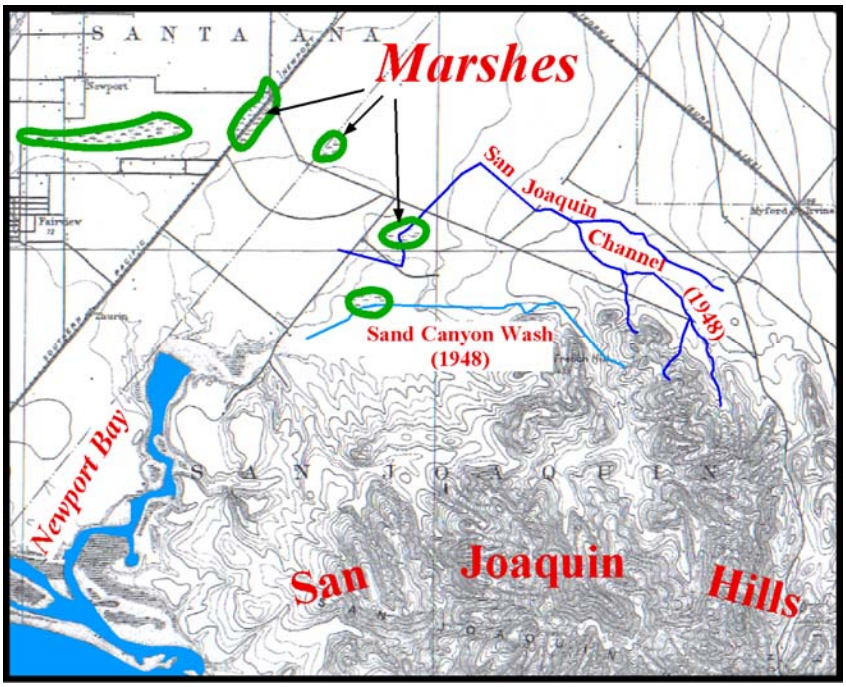


Figure 2.10.7. USGS Topographic map from 1901, indexing inland marshes along drainage ways of latter day San Joaquin Channel. These marshes may account for the strongly negative sulfur isotope signature measured in soils in San Joaquin Channel.

CONCLUSIONS

The geochemical patterns of nitrate, selenium and arsenic exhibit spatial variability within the shallow aquifer of San Diego Creek Watershed. Groundwaters within the boundary of the historic Swamp of the Frogs Marsh show a different geochemical signature than those found outside this boundary. Within the boundary of the historic marsh, the shallow groundwaters are characterized by moderate salinity, high sulfate to chloride ratios (SO_4/Cl) and high levels of selenium (Hibbs and Lee, 2000; Meixner and others, 2004). Outside the historic marsh boundary, shallow groundwaters tend to have lower salinity and lower concentrations of selenium. Nitrate appears to exert important controls on selenium mobility acting in combination with dissolved oxygen to oxidize reduced forms of selenium, thereby releasing selenium into shallow groundwater. The process is particular notable at the outer fringe of the historic marsh, where masses of bound selenium in soils are heavily concentrated.

An arsenic "hotspot", where arsenic concentrations are anomalously high, was identified inside the boundary of the historic swamp (Meixner and others, 2004). New information presented in this investigation suggests that the highest concentration of arsenic arises by evapoconcentration of groundwater that was sourced from a local geologic terrain in the headwaters of San Diego Creek Watershed.

Within the area of historic orchards, groundwaters exhibit higher concentrations of nitrate than in areas that were cultivated with row crops or that have always remained uncultivated. High soil salinity within the boundaries of the

historic marsh prevented some types of agricultural crops from taking root, particularly citrus orchards. These hypersaline areas have much lower concentrations of nitrate and selenium in underlying groundwater today.

Spatial relationships suggest that the important sources of selenium and arsenic came from mountain terrains that drain into different regions in San Diego Creek Watershed. The antecedents to Santa Ana Delhi Channel, Santa Fe Channel, and El Modena Channel drainages were evidently sourced from mountains that are also drained by Santiago Creek. This upland region appears to contain important sources of selenium, but little arsenic. The antecedents to Como Channel and San Diego Creek drainages were connected to channels that extend into the mountains ranging from Hicks Canyon Channel to Borrego Canyon Channel. These uplands appear to be a prominent source of both selenium and arsenic. The antecedents to San Joaquin Channel and Sand Canyon Wash drained the San Joaquin Hills. This upland region appears to contain limited sources of selenium and arsenic, at least where they drained into the precursors to San Joaquin Channel and Sand Canyon Wash.

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Chapter 3

Time Series Analysis of Groundwater Chemistry in San Diego Creek Watershed

with a section on newly installed urban storm drains

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1 May 2008

Prepared for
Santa Ana Regional Water Quality Control Board

by

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Part I: Groundwater Time Series Investigation

INTRODUCTION

Time series monitoring of select groundwater discharge points located both within and outside of the historic marsh boundary was undertaken in order to track seasonal variability in hydrochemical parameters (salinity, sulfate, chloride, nitrate and dissolved selenium). Monitoring over 2006-2007 occurred over one of the driest years on record. However, the availability of a complementary dataset collected over a moderately wet year (2002-2003) gives the unique opportunity to compare changes in these hydrochemical parameters over a wet year and a drought year. This permits a better understanding of processes governing the release of contaminants such as nitrate and selenium from the aquifer matrix into groundwaters. Changes in nitrate and selenium loads in the watershed occur over seasonal cycles. Understanding the changes that affect these constituents in the groundwater environment will aid our understanding of how these changes manifest in surface waters.

METHODS

Groundwater quality was monitored during a moderately wet year (2002-2003) and a drought year (2006-2007) at five groundwater discharge points (Figure 3.1 and Table 3.1). Concomitantly, groundwater levels in the shallow aquifer were monitored at six monitoring wells located throughout the basin (Figure 3.1 and Table 3.2). Depth to the water table was measured in order to observe changes in groundwater elevation.

Water quality data was collected at five sites: weephole 10N along Santa Fe Channel (SFC10N), the spring along San Diego Creek at Harvard (SDCH), the spring at the outlet of Valencia drain (VAL), the spring across from Valencia drain (AVAL), and the weephole along

Como Channel at Yale Avenue (CCY). Table 3.1 gives GPS co-ordinates for each of these groundwater discharge points. Summary statistics of groundwater quality at each of these sites can be found in Appendix 3A.

Three wells were used to represent changes in water table elevation in time series in conjunction with trends in selected water quality parameters: electrical conductivity, sulfate, chloride, nitrate, and selenium. These wells were selected because of their proximity to the sampling site and because the trends in water table level they exhibit seem to give the best reflection of aquifer response on a catchment scale. Table 3.2 gives GPS co-ordinates for the six monitoring wells; the three used to represent changes in water table elevation are highlighted in blue.

Time series graphs reveal how water quality parameters change seasonally (Appendix 3B). The first four sites shown in Table 3.1 are located within the boundary of the historic swamp and tend to exhibit similar seasonal trends with respect to salinity, nitrate and selenium. Different seasonal patterns were observed in salinity, nitrate and selenium at CCY, which is located approximately 0.7 miles outside the boundary of the historic swamp. Comparing water quality parameters in these two sets of time series data (wet-year and drought-year) reveals that the temporal variability in salinity and the concentration of nitrate and selenium relates to land use history.

Table 3.1: GPS Co-ordinates for the Five Groundwater Discharge Points.

Abbreviation	Sampling Site	Latitude	Longitude
VAL	Valencia Spring	N 33.70055	W 117.80942
AVAL	Across Valencia Spring	N 33.70067	W 117.80966
SDCH	SDC Spring @ Harvard	N 33.68367	W 117.81238
SFC10N	Santa Fe Weephole 10N	N 33.710086	W 117.808840
CCY	Como Yale Weephole	N 33.69182	W 117.78226

Table 3.2: GPS Co-ordinates for the Six Monitoring Wells.

Monitoring Well	Latitude	Longitude
Well 63-S	N 33.704590	W 117.795000
Como Well	N 33.706476	W 117. 802810
Well 85-W	N 33.702175	W 117.785628
Well 86-N	N 33.690639	W 117.793868
Well 102-N	N 33.673938	W 117.785114
Well 103-N	N 33.684283	W 117.778965

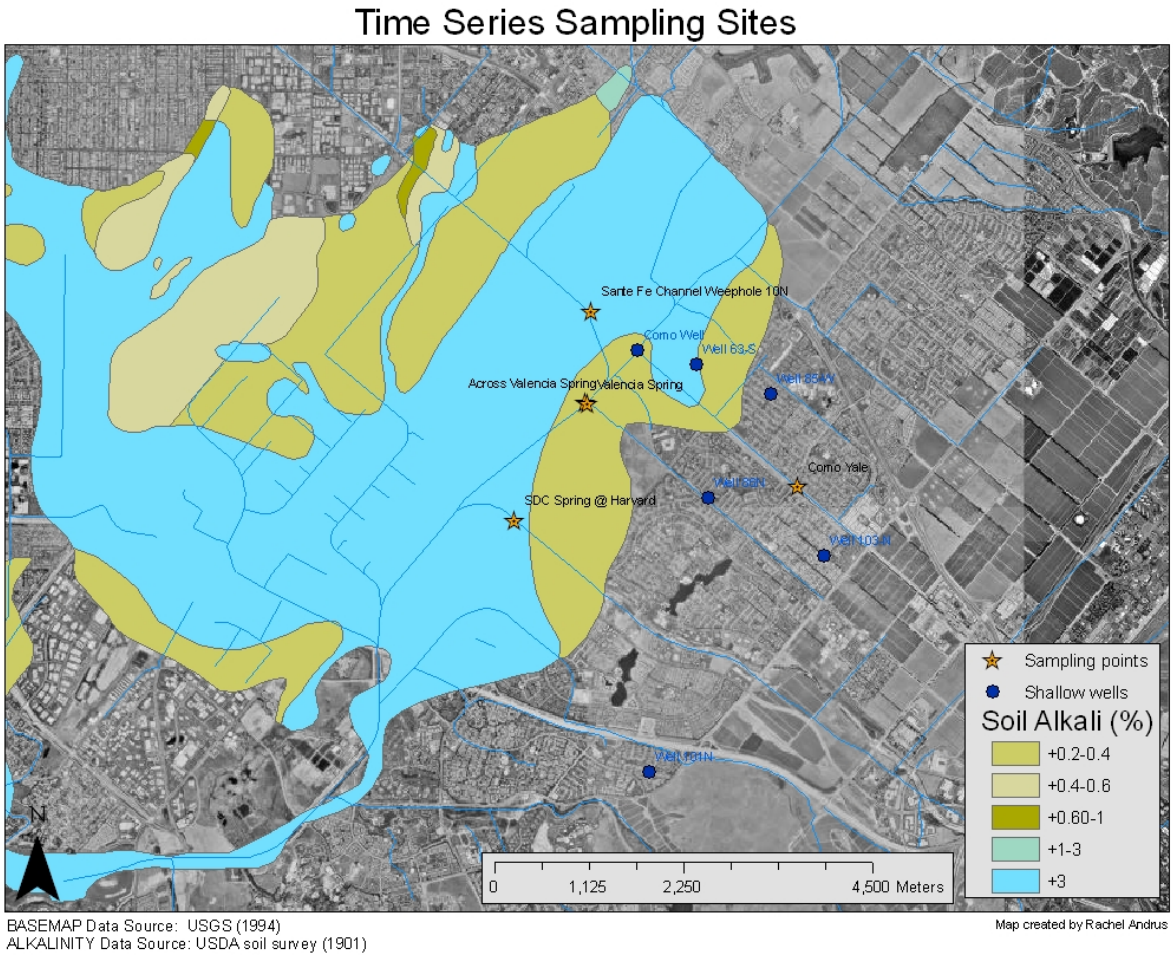


Figure 3.1. Map showing study area. Soil alkali (salinity) contours coincide roughly with the boundary of the historic Swamp of the Frogs. Note that most groundwater sampling points (orange stars) are located within the boundary of the historic marsh. Monitoring wells are shown as blue points.

RESULTS AND DISCUSSION

Precipitation and Aquifer Response

Data gathered over the wet-year (June 2002-March 2004) show that the water table rises in response to precipitation events (Walker, 2006). In total, 10.75 inches precipitation fell in the Irvine area over the 2002-2003 water-year, with 8.72 inches falling between December 2002 and March 2003 (Figure 3.2). During the drought-year, precipitation was minimal, totaling only 2.2 inches over the 2006-2007 water-year. Most rainfall occurred between October 2006 and February 2007 with 1.72 inches falling during this period. The overall trend was a drop in the water table, with most wells exhibiting a drop less than ¼ inch in hydraulic head (Figure 3.3). Two wells exhibited a greater drop of approximately one inch in hydraulic head. The greatest control on the hydraulic head response to precipitation appears to proximity to a constant head barrier such as Peters Canyon Wash. Groundwater levels do not fluctuate as much near these boundaries except during flood stage.

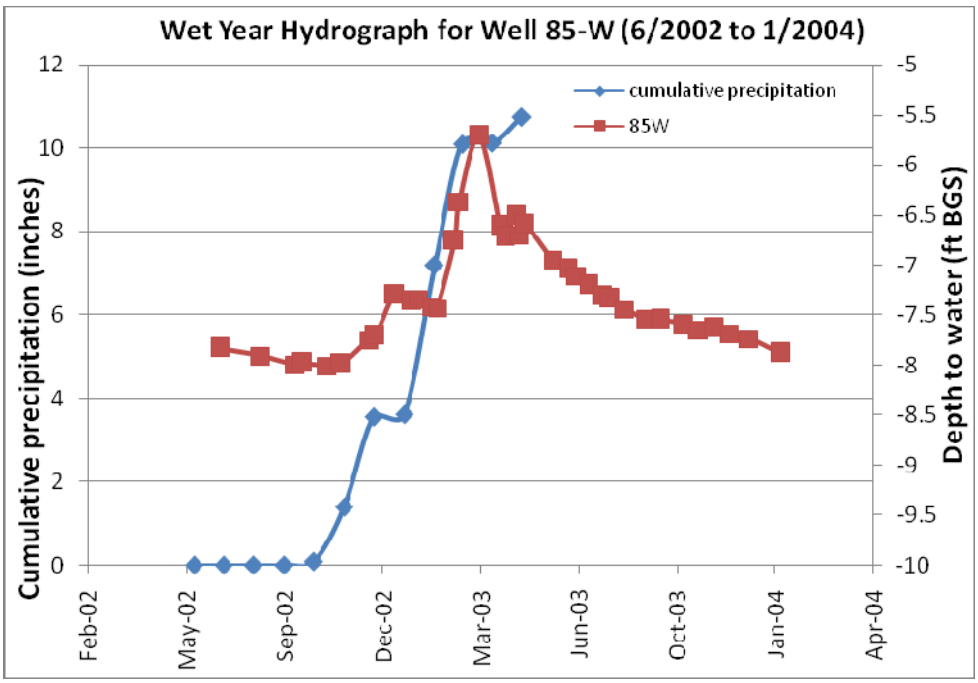


Figure 3.2. Hydrograph showing cumulative precipitation (solid blue line) and depth to water in IRWD well 85-W (solid red line) during the wet year monitoring period.

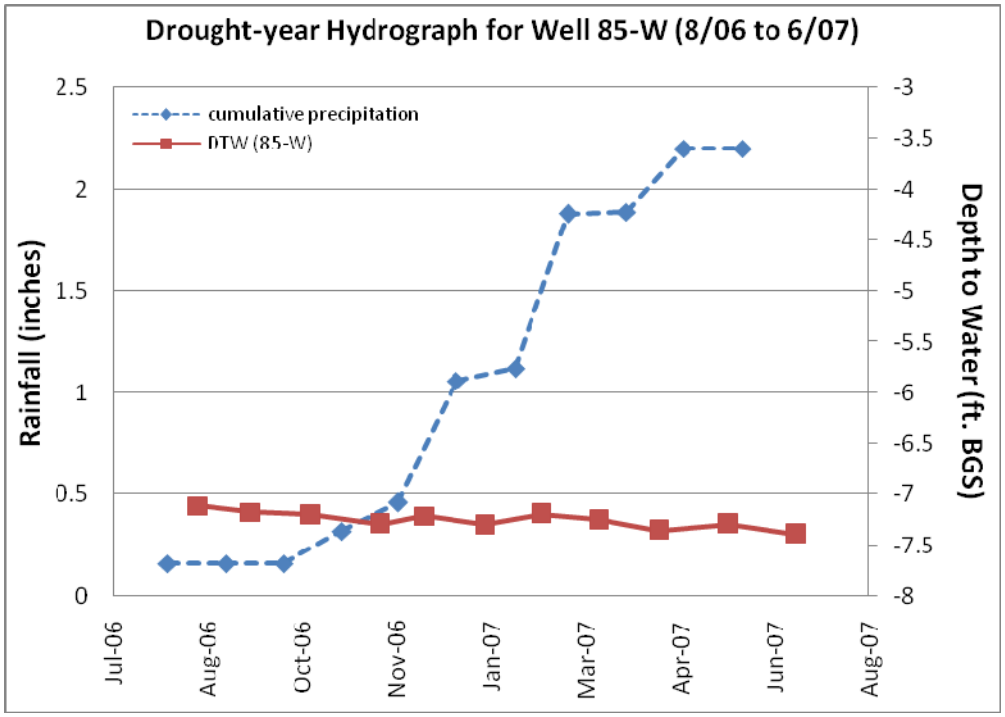


Figure 3.3. Hydrograph showing cumulative precipitation (dashed blue line) and depth to water in IRWD well 85-W (solid red line) during the drought year monitoring period.

Salinity Patterns

Electrical conductivity (EC) is a semi-quantitative proxy for the amount of total dissolved solids. When used in conjunction with sulfate and chloride data, a clear picture of the seasonal variability of salinity emerges. First, salinity data from the wet-year will be presented, including a discussion of sulfate and chloride patterns. Following this discussion, salinity data collected during the drought-year will be presented. When appropriate, representative time series graphs will be used to illustrate broader trends in hydrochemical parameters. An integrated set of these time series graphs organized by site may be found in Appendix 3B.

During the wet year, 4 of the 5 sites initially exhibit decreasing EC during the period of increasing hydraulic head. All four of these are located within the boundary of the historic Swamp of the Frogs. VAL, a representative site for salinity patterns within the historic marsh boundary, shows an example of this pattern whereby EC drops from 5050 µS in July to 4750 µS in December, then increases to about 5100 µS in March (Figure 3.4). This initial drop in salinity is not observed at CCY, outside the boundaries of the historic marsh. Instead, CCY exhibits a positive correlation between water table elevation and salinity, with EC increasing continuously as water table elevation rises in response to precipitation (Figure 3.5). This is most likely due infiltrating precipitation acting to leach salts from the vadose zone. The observed lag between increasing salinity and water table elevation is most likely due to mixing dynamics in the shallow aquifer.

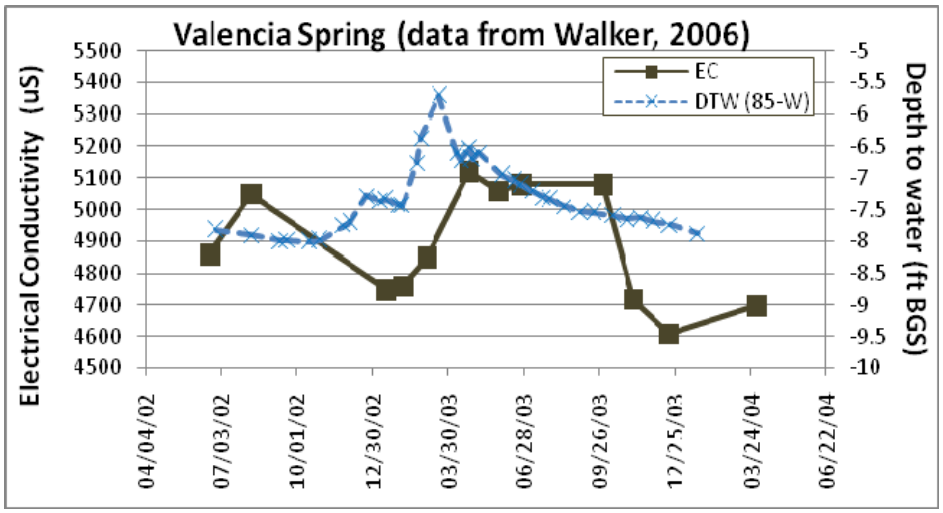


Figure 3.4. Time-series plot of EC at VAL during wet-year monitoring.

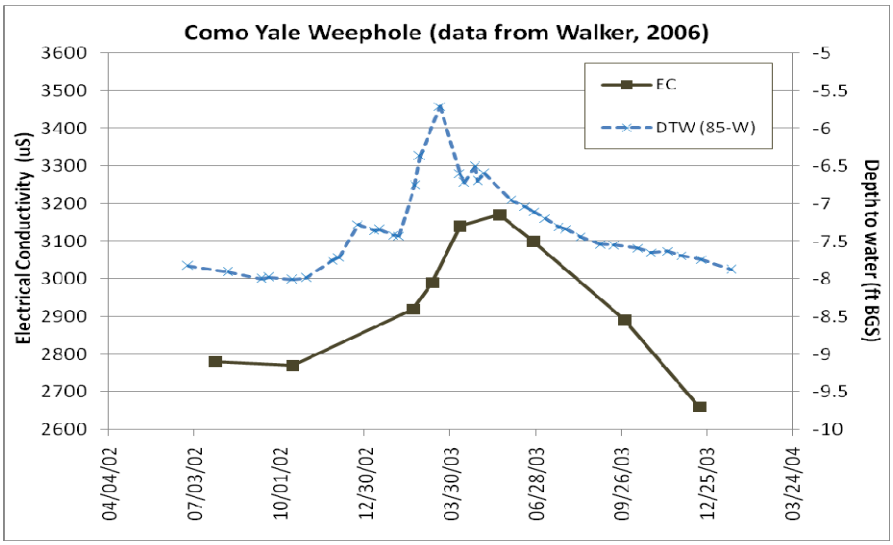


Figure 3.5. Time-series plot of EC at CCY during wet-year monitoring.

Sulfate and chloride can also help to track changes in salinity. The conservative nature of these constituents is well-suited to investigating salinity patterns. It is normally expected that concentrations of sulfate and chloride will mimic the patterns observed for EC. Sulfate is the dominant anion in these waters and therefore tends to mimic patterns observed for EC (Figures 3.6 and 3.7). Chloride, however, tends to increase during the period of increasing hydraulic

head. Plotting sulfate:chloride ratio for the wet-year monitoring period clearly shows this relationship (Figure 3.8).

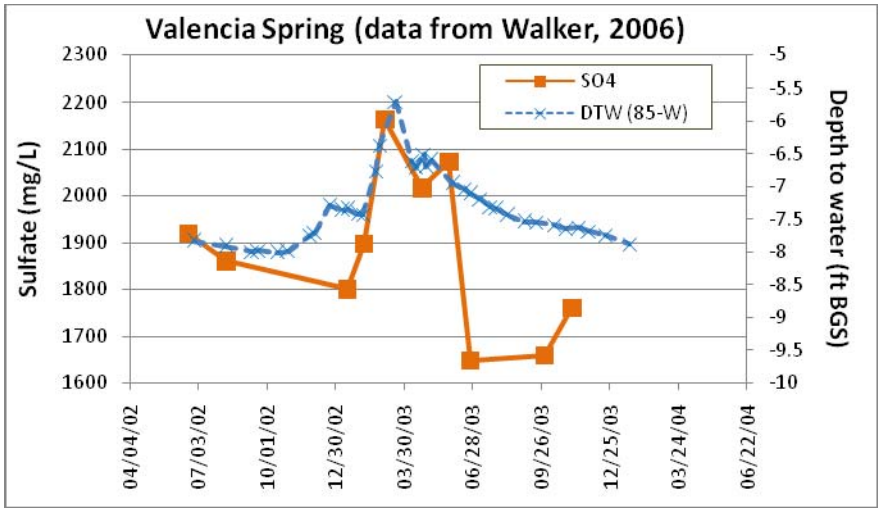


Figure 3.6. Time-series plot of sulfate at VAL during wet-year monitoring. Compare with Figure 3.4.

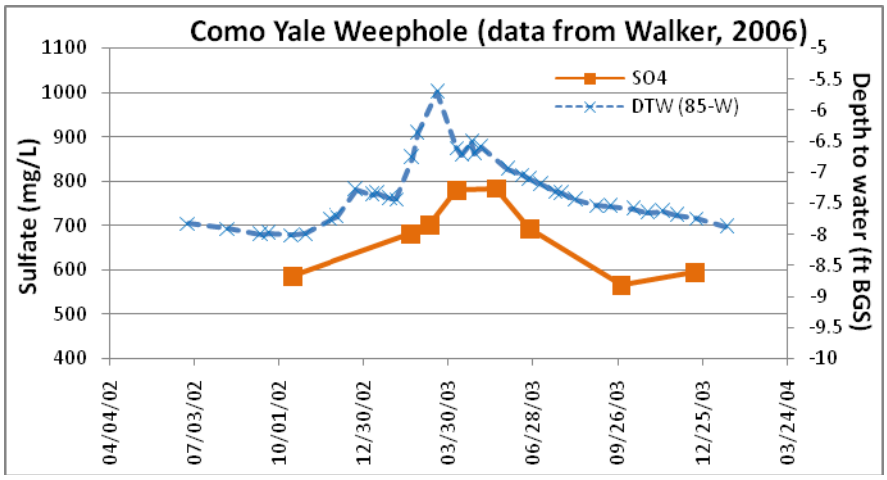


Figure 3.7. Time-series plot of sulfate at CCY during wet-year monitoring. Compare with Figure 3.5.

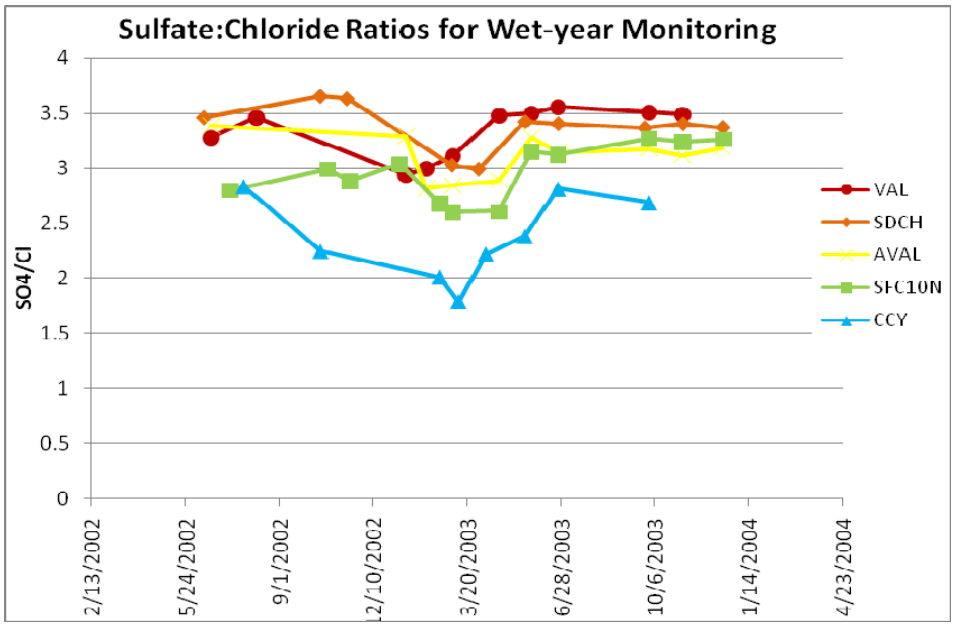


Figure 3.8. Time-series plot of the changes observed in SO_4/Cl ratios.

Chemical precipitation and dissolution kinetics could be one explanation for the uncoupled behavior of sulfate and chloride across the catchment. The four sites within the historic marsh boundary are situated within the San Joaquin black adobe, a very fine-grained soil, while the representative site outside the historic marsh boundary (CCY) is located in the Fullerton sandy adobe, a fine-grained soil with a greater proportion of sand (Figure 3.9). Finer-grained soils have smaller pore spaces, which results in stronger capillary forces that pull the water up a greater distance from the water table. During dry-weather conditions, capillary forces may carry these conservative ions into the capillary fringe to a height above the water table great enough such that moisture can be wicked away via evaporation at land surface, leaving residual moisture enriched in dissolved sulfate and chloride. Thernardite (Na_2SO_4), which has a slightly lower solubility than halite (NaCl), may precipitate in the vadose zone during dry-weather conditions (Valero-Garces et al., 2000). This would create an unsaturated zone that is enriched

in dissolved chloride with pockets of thernardite salts. Infiltrating precipitation then leaches these salts back into the shallow aquifer at rates dependent on dissolution kinetics (Figure 3.10).

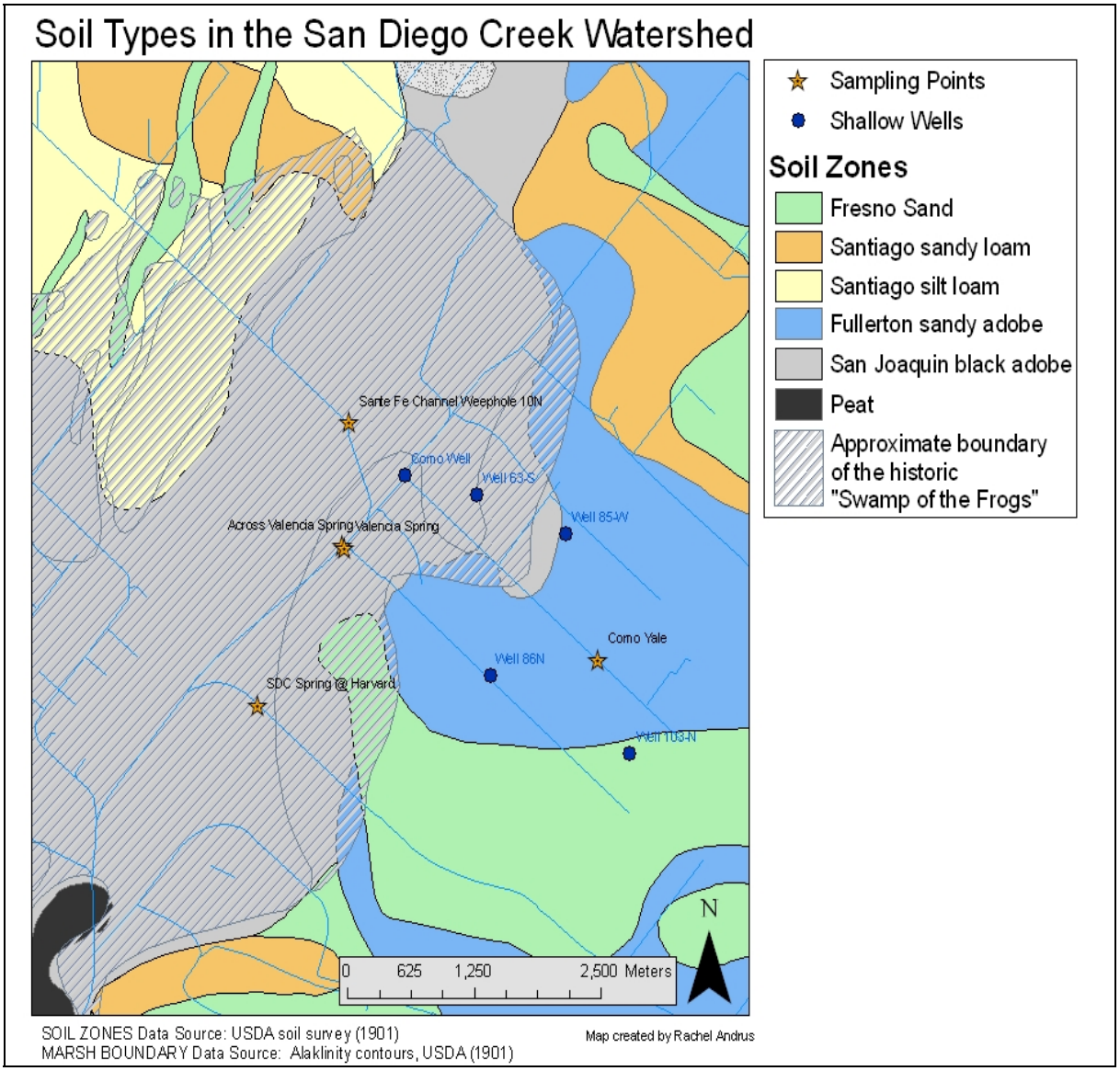


Figure 3.9. Map showing the spatial relationship between soils and sampling sites. Note that most sites are located within the fine-grained San Joaquin black adobe soil.

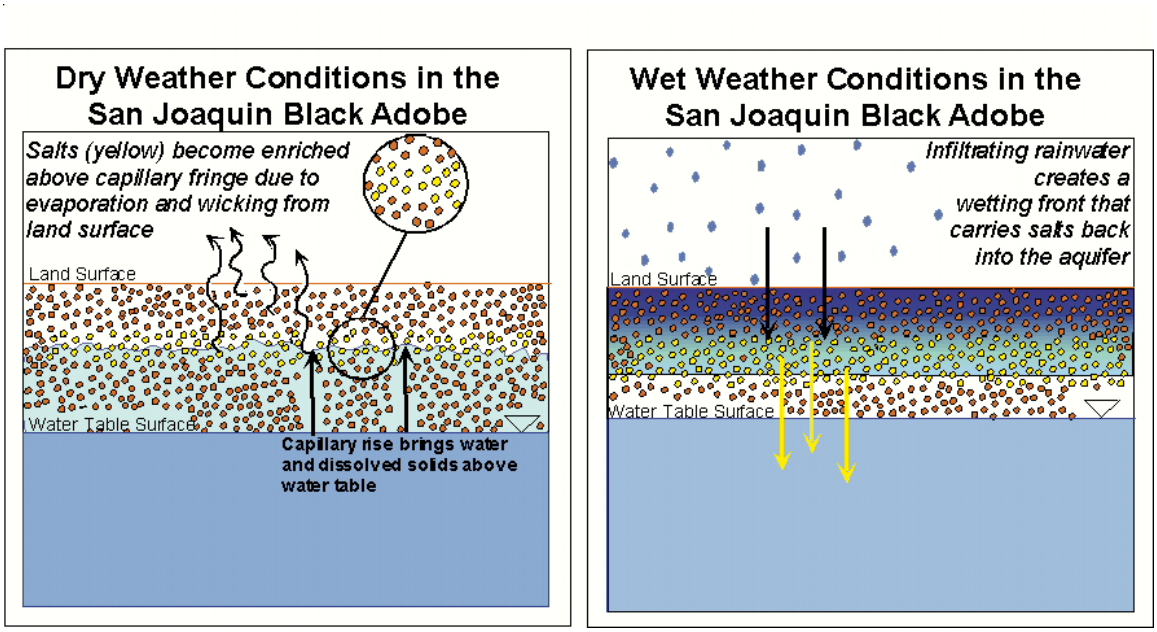


Figure 3.10. Conceptual diagram depicting the effect of capillary rise on seasonal salinity patterns during a typical wet-year. During dry-weather conditions, capillary forces pull water and dissolved solids above the water table to a height great enough that wicking and evaporation of moisture at land surface causes salts to be enriched in the vadose zone. These salts are then carried back to the water table with infiltrating rainwater.

Drought-year data shows that salinity patterns vary across the catchment. Minimal variation in water table elevation during the drought-year implies that the aquifer received very little recharge from infiltrating precipitation (Figure 3.3). Data from SFC10N and SDCH supports the interpretation that infiltrating rainwater has an initial diluting effect on groundwaters within the boundary of the historic swamp. Without the influence of infiltrating rainwater, both water table elevation and EC tend to remain relatively constant at these sites (Figures 3.11 and 3.12).

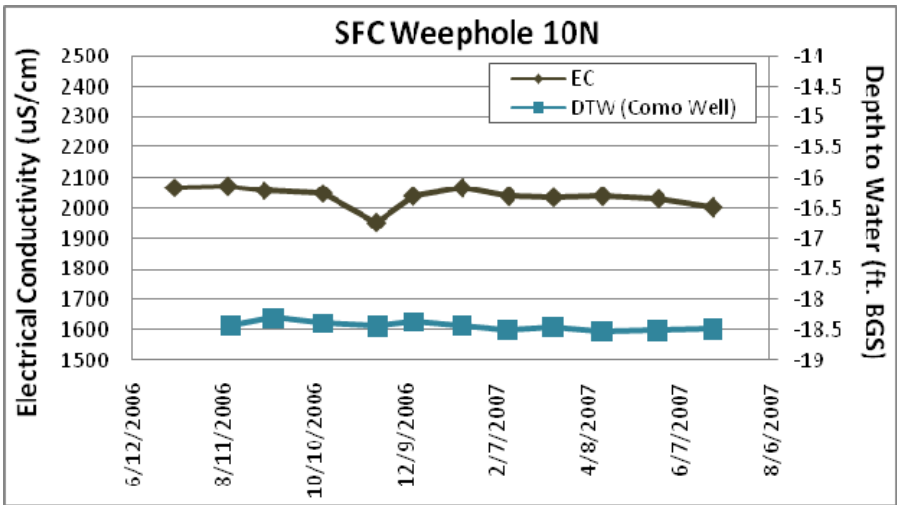


Figure 3.11. Time series plot of EC at SFC10N for drought-year monitoring.

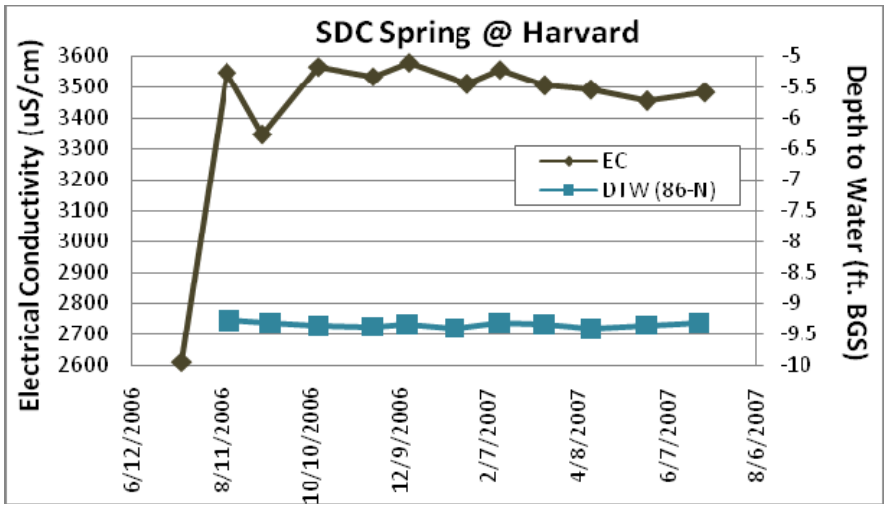


Figure 3.12. Time series plot of EC at SDCH for drought-year monitoring.

Drought-year data for the two other sites located within the historic marsh boundary (VAL and AVAL) suggest that there may be some seasonal control on salinity that is not related to precipitation. During the drought-year, AVAL shows a minor decline in EC, most notably from October to December 2006 and from March to May 2007 (Figure 3.13). This corresponds to an overall decline in sulfate concentrations (Figure 3.14). It appears that salinity at AVAL is dropping continuously over time. Sulfate and chloride plotted in time series from the beginning

of wet-year monitoring (June 2002) to the end of drought-year monitoring (June 2007), while not continuous, illustrates this trend (Figure 3.15).

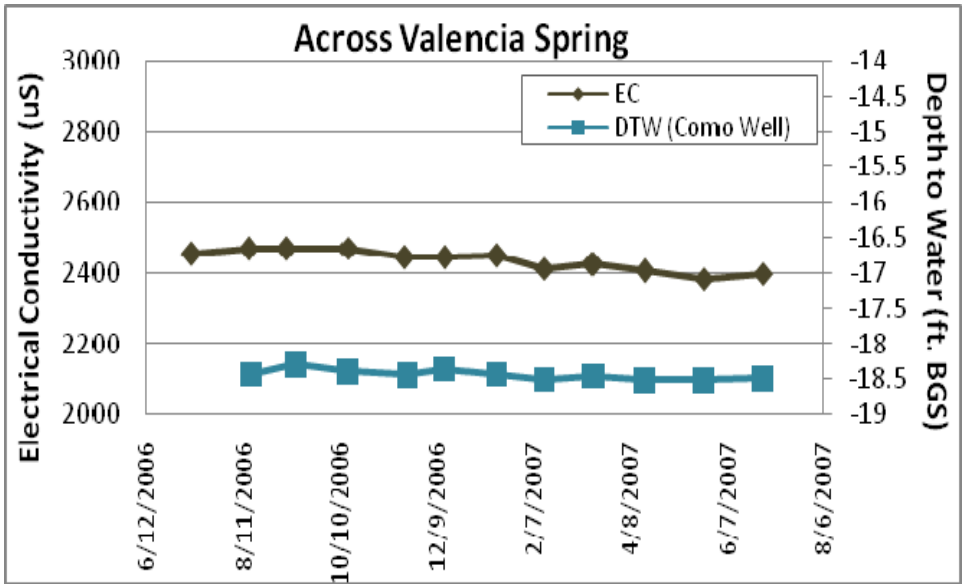


Figure 3.13. Time-series plot of EC at AVAL during drought-year monitoring.

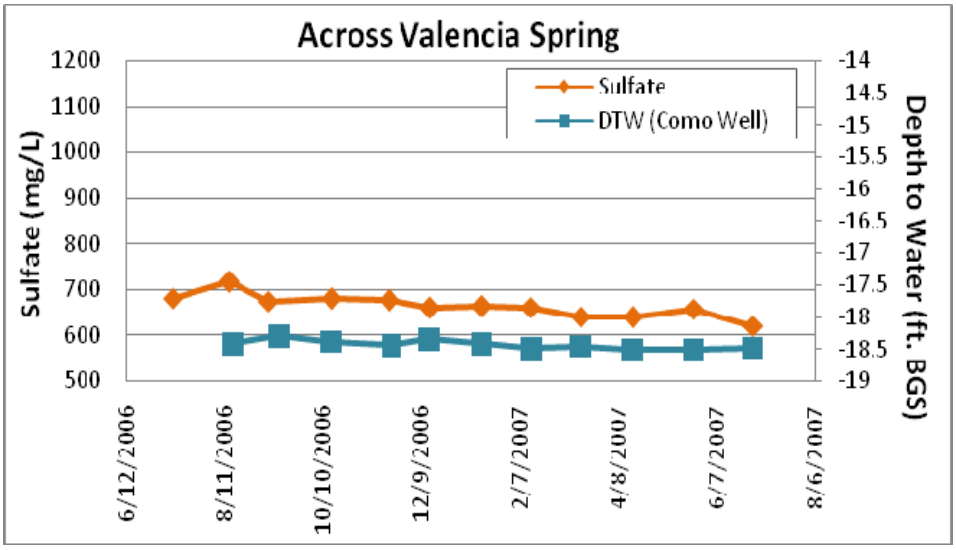


Figure 3.14. Time-series plot of sulfate at AVAL during drought-year monitoring.

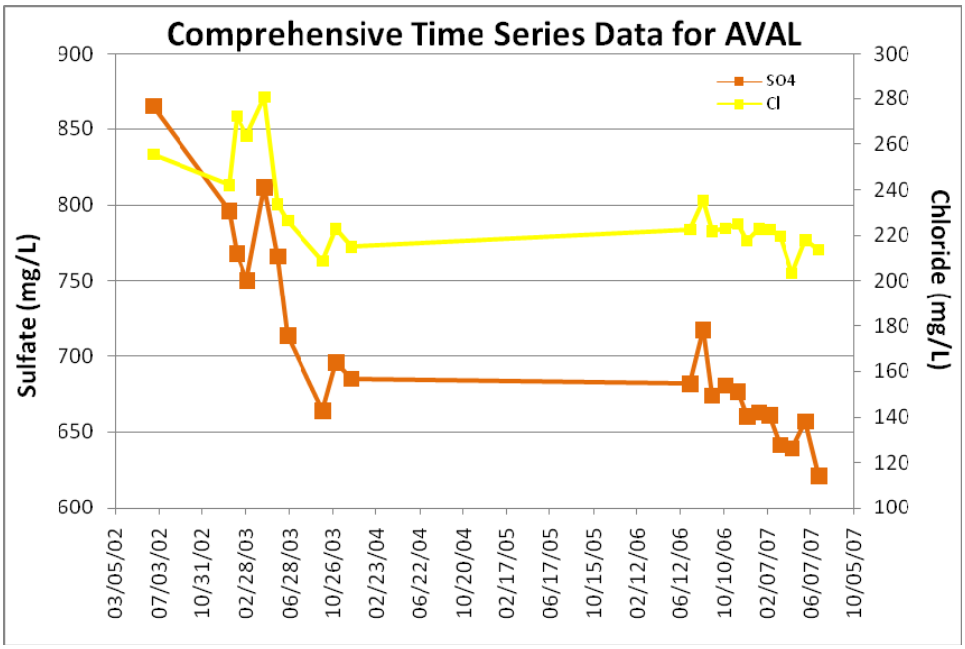


Figure 3.15. Time series data for wet-year and drought-year data plotted together for both sulfate and chloride at AVAL. Note that salinity appears to be dropping continuously over time at this site.

VAL, on the other hand, shows the opposite pattern. During the drought year, EC at VAL increases more or less continuously with minor drops in October 2006 and February 2007 (Figure 3.16). This corresponds to increasing sulfate concentrations from September 2006 to January 2007 and from March to April 2007 (Figure 3.17). For VAL, both wet-year and drought-year data show sulfate concentrations dropping markedly after April. While VAL may exhibit some of the trends associated with leaching of salts from the capillary fringe during the wet-year, drought-year data suggest there may be some seasonal control on the mobility of sulfate that manifests as a springtime peak (March-April) that subsequently declines.

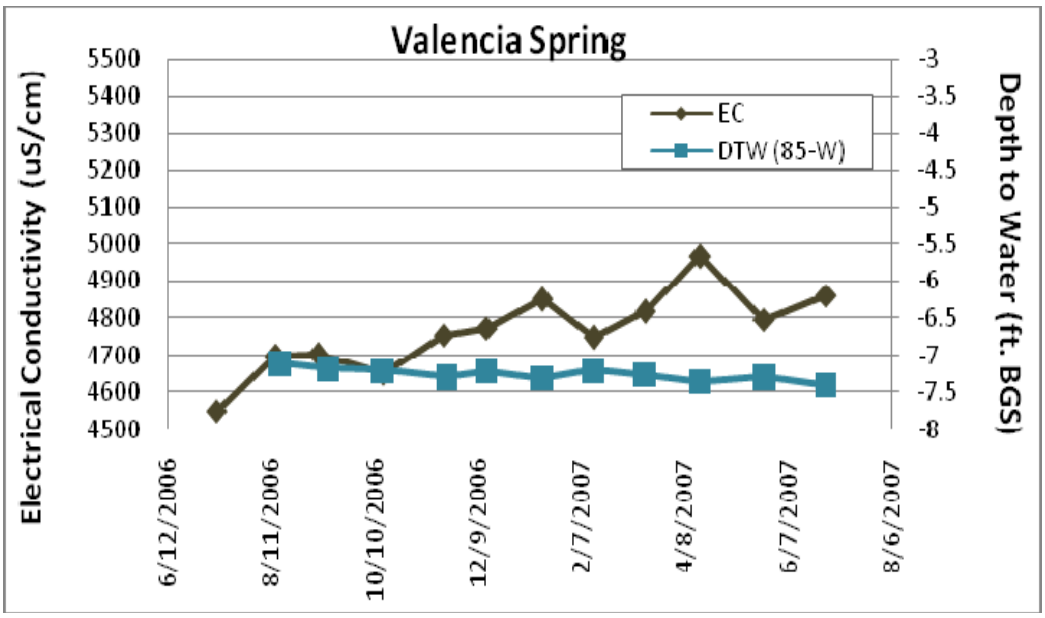


Figure 3.16. Time-series plot of EC at VAL during drought-year monitoring.

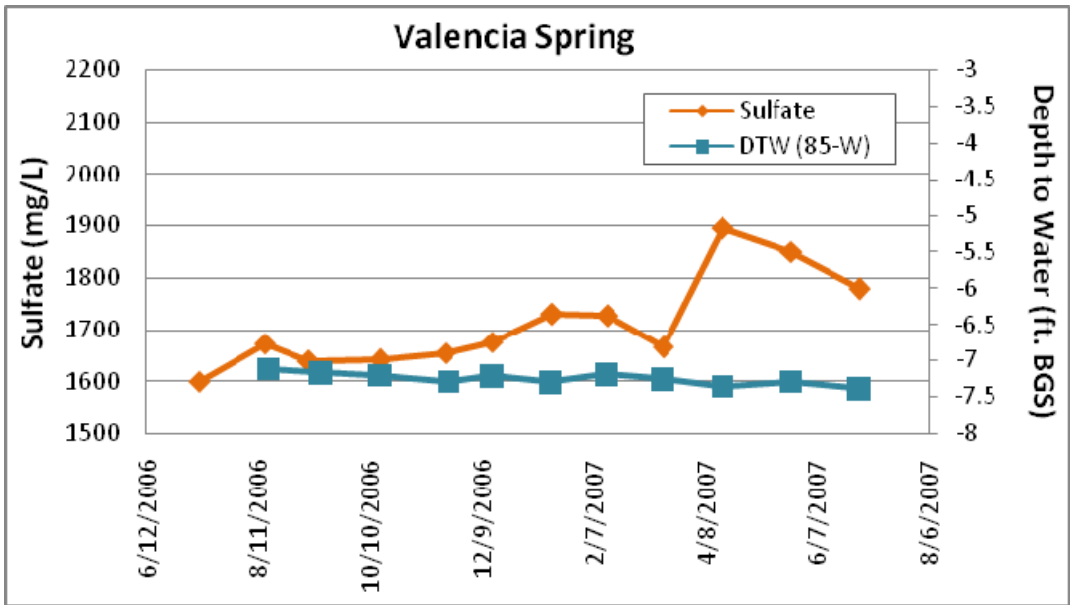


Figure 3.17. Time-series plot of sulfate at VAL during drought-year monitoring.

Plots of time-series changes in the SO_4/Cl ratio during drought-year monitoring also reveal there may be seasonal controls affecting salinity on a catchment scale (Figure 3.18). Sulfate suddenly peaks in April 2007 at all four sites within the boundary of the historic swamp

while chloride concentrations at all of these sites remain steady for the duration of drought-year monitoring. This suggests that VAL is not the only site that exhibits a springtime peak in sulfate.

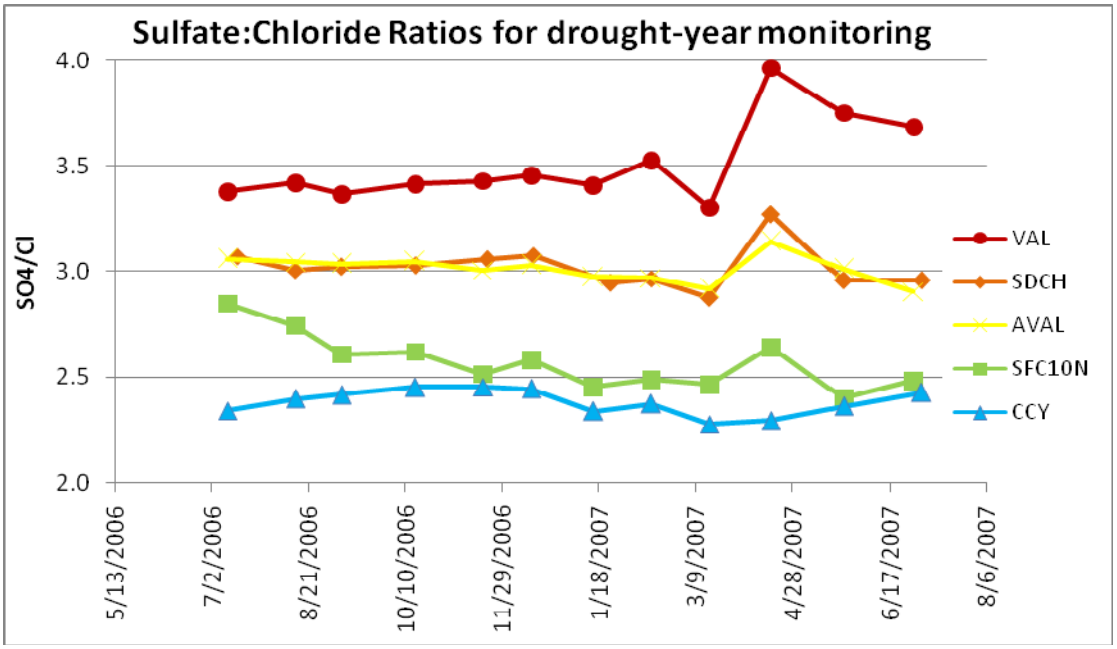


Figure 3.18. Time-series plot of the changes observed in SO_4/Cl ratios at the five sites during drought-year monitoring. Note that all sites within the boundary of the historic marsh exhibit a spike in this ratio in April 2007, which may result from increased plant and microbial productivity.

During the drought-year, EC tends to decrease initially at CCY- the representative site outside the historic marsh boundary- and then begins to rise again in December 2006, stabilizing at an approximate value of 3000 µS (Figure 3.19). This salinity increase follows the first major rain event of the season when 0.2 inch (0.5 cm) of rain fell on December 9, 2006. This small amount of rainfall induced a negligible rise in the water table (0.08 inches in well 85-W), which may have carried sufficient moisture to leach salts from the vadose zone. Walker (2006) suggested that salts may have accumulated in the soils in the vicinity of CCY as a result of historical land use practices. This site sits within the area of historic orchards, which received

abundant application of fertilizers before about 1970 (Figure 3.20). The positive correlation between water table elevation and salinity during wet-weather supports this interpretation as does nitrate data, which are discussed below.

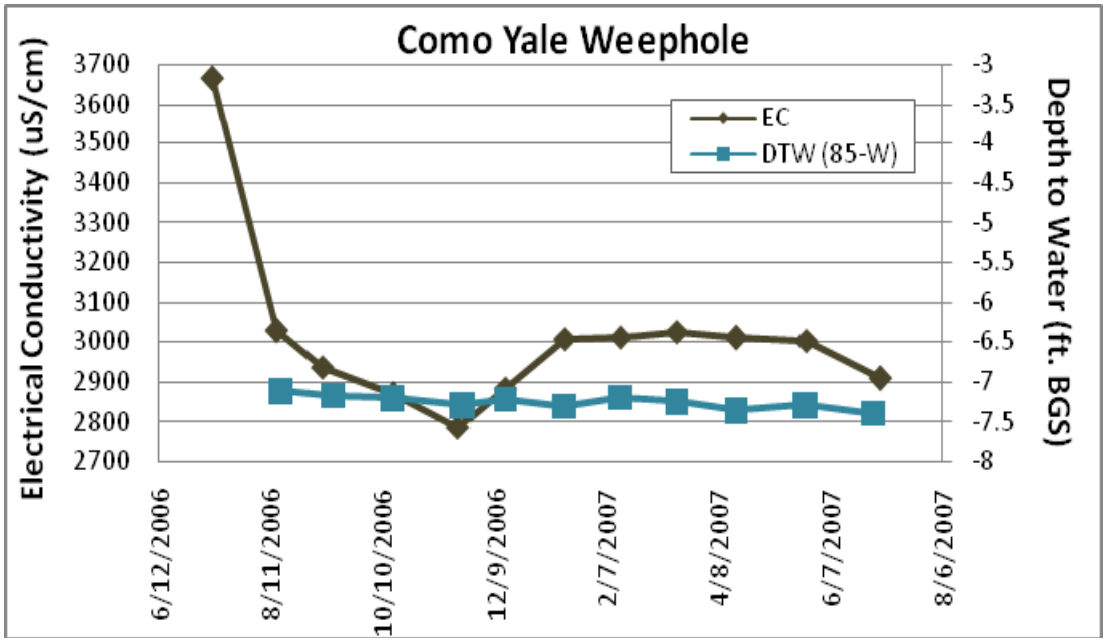


Figure 3.19. Time-series plot of EC at CCY during drought-year monitoring.

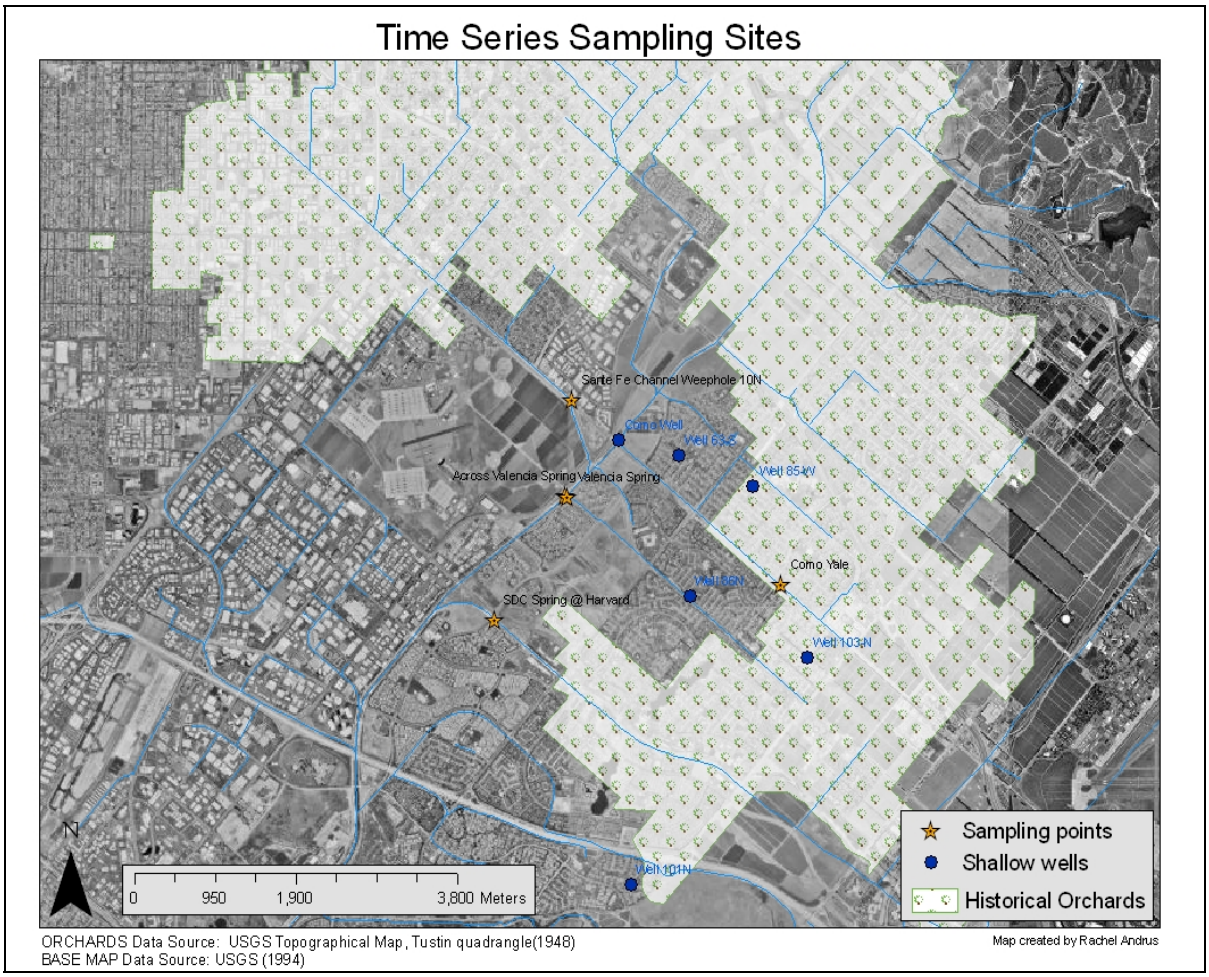


Figure 3.20. Map showing historical distribution of orchards and, by association, fertilizer application circa 1948 (USGS, 1948). The aerial photo base map show agricultural plots that are still active in the eastern part of the watershed in 1994. Note that CCY and IRWD Well 103-N are both located within the region of the historic orchards.

Nitrate and Selenium

There is a very strong geographical influence on the seasonal variation of nitrate relating to land use history. On a catchment scale, nitrate variation is strongly linked to precipitation events. During the wet year, the same four sites that exhibit an initial drop in EC during the period of increasing hydraulic head (VAL, AVAL, SDCH, SFC10N) also show decreasing nitrate concentrations. VAL clearly shows this with nitrate dropping 23% from its dry-weather

value during the period of increasing hydraulic head (Figure 3.21). CCY, which showed a positive correlation between salinity and hydraulic head, shows the same correlation with nitrate concentration (Figure 3.22).

The first four sites are all located within the boundaries of the historic "Swamp of the Frogs" Marsh, which is characterized by high soil alkali (salinity). This area has a limited history of agriculture that predates industrial fertilizer production. Thus, unlike the areas well outside the historic swamp boundary, it does not have a history of extensive fertilizer application. This appears to be the major variable controlling seasonal nitrate concentrations on a catchment scale (Figure 3.23).

Nitrate associated with historic fertilizer application is presumably enriched in the vadose zone and in groundwaters underlying the area of the historic orchards. Nitrate-enriched groundwaters flow down the hydraulic gradient into the area overlain by saline soils, which had limited agriculture. In the area of historic orchards, infiltrating rainwater leaches nitrate from the vadose zone resulting in increased nitrate concentration in groundwater. Infiltrating rainwater in the alkali region has the opposite effect, effectively diluting nitrate concentrations in groundwater. Sites such as CCY and IRWD Well 103N, which are located within the area of historic fertilizer application, both exhibit a positive correlation between nitrate concentration and hydraulic head (Figures 3.22 and 3.23), supporting the interpretation illustrated in Figure 3.24. Investigations in Orange County estimate that it may take anywhere from 10 to 35 years for irrigation waters applied to fields to reach the shallow aquifer, depending on depth to the water table (French et al., 2006; Rible et al., 1974).

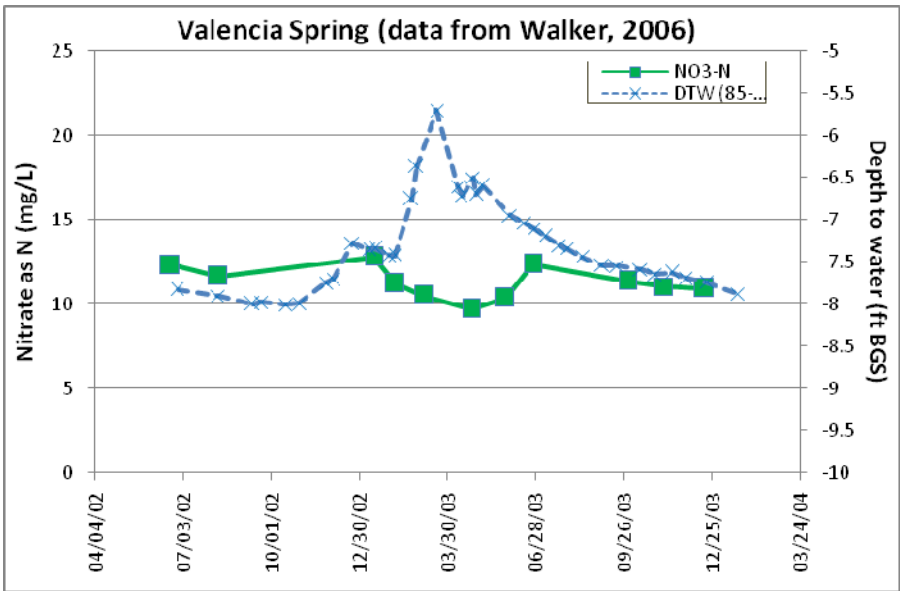


Figure 3.21. Time-series plot of nitrate as nitrogen at VAL during wet-year monitoring.

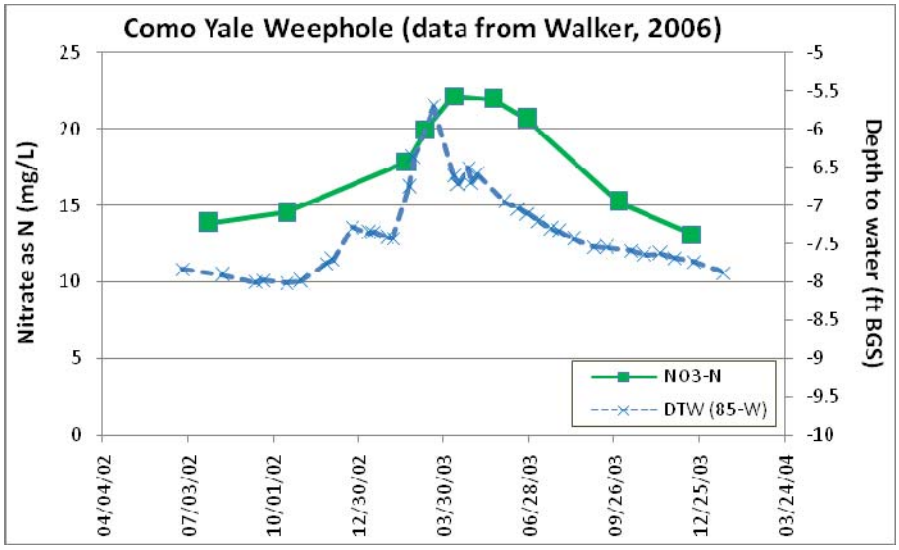


Figure 3.22. Time-series plot of nitrate as nitrogen at CCY during wet-year monitoring.

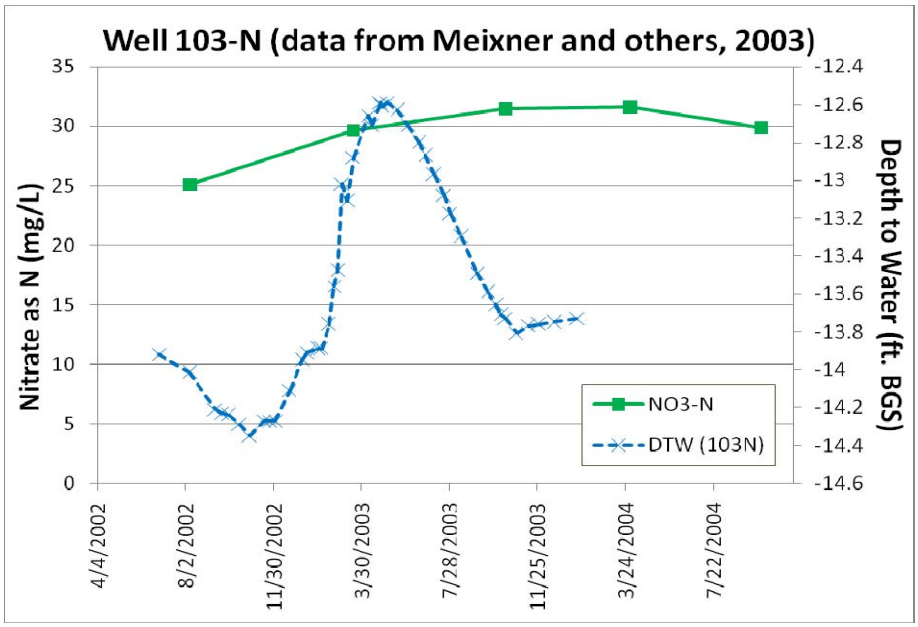


Figure 3.23. Time series plot of nitrate as nitrogen at Well 103-N, which is located within the area of historic orchards.

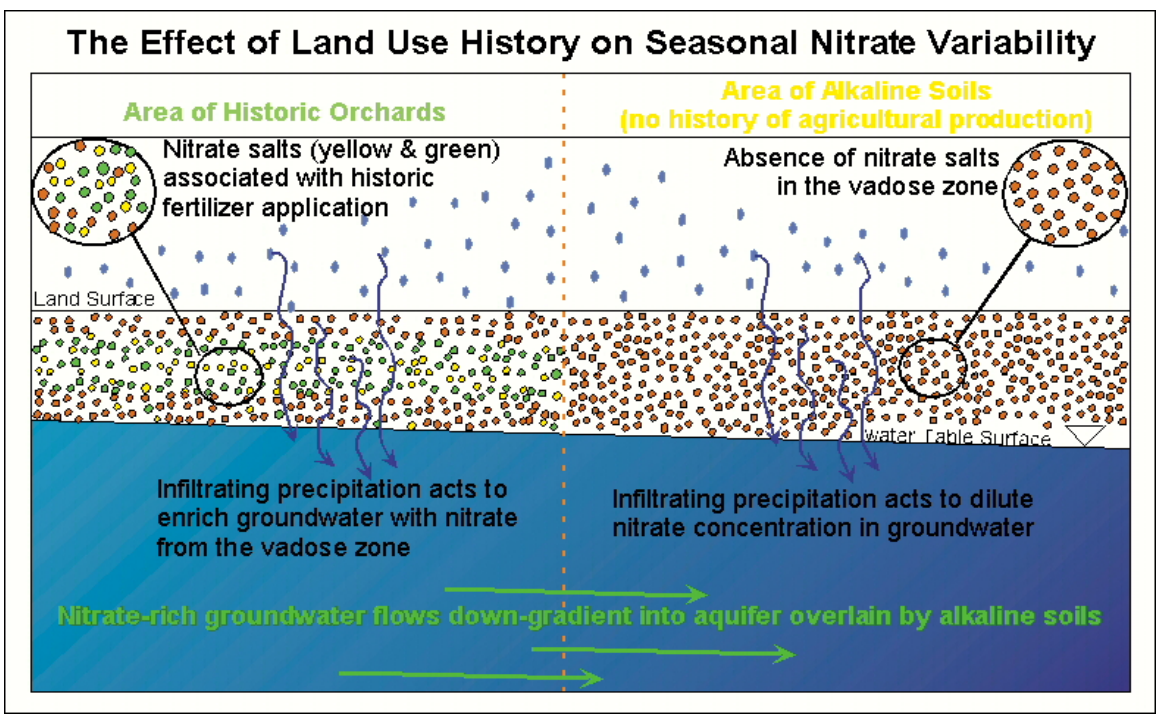


Figure 3.24. Conceptual diagram of the effects of historical land use on nitrate variability associated with precipitation.

During the drought-year, nitrate concentrations remain relatively constant at all sites within the boundary of the historic swamp. VAL adequately illustrates this pattern (Figure 3.25). This "baseline" value is most likely controlled by the up-gradient supply of nitrate-rich groundwaters from the zone of historic agriculture. CCY, which lies within the area of historic fertilizer application, exhibits marginally decreasing nitrate concentrations during the drought-year, reaching a low value of about 18 mg/L in November 2006. Then in December 2006, like EC, nitrate concentrations increase (Figures 3.26). This supports the interpretation that leachable salts from the vadose zone are being carried down to the aquifer with infiltrating rainwater.

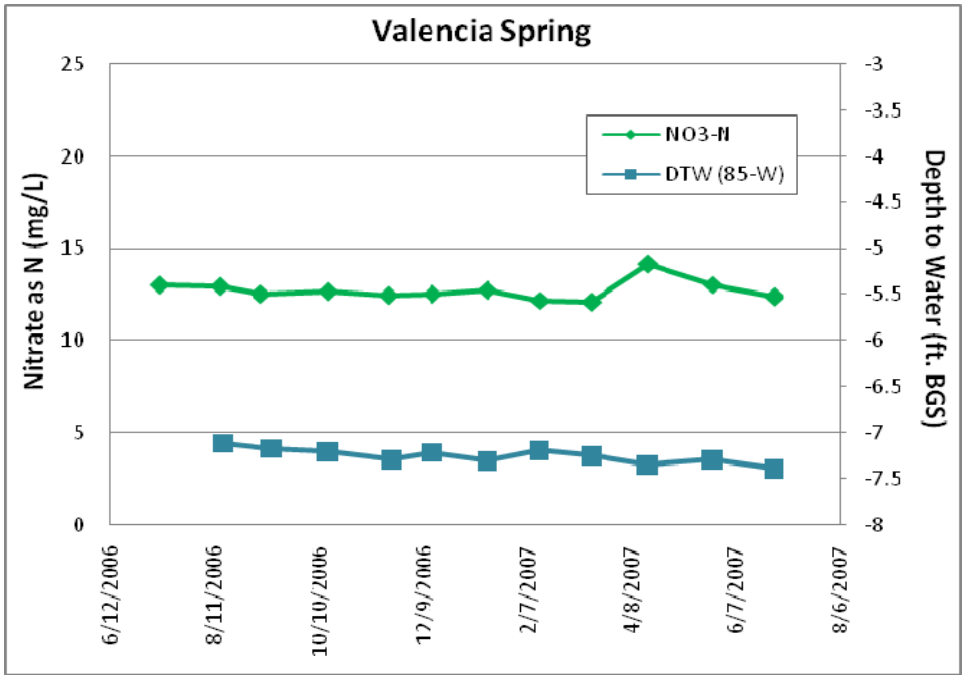


Figure 3.25. Time-series plot of nitrate as nitrogen at VAL during drought-year monitoring.

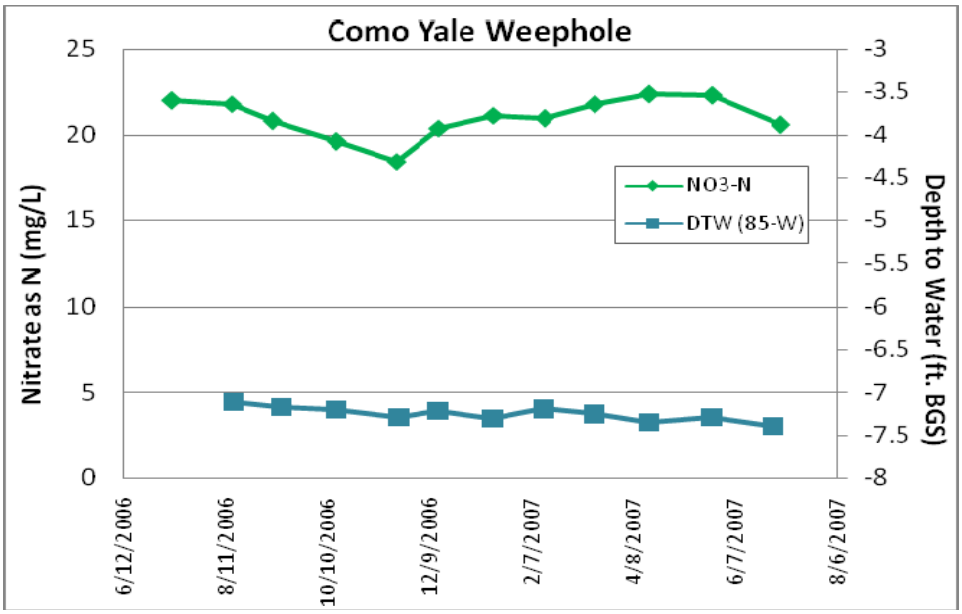


Figure 3.26. Time-series plot of nitrate as nitrogen at CCY during drought-year monitoring.

During the wet-year, all sites across the catchment exhibit an increase in selenium concentrations following the period of highest hydraulic head. Figures 3.27 and 3.28 respectively illustrate this pattern both within (VAL) as well as outside (CCY) the historic marsh boundary. Note that selenium concentrations are nearly double the dry-weather value during peak hydraulic head at both sites. CCY increases from a low value of 16 µg/L in July 2002 to 27.6 µg/L in April 2003. VAL is considered one of the selenium "hot spots" identified by Hibbs and Lee (2000). Selenium concentrations at VAL increase from a low value of 142 µg/L in July 2002 to 270 µg/L in May 2003. After these springtime highs, selenium drops off to values near those observed in July 2002 at the beginning of the monitoring period (140 µg/L in November 2003).

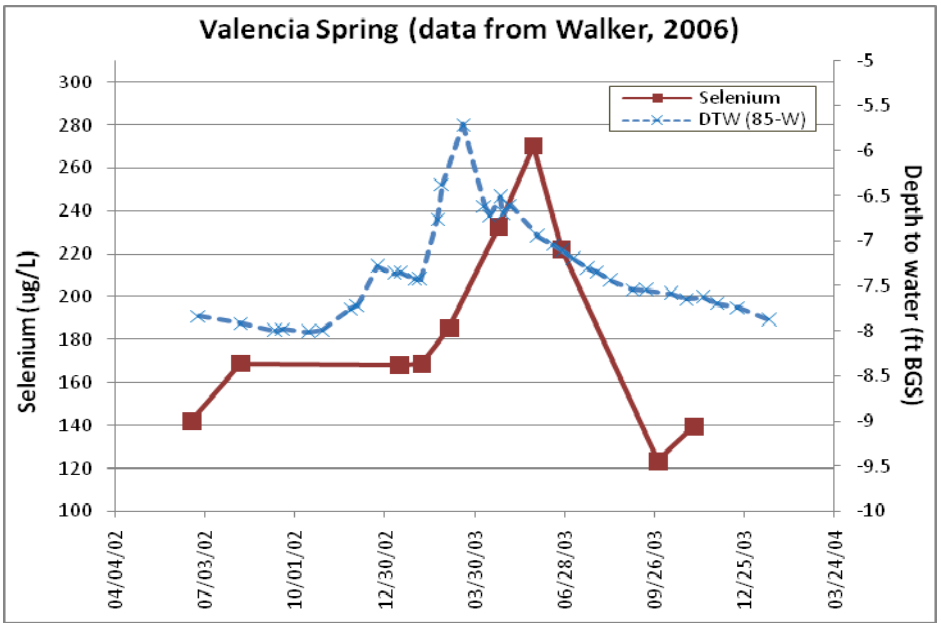


Figure 3.27. Time-series plot of selenium at VAL during wet-year monitoring. *Note the scale has been enlarged seven-fold to show the fluctuation in selenium at this site*.

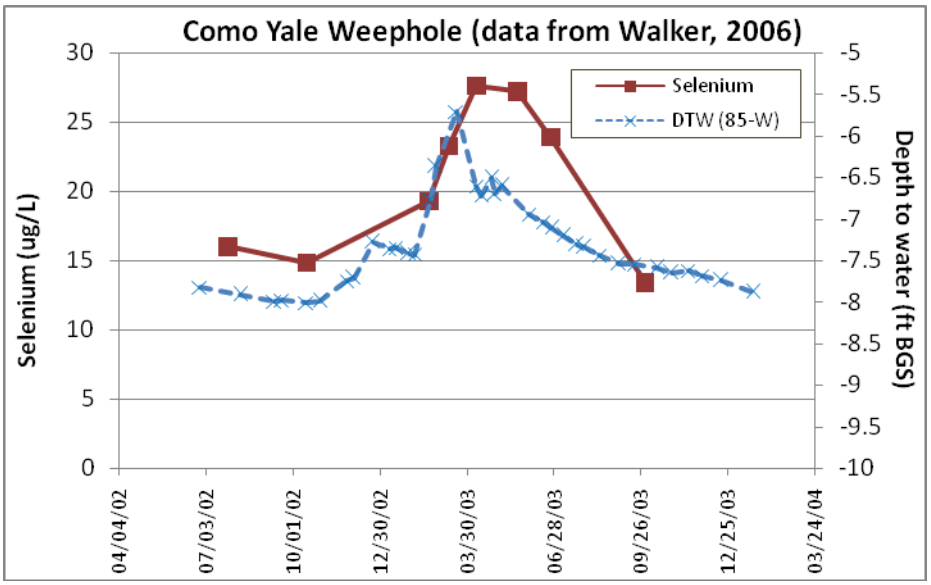


Figure 3.28. Time-series plot of selenium at CCY during wet-year monitoring.

While AVAL exhibits a similarly dramatic increase of selenium concentration in response to precipitation (Figure 3.29), SDCH and SFC10N, also located within the boundary of the historic swamp, show only moderate increases in selenium (Figure 3.30 and 3.31 respectively). During the wet-year, selenium at AVAL increases from a dry-weather value of 11 µg/L in June 2002 to a wet-weather value of 22 µg/L in April 2003. Selenium concentrations at the other two sites do not similarly exhibit a strong positive correlation with water table elevation. SDCH exhibits an initial decline in selenium concentrations during the period of increasing hydraulic head with a marginal increase in selenium following the period of highest hydraulic head (Figure 3.30). SFC10N exhibits a better correlation between selenium and water table elevation, exhibiting an increase of roughly 2 µg/L following the period of highest hydraulic head (Figure 3.31).

Across the catchment, both within and outside of the boundary of the historic swamp, it appears that infiltrating rainwater acts to leach selenium from the vadose zone. However, there is spatial variability in the amount of selenium available to be leached. Elevated selenium concentrations at VAL (drought-year average = 160 µg/L) are thought to be related to its position along the outer margin of the historic swamp. SDCH and SFC10N are both well inside the boundary of the historic swamp. AVAL, while positioned near VAL in the outer margin of the historic marsh, most likely receives flow along another flowpath from waters passing through the interior part of the historic marsh. CCY is well outside this boundary. Relative to sites located along the fringe of the historic marsh boundary (like VAL and Bar-Alt Spring, see Appendix 3A and 3B), all four of these sites (CCY, AVAL, SDCH and SFC10N) have lower selenium concentration on the order of about 20 to 30 µg/L.

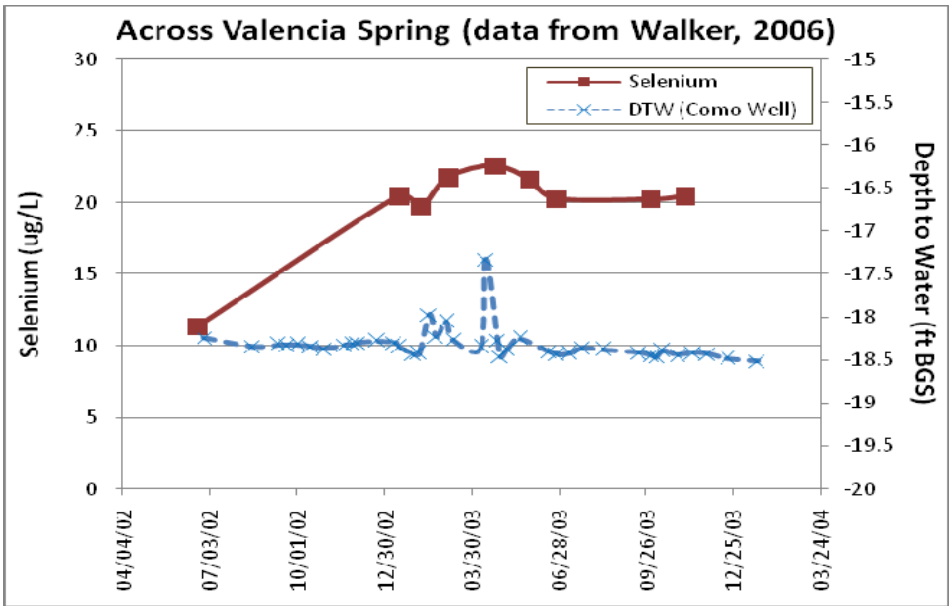


Figure 3.29. Time-series plot of selenium at AVAL during wet-year monitoring.

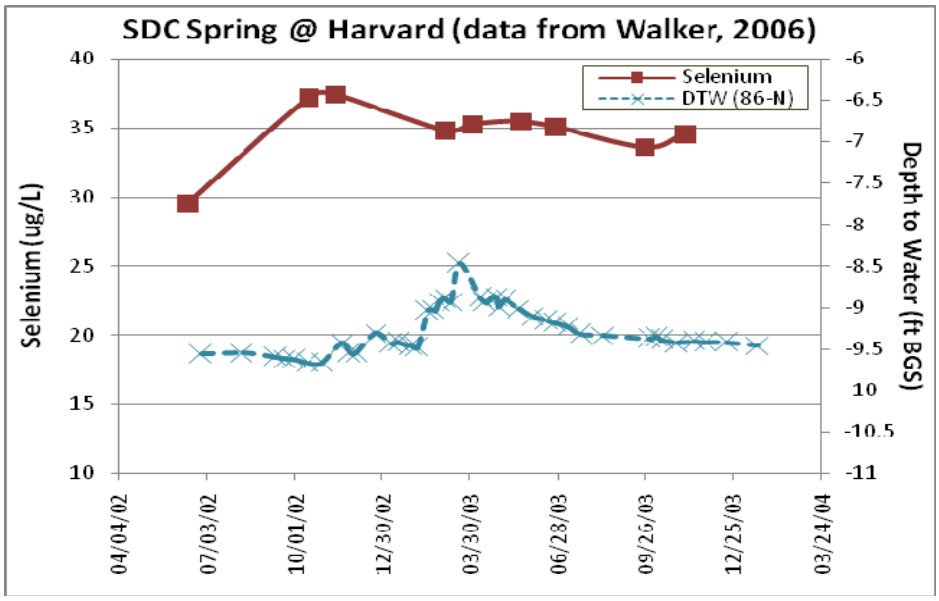


Figure 3.30. Time series plot of selenium at SDCH for wet-year monitoring.

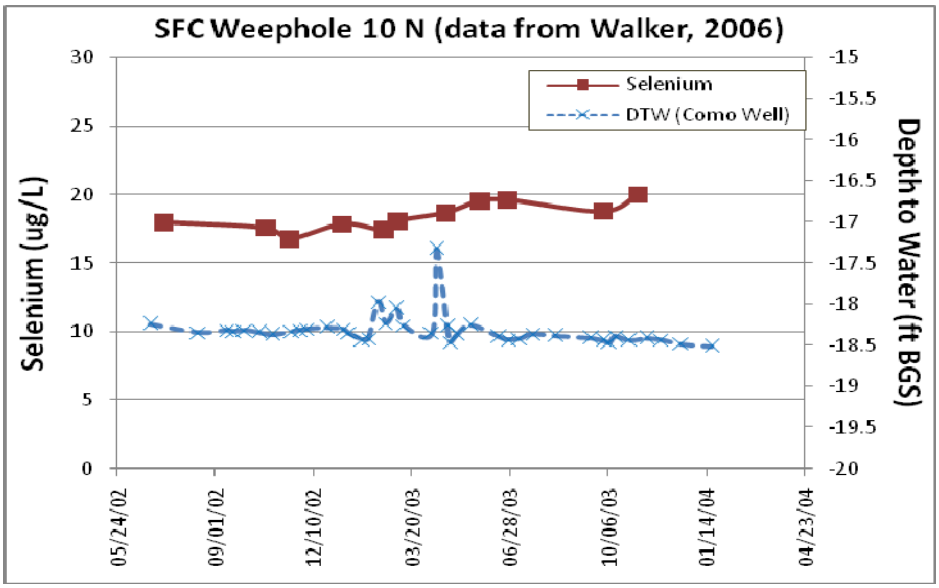


Figure 3.31. Time series plot of selenium at SFC10N for wet-year monitoring.

One scenario that might explain this spatial variation relates to historic redox conditions in the swamp. Selenium, sourced from marine shales in the highlands, was carried downstream to the lowlands in both particulate and dissolved phases. Some of the particulate selenium would have settled out along the historic floodplain resulting in moderate to low concentrations outside of the marsh. Low concentrations of dissolved selenium advected with surface and/or groundwater flow. This selenium would have been in the highest oxidation state as selenate (Se^{6+}). When this dissolved selenium reached the reducing waters of the historic swamp most of it underwent chemical reduction to less mobile forms and was sequestered in the outer margin of the historic swamp as adsorbed selenite (Se^{4+}), elemental selenium (Se^{0}) or as metal selenides (Se^{2-}). The majority of the dissolved selenium would have been removed in the outer margin of the historic marsh, resulting in only a small fraction of soluble selenium reaching the interior. This could explain why we see very high concentrations along the outer margin of the historic

swamp (such as at VAL) and lower concentration deeper within its interior (such as at SDCH and SFC10N).

While all sites exhibit increasing selenium concentrations during the wet-year, only VAL maintains this trend during the drought-year. During the drought-year, selenium concentrations at VAL increase steadily from June 2006 (142 µg/L) to March 2007 (183 µg/L), then begins to taper off (Figure 3.32). This pattern closely matches that observed for sulfate, which may suggest a mechanistic link between the seasonal mobility of these two constituents.

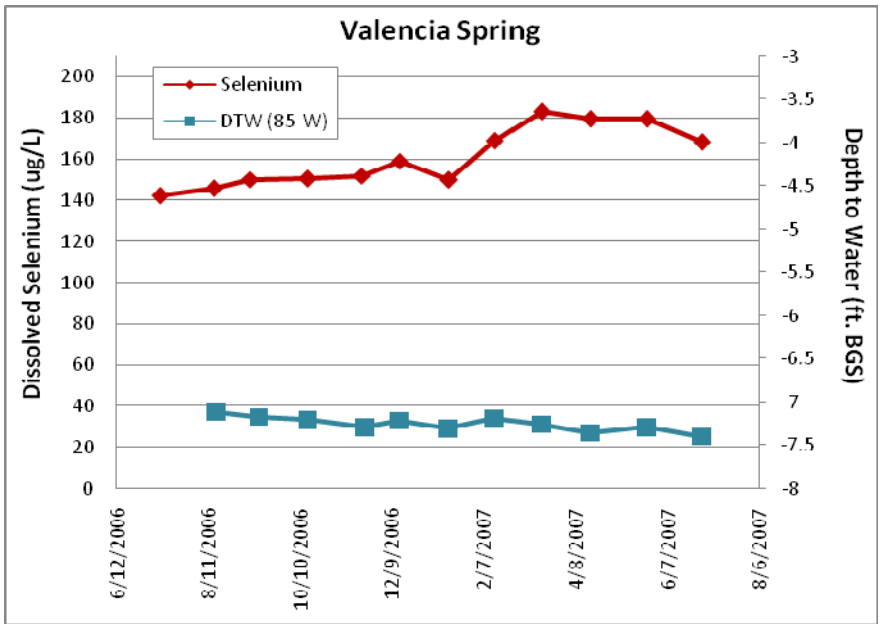


Figure 3.32. Time-series plot of selenium at VAL during drought-year monitoring. *Note the scale has been enlarged nearly seven-fold to show the fluctuation in selenium at this site.*

During the drought-year, selenium decreases at CCY (outside the historic marsh boundary), from 26.6 µg/L in July 2006, reaching a low of 15.2 µg/L in November 2006, which recovers to a steady value of about 23 µg/L by February 2007 (Figure 3.33). The observed increases in both nitrate and selenium following November 2006 at CCY may be related to

leaching associated with minor rain events during this period as described in the section on salinity patterns.

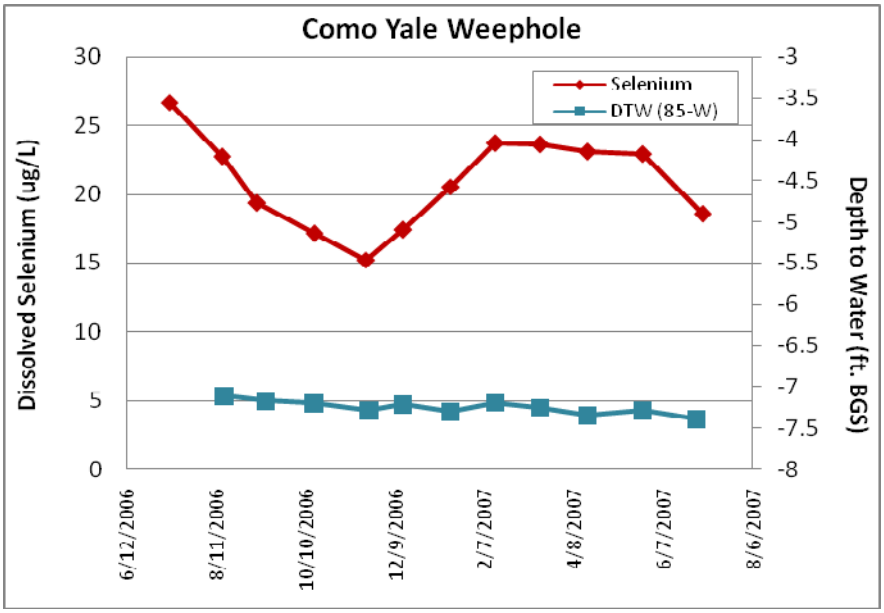


Figure 3.33. Time-series plot of selenium at CCY during drought-year monitoring.

Drought-year data suggests that there may be a seasonal control on selenium mobility within the boundaries of the historic swamp. SDCH and SFC10N both exhibit selenium peaks in October 2006 and March/April 2007 (Figures 3.34 and 3.35 respectively). Selenium also peaks at AVAL in October, while VAL appears to peak in December and April (Figures 3.36 and 3.32 respectively). These same patterns are also clearly observed at SDCH and SFC10N during wet-year monitoring (Figures 3.30 and 3.31). Many of the chemical transformations of selenium are microbially-mediated. Changes in microbial activity could explain this seasonality.

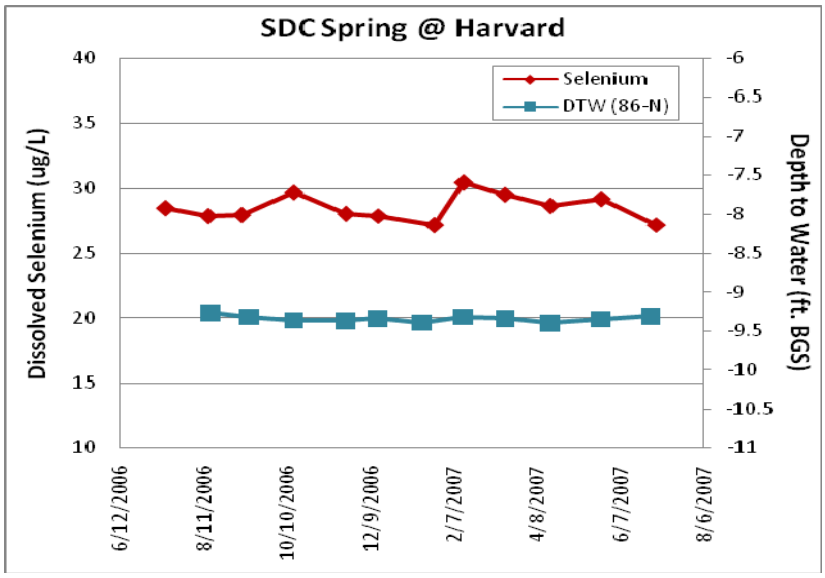


Figure 3.34. Time series plot of selenium at SDCH for drought-year monitoring.

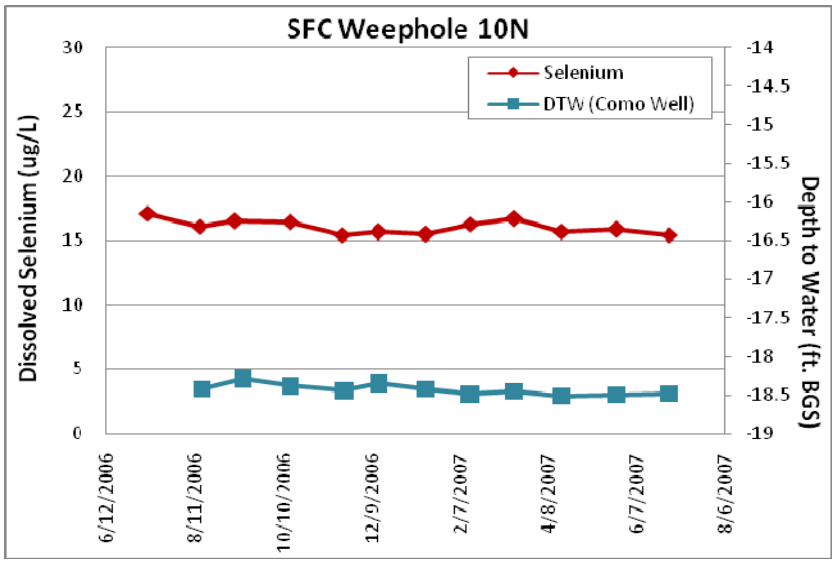


Figure 3.35. Time series plot of selenium at SFC10N for drought-year monitoring.

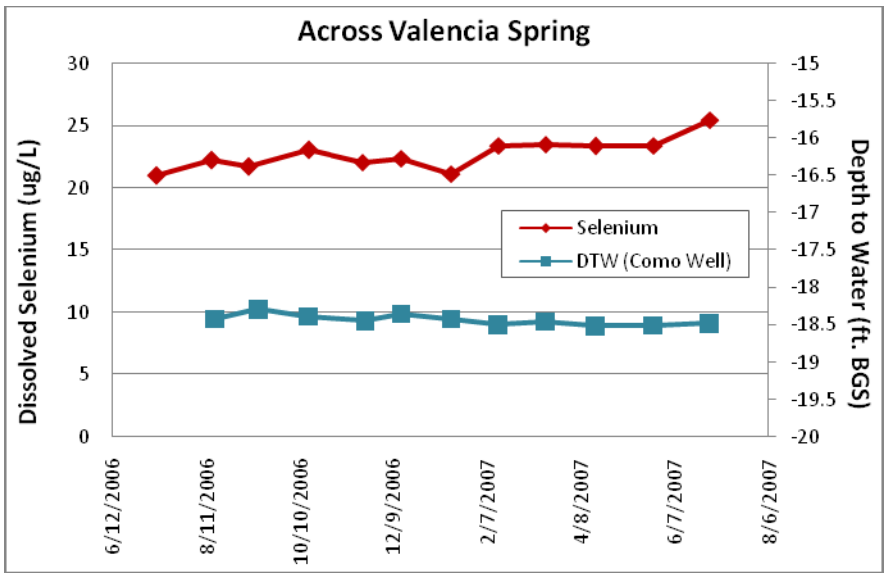


Figure 3.36. Time-series plot of nitrate at AVAL during drought-year monitoring.

CONCLUSIONS FOR TIME SERIES INVESTIGATION

Throughout the catchment there is a spatial dimension to the seasonal variations in all water quality parameters. Within the boundaries of the historic swamp, nitrate decreases during the wet season while selenium, sulfate and chloride increase. Without the influence of infiltrating precipitation, most sites within the boundary of the historic marsh exhibit negligible variation in salinity and nitrate. Selenium, however, appears to peak in the fall (October) and spring (March/April). This seasonal variation may result from changes in plant or microbial activity.

Outside of the historic marsh boundary a very different seasonal pattern emerges. During the wet season, overall salinity increases as does sulfate, chloride, nitrate and selenium. Natural salts and nitrate salts associated with fertilizer application in the historic orchards are leached from the vadose zone and carried to the water table with infiltrating rainwater. During the drought-year, a decrease in all of these water quality parameters is observed until December,

when minor precipitation induced a marginal rise in the water table that permitted salts to be leached from the vadose zone. Across the catchment, the response of nitrate and selenium to fluctuations in the water table is influenced by the history of the land.

Part II: New Drain Studies

INTRODUCTION AND METHODS

In early 2006, during reconnaissance along Peters Canyon Wash, the construction of new residential storm drains was noted (Figure 3.37). Initially, four drains were investigated internally to determine what the nature of the source flows emanating from the drains is (Figure 3.38). It was discovered that groundwater issues from these storm drains leaking between joints in the concrete lining. These drains act as a point source discharge of ground water into Peters Canyon Wash. Construction of these drains intercepts natural groundwater flowpaths (Figure 3.39), which inhibits the natural removal of nitrate and selenium during natural seepage of groundwater through organic rich streambed sediments, where nitrate and selenium are normally removed by plant uptake, denitrification, and redox processes.

Monitoring of water emanating from drains began March 2006 and terminated January 2007, comprising three sampling events in which water emanating from each drain outlet was sampled to obtain an integrated value of all source flows contributing to flow in the drains. Additionally, two internal seeps were sampled at Warner-Val Drain 2 and Warner-Val Drain 3. An expanded sampling campaign was also conducted in September 2006. We performed a detailed analysis to determine the nature of flows at the strongest flowing drain (Warner-Val Drain 3). One additional internal seep was also sampled within Warner-Val Drain 1.

A.

B.

Figure 3.37. Newly constructed storm drain at a new residential development located between Warner Drain and Valencia Drain (A). Graduate student assistants sample new storm drains with peristaltic pump (B).

Figure 3.38. Locations of new storm drains in San Diego Creek Watershed along Peters Canyon Wash.

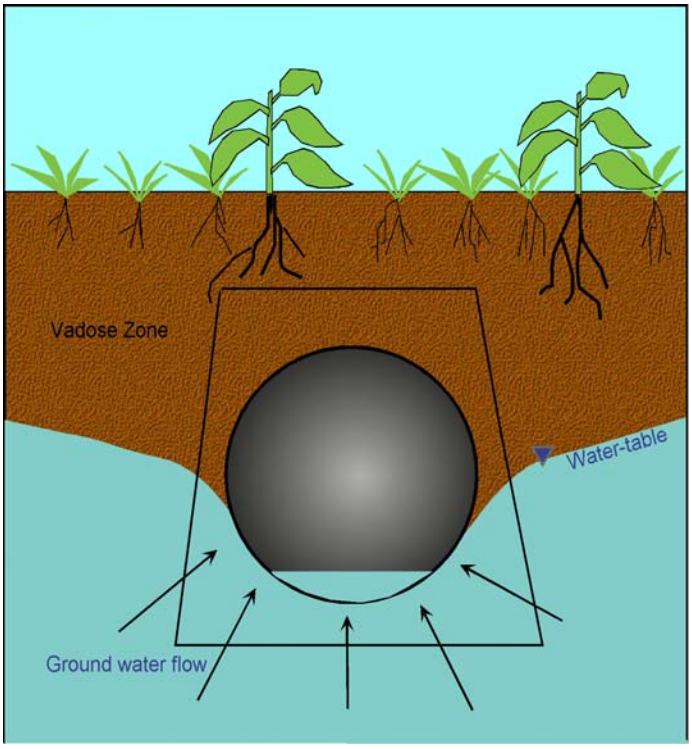


Figure 3.39. Conceptual model of leakage of groundwater into storm drains due to high water tables in San Diego Creek Watershed.

RESULTS AND DISCUSSION

During March 2006 sampling, almost all of the flows from the drains were from groundwater seepage. In March 2006, cumulative flows from all four drains amounted to about 0.40 cubic feet per second of flow. We therefore sampled the drains to determine what the concentration of nitrate and selenium flowing from the outlet of each drain is. One direct groundwater seep was also sampled in Warner-Val Drain 2. The number and volume of new flows were so much greater than in March that it was initially thought that these flows were derived from temporary perched water, associated with watering of newly landscaped areas in the new developments where the drains were installed. In March 2006, the water table might have been falling (transient) in response to leakage into the newly constructed drains. However, sufficient time had passed to establish water table equilibrium by late summer 2006 when the

expanded sampling campaign was conducted. Continued monitoring of water emanating from the outlets of these drains in June 2006 reveals signatures that are consistent with native groundwaters. However, in January 2007 Warner-Val Drain 2 appears to have a greater proportion of urban run-off (Figure 3.40). Data show that there is considerable groundwater loading of nitrate (NO_3) and selenium (Se) to Peter Canyon Wash through these newly installed underground storm drains (Figures 3.41 and 3.42).

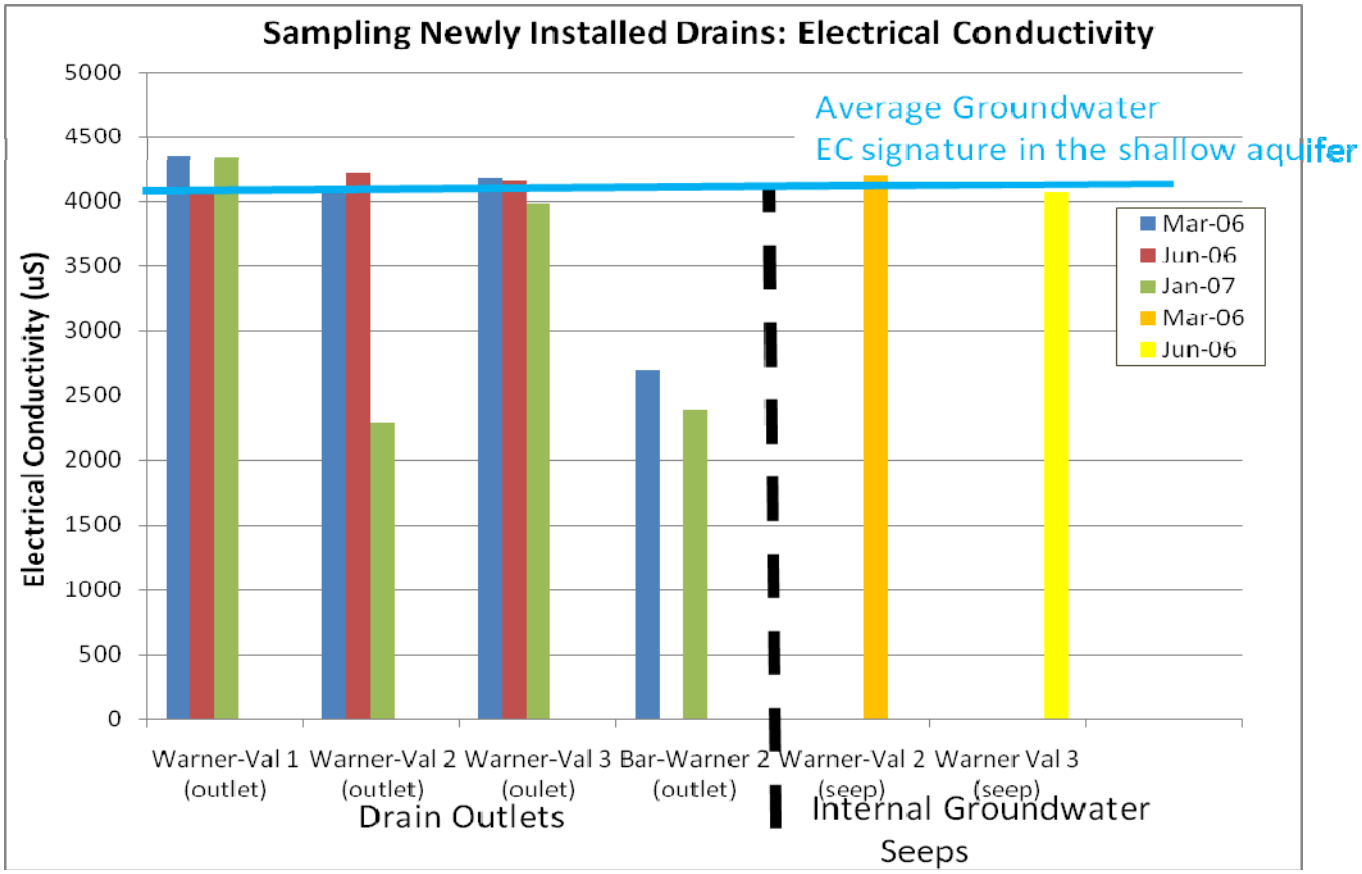


Figure 3.40. Electrical conductivity for surface flows at drain outlets (left) and for internal groundwater seeps (right).

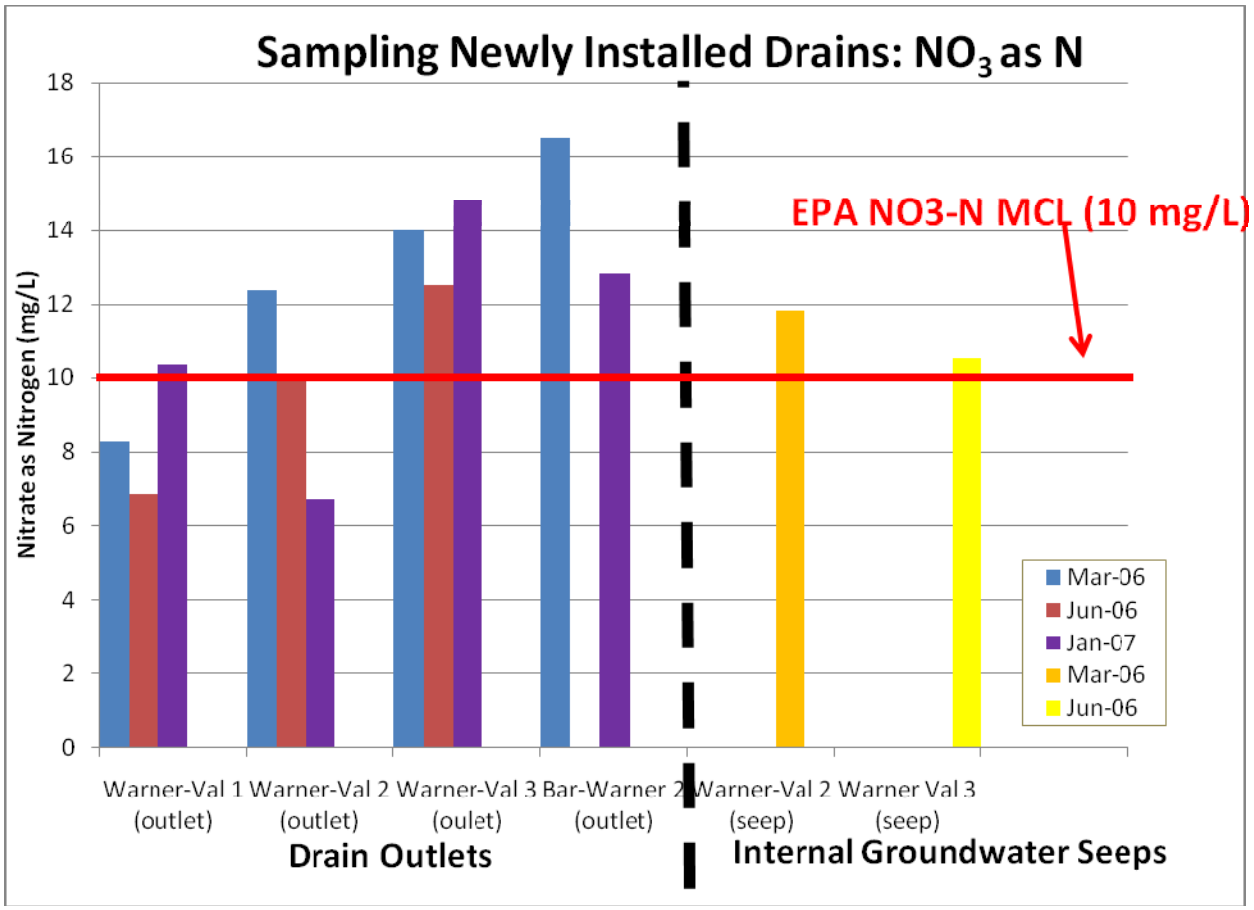


Figure 3.41. Nitrate as nitrogen concentrations for surface flows at drain outlets (left) and for internal groundwater seeps (right).

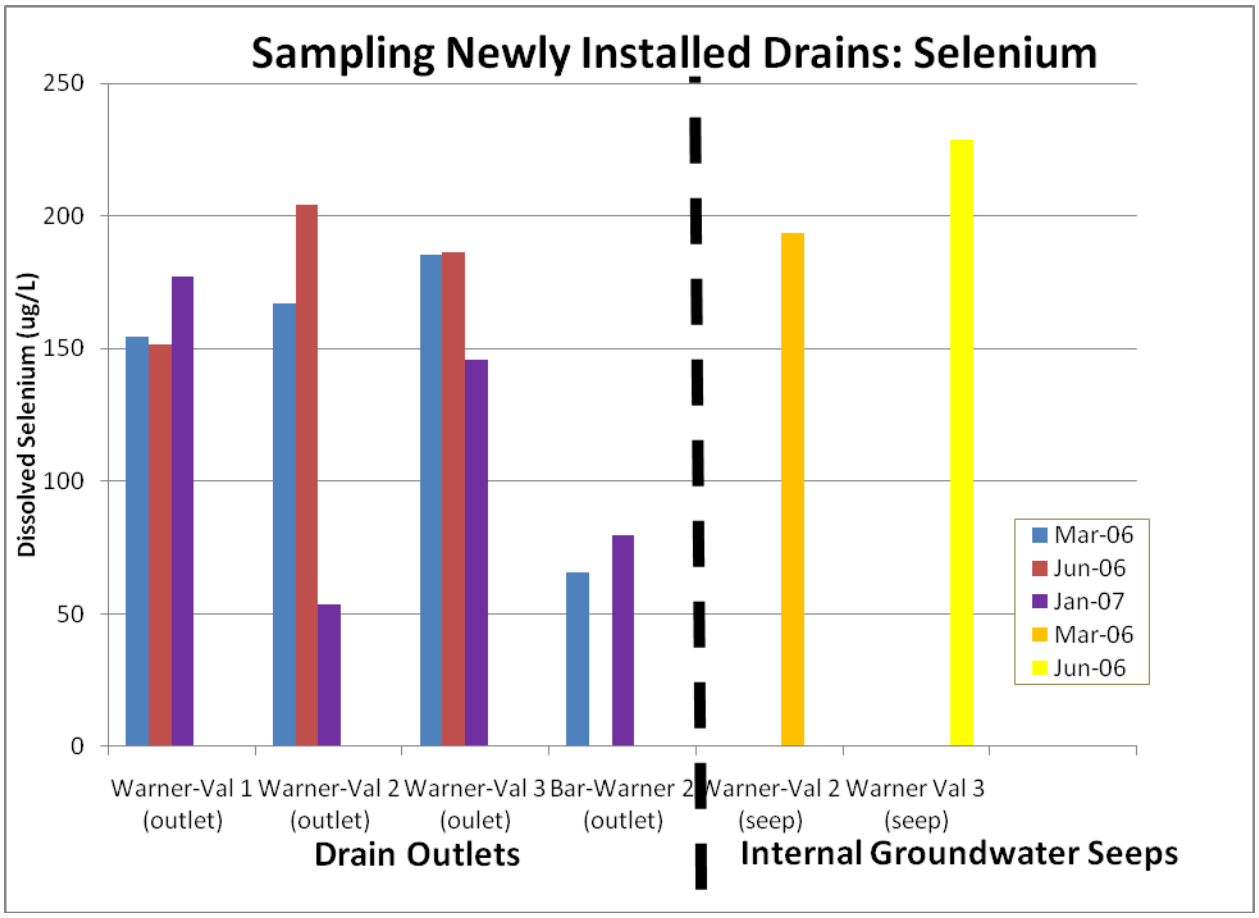


Figure 3.42. Dissolved selenium concentrations for surface flows at drain outlets (left) and for internal groundwater seeps (right).

Selenium levels in surface water collected in March 2006 at the outlets of the storm drains ranged from 66 µg/L to 185 µg/L Se. The highest concentration of selenium found in March 2006 was at the Warner-Val 2 internal groundwater seep (193 µg/L Se) where groundwater seeps through the joint between segments of concrete drainpipe (Figure 3.42). The outlet of Warner-Val Drain 2 had been sampled in 2005 prior to the construction of the other drains. The 2005 sample at Warner-Val Drain 2 yielded a selenium concentration of 316 µg/L. The lowest concentration of selenium observed was 66 µg/L at Bar-Warner Drain 2, which is located below Warner Drain. All other drains had selenium concentrations above 150 µg/L Se

and are located upstream of Warner Drain (Figure 3.38 and 3.42). During the June sampling campaign, selenium levels in surface water collected at the outlets of the storm drains were slightly elevated relative to March values. The highest concentration of selenium found in June 2006 was at Warner-Val Drain 3 internal groundwater seep (229 µg/L). During the January 2007 sampling campaign, selenium concentrations in surface water collected at two of the four drain outlets were lower than the summer values (Warner-Val 2 and 3), while surface waters in two drains show elevated concentrations of selenium (Warner-Val 1 and Bar-Warner 2). Electrical conductivity values suggest that the lower concentrations of selenium observed in two of the drains resulted from a greater proportion of urban run-off contributing flow to the drains (Figure 3.40 and 3.42).

Data collected during 2006 show variations of nitrate concentrations in the storm drain outlets. Nitrate concentrations ranged from 8 mg/L NO_3-N to 17 mg/L NO_3-N in March and from 7 mg/L NO_3-N to 13 mg/L NO_3-N in June. The highest nitrate concentration is from Bar-Warner Drain 2, which also had the lowest selenium concentration (compare Figures 3.41 and 3.42). Nitrate concentrations increase in a downstream direction. Warner-Val Drain 1, the most upstream of the four storm drains, exhibits nitrate concentrations that fall below the EPA MCL of 10 mg/L NO3-N, whereas more downstream sites (Warner-Val Drain 2 and 3 and especially Bar-Warner Drain 2) exceed this criterion (Figure 3.41). Data collected in January 2007 diverge slightly from this trend, Warner-Val 2, with a greater input of urban run-off, shows lower nitrate concentrations. However, Warner-Val 1 (the most upstream drain) has elevated nitrate concentrations that exceed the EPA criterion. This variability in nitrate concentrations is most likely the result of variability of nitrate concentrations in up-gradient groundwaters.

All surface water samples located upstream of Warner Drain (Warner-Val Drain 1, 2, and 3) show a positive selenium-nitrate correlation in the April 2006 samples (Figure 3.43). This correlation breaks down in the Bar-Warner Drain 2 sample. Salinity reveals that Bar-Warner Drain 2 is a distinct water type. These waters have a salinity of only 2400 µS/cm. Other drain samples upstream of Warner Drain (Warner-Val Drain series) had salinities in the range of 3300 to 3500 µS/cm (Figure 3.40). Geochemical data reveal that the Bar-Warner Drain sample is a distinct water type (Figures 3.40, 3.41, 3.42, and 3.43). For example, notice the sulfate-chloride ratios are similar in Warner-Val Drain samples but are different in the Bar-Warner Drain 2 sample (Figure 3.44).

Within any small set of samples, the positive selenium-nitrate correlation is not perfectly linear. A selenium value of 66 µg/L Se and a nitrate value of 73 mg/L NO_3 at Bar-Warner Drain 2 is still a positive correlation. Scatter is always observed in this selenium-nitrate correlation, and the two different water types at the drain locations (one set of samples collected above Warner Drain and one sample collected below Warner Drain) implies that we cannot look for perfect linearity in the selenium-nitrate correlation.

Sulfate to chloride ratios have been used to discriminate between groundwaters sourced from the historic Swamp of the Frogs marsh versus waters sourced from areas outside of the marsh region (Hibbs and Lee, 2000). When sulfate to chloride ratios are greater than about 2.0, they usually are sourced from the Swamp of the Frogs marsh area (Hibbs and Lee, 2000). The drain samples have sulfate to chloride ratios greater than 2.5 (Figure 3.44). These ionic ratio data help to explain why selenium flowing out of the recently constructed drains is usually greater than 100 µg/L Se. The waters flowing from the drains are sourced from groundwaters from within the Swamp of the Frogs marsh region.

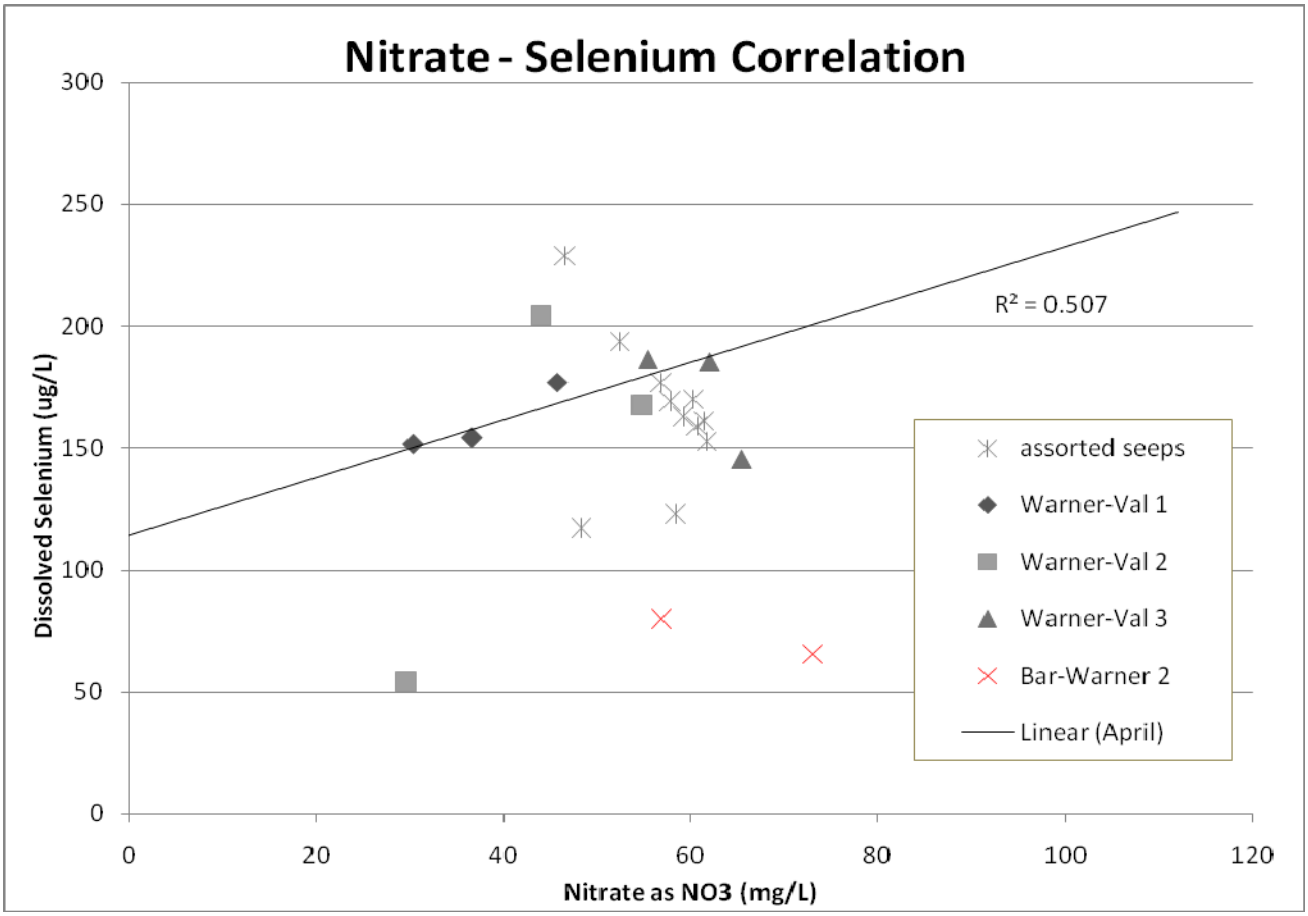


Figure 3.43. Scatter plot showing rough correlation between nitrate and selenium in the storm drain surface waters and groundwater seeps. Correlation co-efficient (R^2=0.507) corresponds to samples collected within the Warner-Val drain series in April 2006.

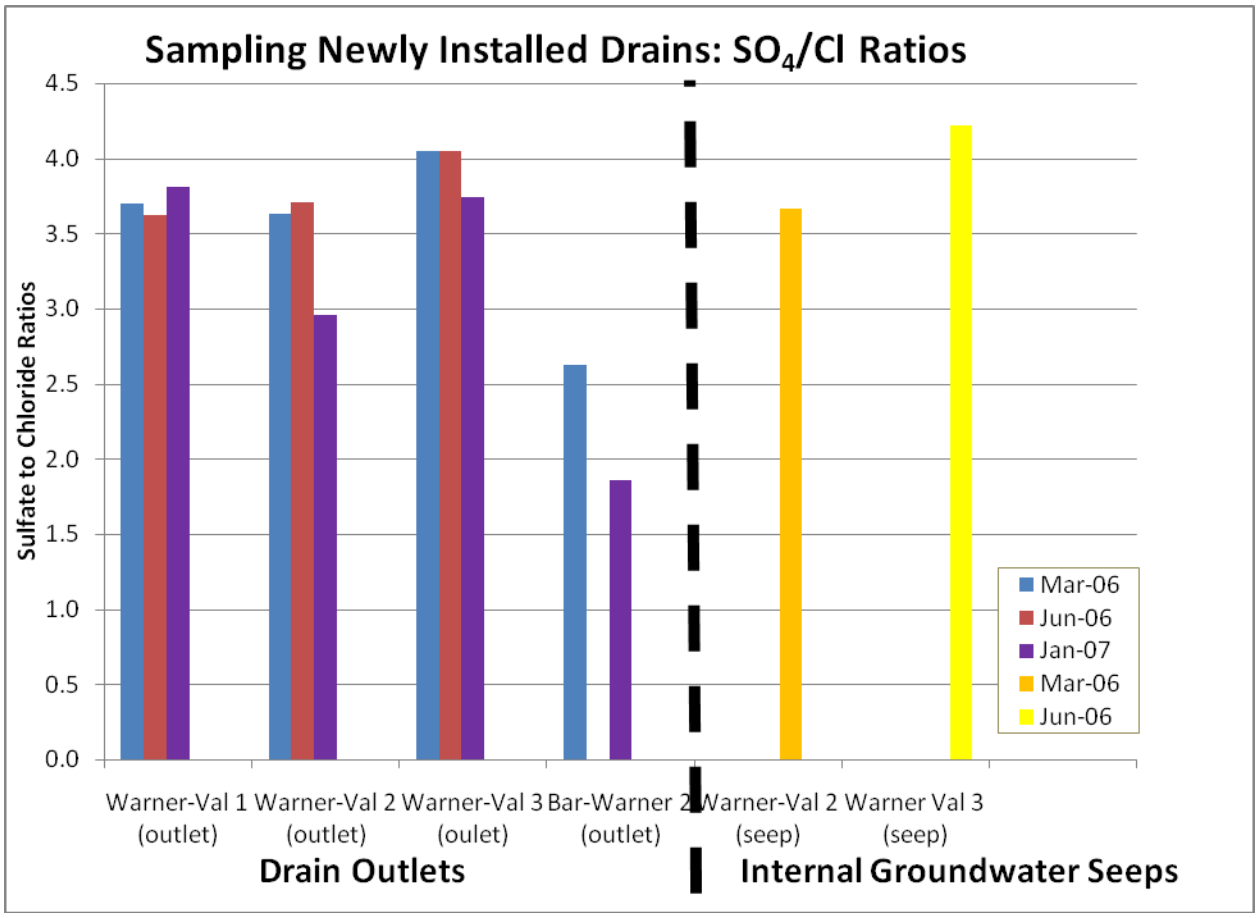


Figure 3.44. Sulfate-chloride ratios for surface flows at drain outlets (left) and for internal groundwater.

A comprehensive investigation of the strongest flowing drain (Warner-Val Drain 3) was undertaken in September 2006. We wanted to wait until the system established more of a water table equilibrium before conducting this more detailed investigation. By September 2006, many new groundwater seeps and flows were observed inside the drain. Upon sampling these seeps, we discovered that water quality was similar to native groundwater in this vicinity, and was fairly homogeneous between stations (Table 3.3). Therefore, we excluded temporary perching of groundwater as a possible source of the flows. We wouldn't expect such homogeneous water quality parameters from temporary perching in the vadose zone. Instead we believe that native

groundwater had eroded the seal between joints in concrete pipe in the storm drain (Figure 3.45). This resulted in greater flows in the drain.

Table 3.3: Hydrochemical Parameters in Groundwater Seeps And Outlet Flows in Warner-Val Drain 3

Groundwater Station #	Distance From Outlet (ft)	Conductivity (µS/cm)	Dissolved Selenium (µg/L)	Total Nitrate (mg/L)
-1	272	4047	152.9	61.7
0	191	4130	159.2	60.7
6	112	4012	161.3	61.4
9	75	3988	162.7	59.3
10	46	4019	168.9	57.9
11	30	4010	170.3	60.3
Surface Outlet to PCW	0	3737	122.7	58.5

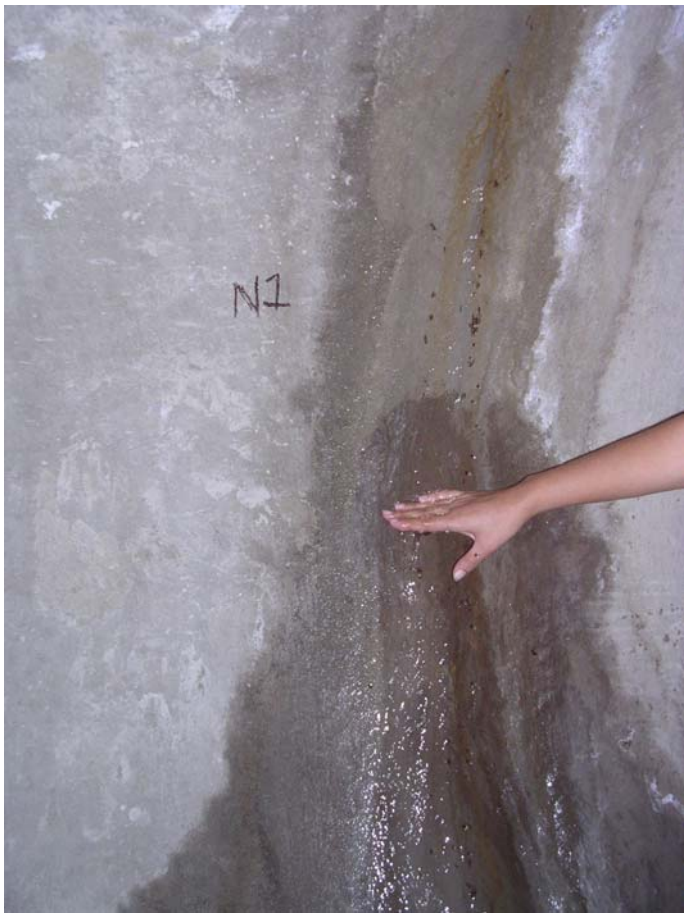
Figure 3.45. Groundwater seeping through eroded seal between joints of two concrete pipes.

The concentration of selenium issuing from these seeps was very high (153 to 170 µg/L Se) and the concentration of nitrate was moderately high (10 to 14 mg/L NO_3-N). Total surface flows were 0.21 cfs at the drain outlet. Concentrations of selenium in surface flows were lower than in the groundwater seeps that were sampled, while nitrate was about the same (Table 3.2). Some of the flows in the drain above the upstream groundwater seep (sample point -1, at 272 feet above Peters Canyon Wash) were derived from other groundwater seeps where selenium concentrations are lower, and this resulted in a lower overall selenium concentration in surface flows at the drain outlet (123 ug/L Se). These seeps could not be sampled because the diameter of the drain became constricted to an inaccessible diameter upstream of sample point –1. Note that the selenium concentrations in groundwater is higher at seeps located closer to Peters Canyon Wash, as shown in previous studies in Valencia Drain (Table 3.3). Formerly, groundwater at this location seeped into Peters Canyon Wash from above channel springs that flowed freely into the channel). These springs had selenium concentrations reaching 400 to 600 µg/L dissolved selenium.

A few weeks after Warner-Val Drain 3 was sampled, we noticed that construction workers had attempted to seal the leaks in the concrete pipe with plastic cement (Figure 3.46). In the short term these seals had reduced groundwater flows into the drain by a significant amount. However, a few new seeps had started to break through seals in other locations in the drain. We have not returned to the drain to determine if these leaks have also been patched. Finally, where the diameter of the drains is too small for a person to seal the leaks, it is difficult to envision any practical means by which to seal the groundwater seeps.

A.

B.



C.

Figure 3.46. Patching of leaks in Warner-Val Drain 3 using plastic cement (A) appeared to be fairly successful for blocking leaks, at least in the short term (B), though new seeps were observed inside the drain in October (C).

CONCLUSIONS FOR NEW DRAIN STUDIES

These data show that there was moderate loading of nitrate and high loading of selenium to Peter Canyon Wash through this newly installed underground storm drain. The drain penetrates the water table, which allows groundwater to seep into the drains through joints between segments of concrete pipe (Figure 3.45). These drains are now artificial outlets for point source discharge of ground water into Peters Canyon Wash. Construction of many drains in San Diego Creek Watershed intercepts natural groundwater flowpaths (Figure 3.39), which

inhibits the natural removal of nitrate and selenium during natural seepage of groundwater through organic rich streambed sediments, where nitrate and selenium are normally removed by plant uptake, denitrification, and redox processes. On the other hand, selenium concentration at Warner-Val Drain 3 becomes very high close to Peters Canyon Wash, so this particular storm drain may actually partially dewater selenium-bearing sediments that normally are saturated with groundwater.

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APPENDIX 3A:
SUMMARY STATISTICS FOR TIME SERIES INVESTIGATION

----------Wet-Year Data ----------

Location	Number of Measurements	Summary Statistics	pH	EC (µS)	Cl (mg/L)	SO_4 (mg/L)	NO_3-N (mg/L)	Diss. Se (µg/L)
Across Valencia Spring	**11**	**MEAN**	7.067273	2562.727	242.194	751.776	16.60091	19.83667
		MEDIAN	6.96	2560	237.96	758.445	16.81	20.47
		SD	0.195606	82.5943	24.84604	62.87443	0.562485	3.305011
		MIN	6.93	2460	208.97	664.28	15.47	11.36
		MAX	7.5	2720	280.65	865.24	17.27	22.56
Como-Yale Weephole	**9**	**MEAN**	7.092222	2935.556	294.6238	673.3425	17.70444	20.69625
		MEDIAN	7.03	2920	296.72	687.055	17.88	21.27
		SD	0.150978	179.1027	82.76453	85.003	3.602021	5.589055
		MIN	6.9	2660	200.75	565.31	13.1	13.42
		MAX	7.28	3170	434.96	784.62	22.16	27.64
SDC Spring @ Harvard	**11**	**MEAN**	7.096364	3800.909	352.384	1183.672	48.99545	34.76778
		MEDIAN	7.08	3800	338.85	1187.63	48.88	35.07
		SD	0.118345	138.2356	31.04441	50.06603	2.62588	2.30386
		MIN	6.98	3450	325.06	1106.75	45.19	29.55
		MAX	7.4	3980	422.77	1264.44	55.05	37.41
SFC Weephole 10N	**13**	**MEAN**	6.746154	2176.923	181.8042	537.7175	17.34538	18.40091
		MEDIAN	6.77	2170	178.695	537.01	17.63	18.08
		SD	0.215079	50.39587	14.34629	22.84035	0.845898	1.017816
		MIN	6.08	2060	161.16	500.82	15.87	16.78
		MAX	6.92	2250	201.96	581.28	19.05	20.03
Valencia Drain Spring @ outlet	**12**	**MEAN**	7.185	4886.667	567.424	1880.459	11.29182	182.238
		MEDIAN	7.145	4855	582.5	1879.745	11.2	169.01
		SD	0.145758	181.3752	73.27434	170.5047	0.933111	46.37142
		MIN	7.03	4610	463.19	1648.65	9.72	123.7
		MAX	7.55	5120	694.8	2163.96	12.8	270.4

----------Drought-Year Data ----------

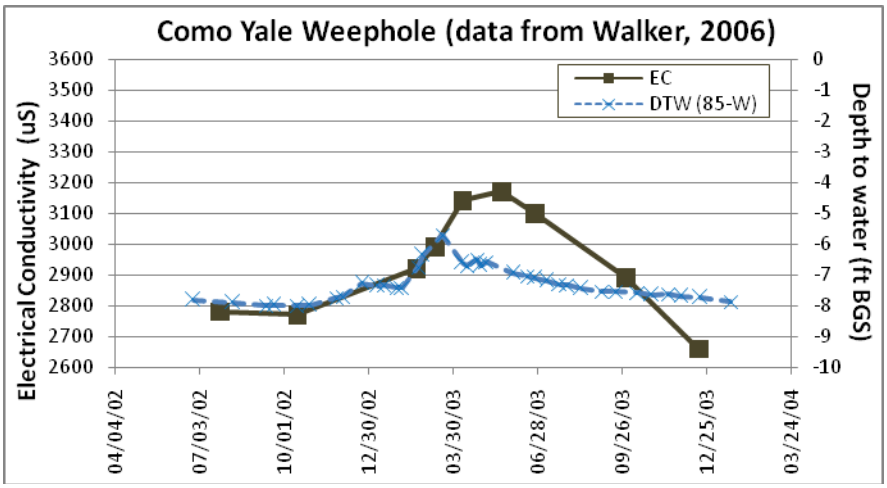
Location	Number of Measurements	Summary Statistics	pH	EC (µS)	Cl (mg/L)	SO_4 (mg/L)	NO_3-N (mg/L)	Diss. Se (µg/L)
Across Valencia Spring	12	MEAN	7.1438	2439.0769	220.0516	666.1918	16.1711	22.6065
		MEDIAN	7.1900	2445.0000	221.8689	663.0369	16.1399	22.3610
		SD	0.1095	31.2342	7.4650	24.3846	0.4154	1.2689
		MIN	6.9400	2384.0000	203.3850	621.1335	15.5553	20.9680
		MAX	7.2500	2486.0000	235.5574	717.3470	17.3652	25.4700
Bar-Alt Spring	13	MEAN	7.0346	6046.1538	682.3044	2051.2705	57.0085	172.0503
		MEDIAN	7.0200	6100.0000	687.2530	2078.5090	56.4865	169.3930
		SD	0.0672	189.8481	40.9863	81.1781	1.7090	16.5531
		MIN	6.9300	5490.0000	565.8572	1821.1335	54.5797	153.0320
		MAX	7.1400	6250.0000	734.5271	2134.6549	60.0559	221.9710
Barranca Weephole 1	7	MEAN	7.3086	3883.1429	261.6273	1683.2154	7.3621	29.1963
		MEDIAN	7.2900	3927.0000	257.1465	1694.8671	7.1638	30.1610
		SD	0.0830	209.1327	14.6826	128.2045	1.6740	6.6703
		MIN	7.2200	3620.0000	245.6991	1517.0363	4.4426	16.4460
		MAX	7.4600	4241.0000	288.4225	1896.8594	9.6901	35.9140
Como Harv-Cul Weephole	13	MEAN	7.2454	2773.8462	243.8757	629.8869	21.6269	27.5751
		MEDIAN	7.2300	2771.0000	244.3406	630.3374	21.7114	27.7390
		SD	0.0791	26.2674	7.8367	22.8902	0.3956	1.1220
		MIN	7.1100	2733.0000	227.9929	598.2117	20.5547	26.1000
		MAX	7.3400	2813.0000	255.9975	666.0774	22.1174	30.1790
Como Yale Weephole	13	MEAN	7.1223	3013.1538	290.6080	690.8051	21.0340	21.0401
		MEDIAN	7.1100	3008.0000	292.7385	684.9152	20.9997	22.6360
		SD	0.0610	209.7017	20.5456	39.3334	1.1217	3.2877
		MIN	7.0300	2788.0000	253.4578	621.7184	18.4817	15.2360
		MAX	7.2100	3663.0000	326.8759	765.4509	22.4144	26.6680

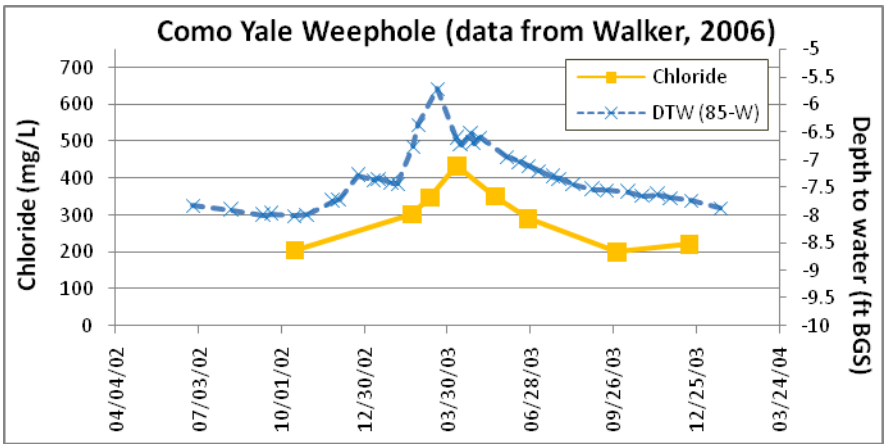
Location	Number of Measurements	Summary Statistics	pH	EC (µS)	Cl (mg/L)	SO_4 (mg/L)	NO_3-N (mg/L)	Diss. Se (µg/L)
El Modena Weephole B3	**12**	**MEAN**	7.3350	2657.8333	196.6028	687.4020	28.8152	67.1893
		MEDIAN	7.3050	2655.5000	194.2805	685.9894	28.6339	64.4675
		SD	0.0830	31.1706	6.7419	26.1990	0.7225	10.4674
		MIN	7.2200	2598.0000	184.9726	642.4814	28.0980	55.6710
		MAX	7.4900	2708.0000	211.4216	750.3649	30.9088	88.2000
PCW Spring @ confluence	**7**	**MEAN**	7.5729	4833.2857	513.5859	1712.6102	4.4096	14.1353
		MEDIAN	7.5700	4961.0000	521.8064	1806.4466	3.6755	13.8110
		SD	0.1083	423.7569	55.4000	230.0531	1.2430	2.2183
		MIN	7.4000	3948.0000	404.1788	1237.6729	3.3985	11.2180
		MAX	7.6900	5310.0000	588.3721	1935.1046	6.7925	17.2710
SADC Weephole 1	**12**	**MEAN**	7.1233	3953.5833	342.7807	1707.3710	9.2228	23.8858
		MEDIAN	7.1050	3963.5000	341.6060	1713.0822	9.1556	23.8770
		SD	0.0725	30.5419	8.7543	30.9196	0.2135	1.5530
		MIN	7.0000	3905.0000	330.7447	1661.0122	8.9569	21.3320
		MAX	7.2300	3993.0000	362.2157	1769.5071	9.6830	25.9290
SADC Weephole 3 by golf course	**13**	**MEAN**	7.1146	2233.0769	247.8182	416.2903	2.9103	6.6174
		MEDIAN	7.1100	2235.0000	245.3507	411.8949	2.9293	6.7610
		SD	0.0714	79.3268	13.5340	28.2203	0.2258	0.9029
		MIN	7.0100	2040.0000	221.1374	351.0200	2.4528	5.1000
		MAX	7.2200	2333.0000	268.5747	460.0615	3.1999	8.0790
Santa Fe Weephole 1	**12**	**MEAN**	6.9067	2507.7500	167.1816	846.5747	16.2707	30.8849
		MEDIAN	6.9050	2511.5000	168.0040	842.6938	16.2301	30.9645
		SD	0.0661	31.2675	5.3267	20.8233	0.3227	1.3696
		MIN	6.8000	2458.0000	154.1960	815.9396	15.7969	28.7680
		MAX	7.0000	2557.0000	174.3157	890.6989	16.6903	32.6680

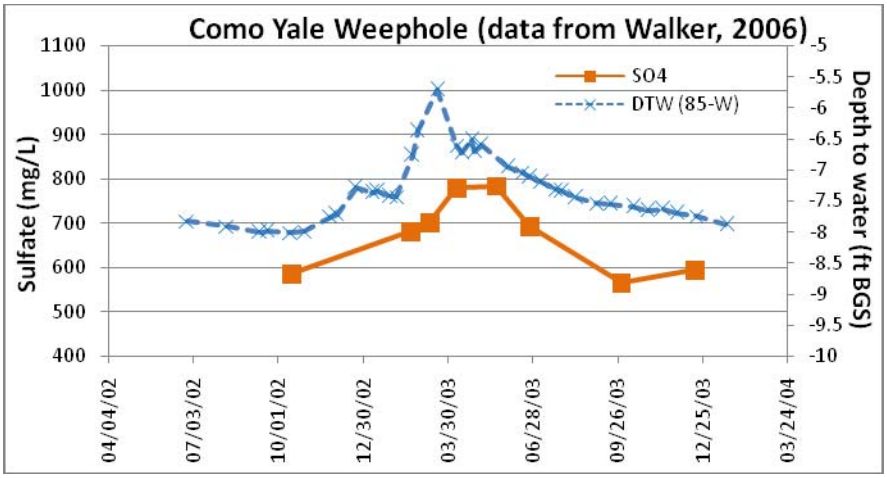
Location	Number of Measurements	Summary Statistics	pH	EC (µS)	Cl (mg/L)	SO_4 (mg/L)	NO_3-N (mg/L)	Diss. Se (µg/L)
Santa Fe Weephole 10N	**12**	**MEAN**	6.8775	2038.6667	177.1002	455.3734	17.6824	16.0483
		MEDIAN	6.8950	2040.0000	177.3596	443.9168	17.5587	15.9590
		SD	0.0666	33.6974	5.6620	26.4873	0.4887	0.5502
		MIN	6.7700	1952.0000	165.9499	436.5142	17.2143	15.4180
		MAX	6.9700	2073.0000	188.7512	517.8226	18.9819	17.1000
SDC Spring @ Harvard	**12**	**MEAN**	7.1400	3431.0000	330.9842	998.7439	37.6994	28.4403
		MEDIAN	7.1400	3506.5000	334.4871	1003.1617	37.5151	28.2000
		SD	0.1168	265.0365	12.1738	13.8617	0.5032	1.0261
		MIN	6.9500	2613.0000	294.7587	963.7100	37.1868	27.0860
		MAX	7.3300	3578.0000	342.2676	1012.4704	38.5060	30.4180
SDC Spring @ Mervyn's	**12**	**MEAN**	7.0342	2413.7500	298.2363	415.6156	20.1496	5.1732
		MEDIAN	7.0200	2399.5000	297.1463	409.1766	19.8557	5.1590
		SD	0.0883	54.4529	8.9185	15.6218	1.0830	0.4242
		MIN	6.8800	2343.0000	285.0614	398.9994	19.2219	4.5640
		MAX	7.2000	2502.0000	320.3852	450.4267	23.1539	6.0210
SDC Weephole 40 @ Valley Oak	**13**	**MEAN**	7.0446	2440.0000	252.0167	454.2638	36.6775	7.8676
		MEDIAN	7.0400	2447.0000	253.3541	455.1443	37.1251	7.7790
		SD	0.0983	33.7935	6.6513	8.6264	1.1865	0.3879
		MIN	6.8500	2343.0000	233.8892	431.7917	33.4488	7.2860
		MAX	7.1800	2474.0000	259.3994	466.8000	37.7290	8.6250
Valencia Drain Spring @ outlet	**12**	**MEAN**	7.2958	4764.8333	487.4773	1710.7501	12.7566	160.7667
		MEDIAN	7.2700	4765.0000	485.5680	1674.7552	12.6287	155.6070
		SD	0.1062	108.3302	9.9270	89.6055	0.5437	14.4779
		MIN	7.1200	4551.0000	473.4681	1600.2711	12.1308	142.3290
		MAX	7.4400	4966.0000	506.8264	1894.6628	14.1920	183.0600
Warner-Val Drain 2 North Spring @ outlet	**12**	**MEAN**	7.1975	4152.0000	397.8772	1448.8413	11.7284	172.4356
		MEDIAN	7.1750	4153.0000	400.3274	1436.8904	11.8104	169.4605
		SD	0.0938	49.4313	7.4968	44.8637	0.5064	10.3026
		MIN	7.0600	4022.0000	385.4730	1360.0083	10.3879	158.9140
		MAX	7.3800	4238.0000	405.9132	1508.8665	12.5185	192.4650

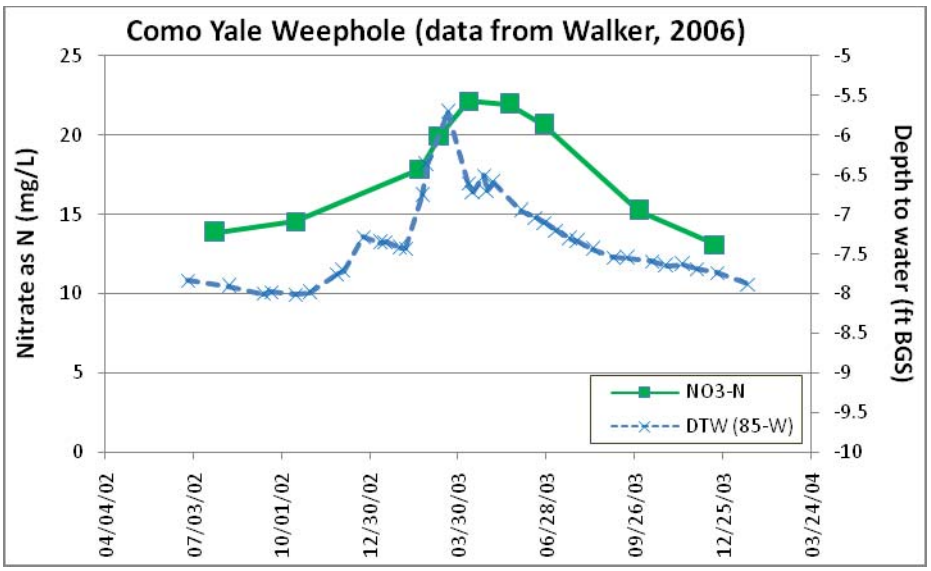
APPENDIX 3B:
TIME SERIES GRAPHS OF WATER QUALITY DATA

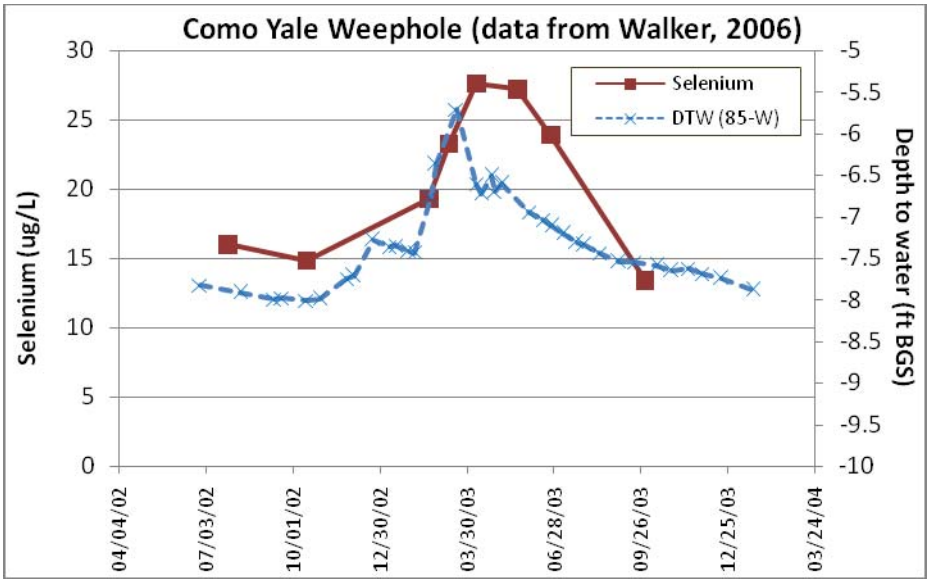
----------Wet-Year Data for Como-Yale Weephole----------



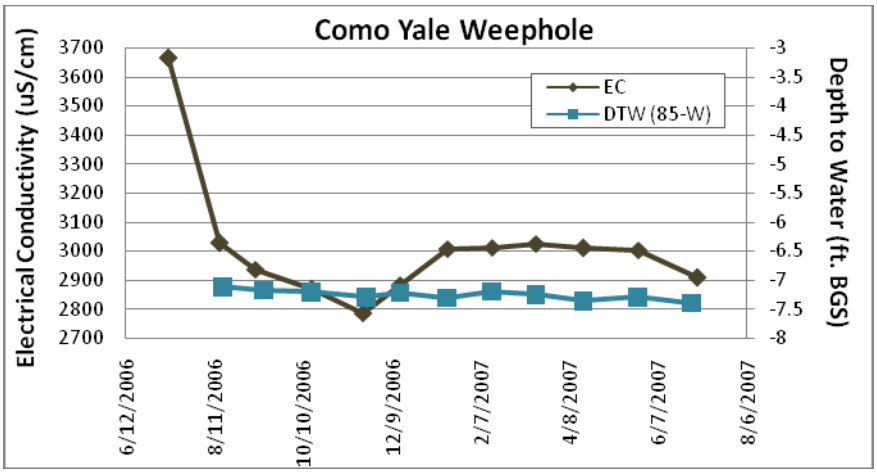


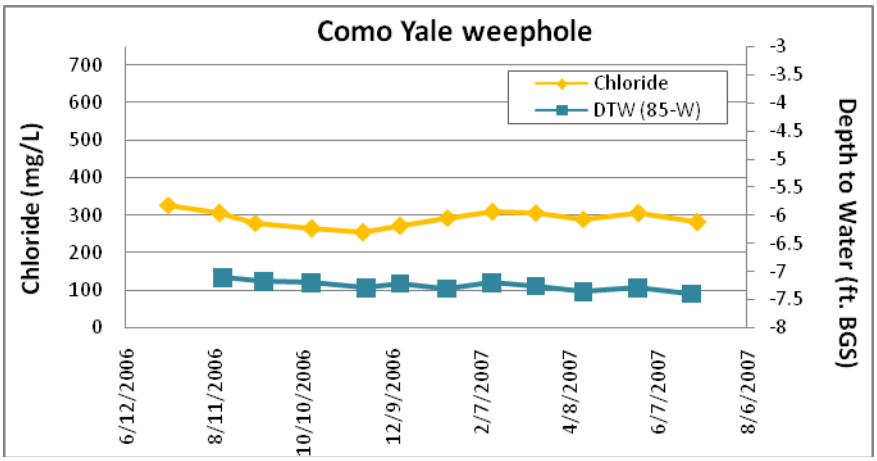


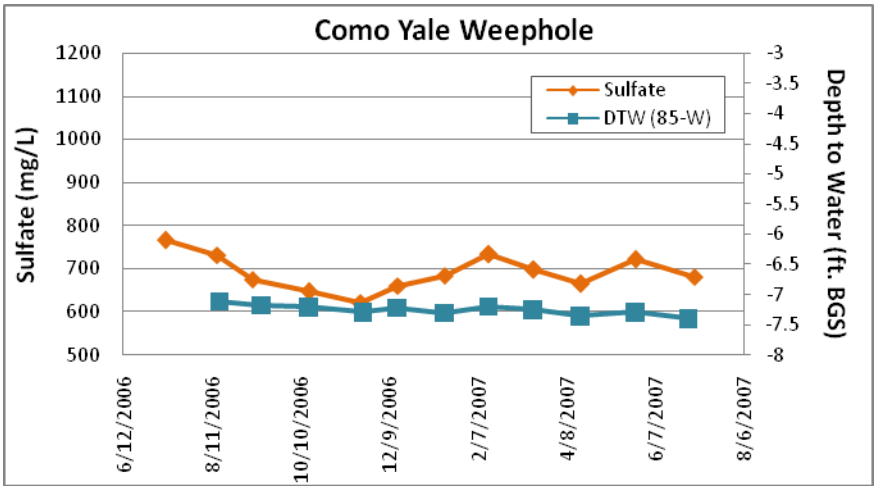

Como Yale Weephole (data from Walker, 2006)
Nitrate as N (mg/L)
Depth to water (ft BGS)
NO3-N
DTW (85-W)
25
20
15
10
5
0
-5
-5.5
-6
-6.5
-7
-7.5
-8
-8.5
-9
-9.5
-10
04/04/02
07/03/02
10/01/02
12/30/02
03/30/03
06/28/03
09/26/03
12/25/03
03/24/04

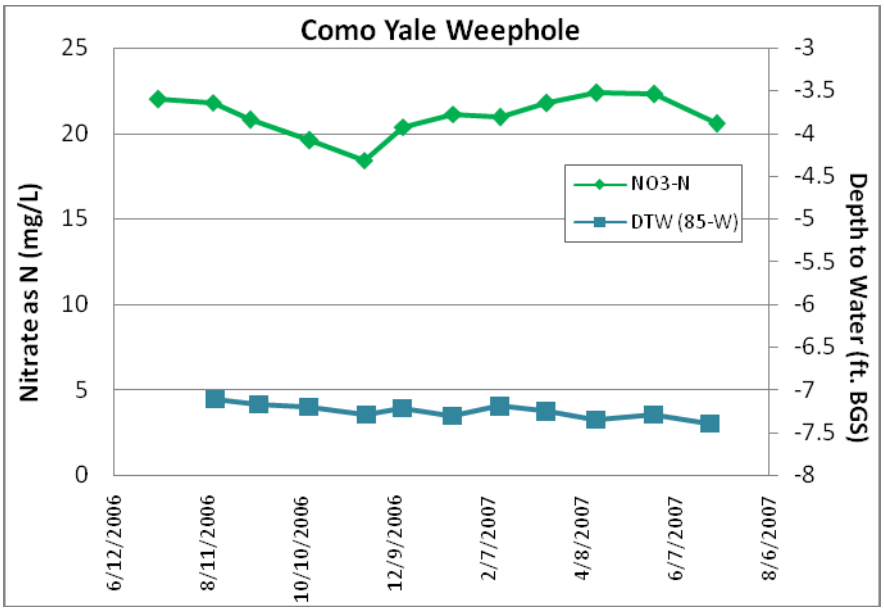

Como Yale Weephole (data from Walker, 2006)
Selenium (ug/L)
Depth to water (ft BGS)
Selenium
DTW (85-W)
30
25
20
15
10
5
0
-5
-5.5
-6
-6.5
-7
-7.5
-8
-8.5
-9
-9.5
-10
04/04/02
07/03/02
10/01/02
12/30/02
03/30/03
06/28/03
09/26/03
12/25/03
03/24/04

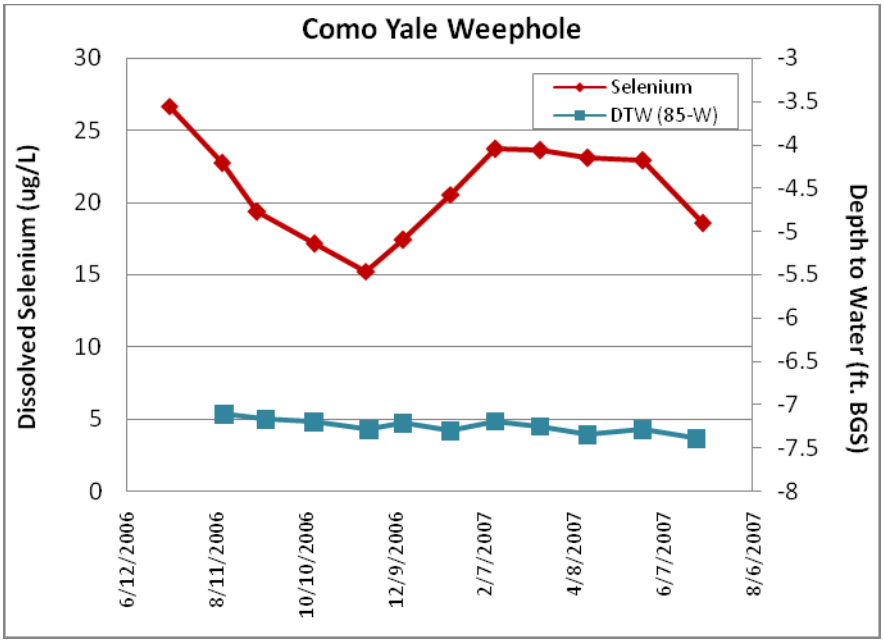
----------Drought-Year Data for Como-Yale Weephole ----------



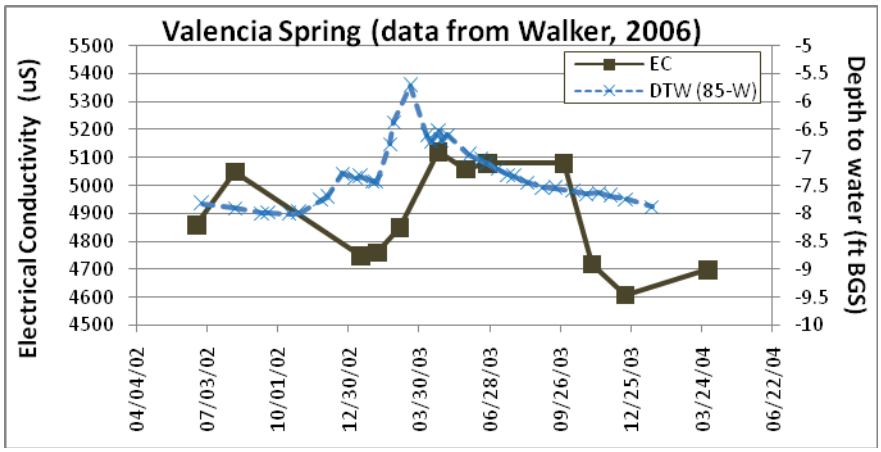


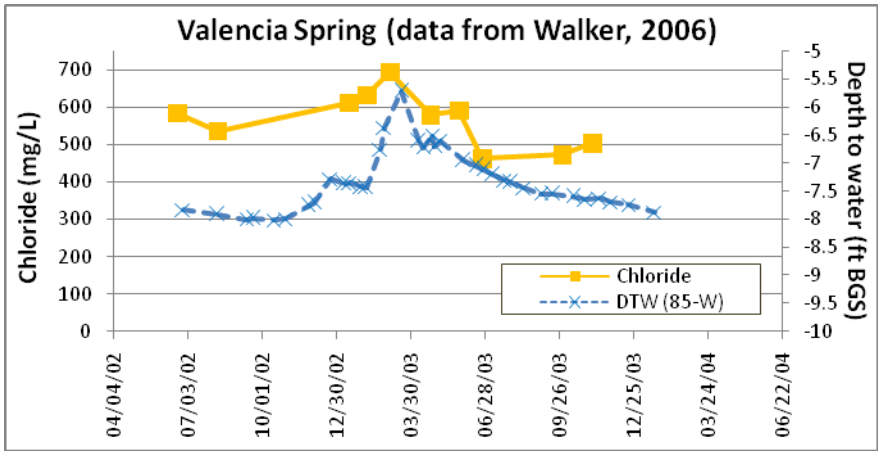


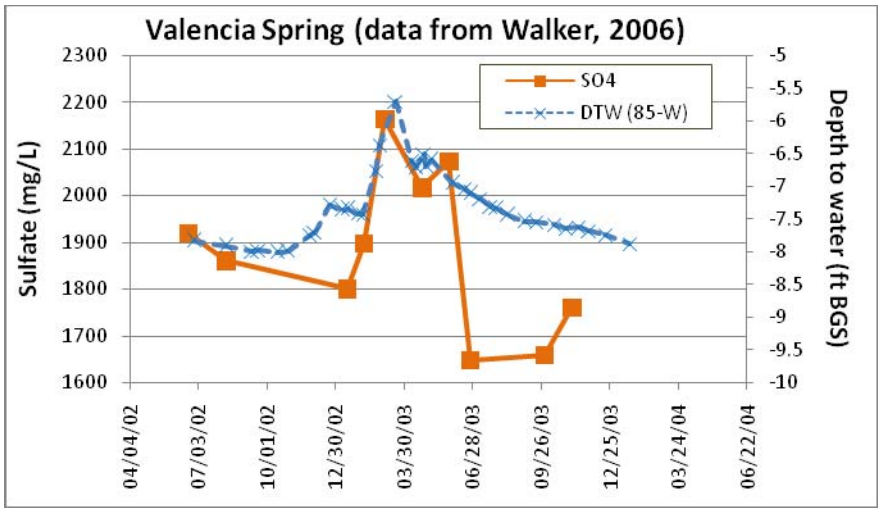

Como Yale Weephole
Nitrate as N (mg/L)
Depth to Water (ft. BGS)
NO3-N
DTW (85-W)
25
20
15
10
5
0
-3
-3.5
-4
-4.5
-5
-5.5
-6
-6.5
-7
-7.5
-8
6/12/2006
8/11/2006
10/10/2006
12/9/2006
2/7/2007
4/8/2007
6/7/2007
8/6/2007

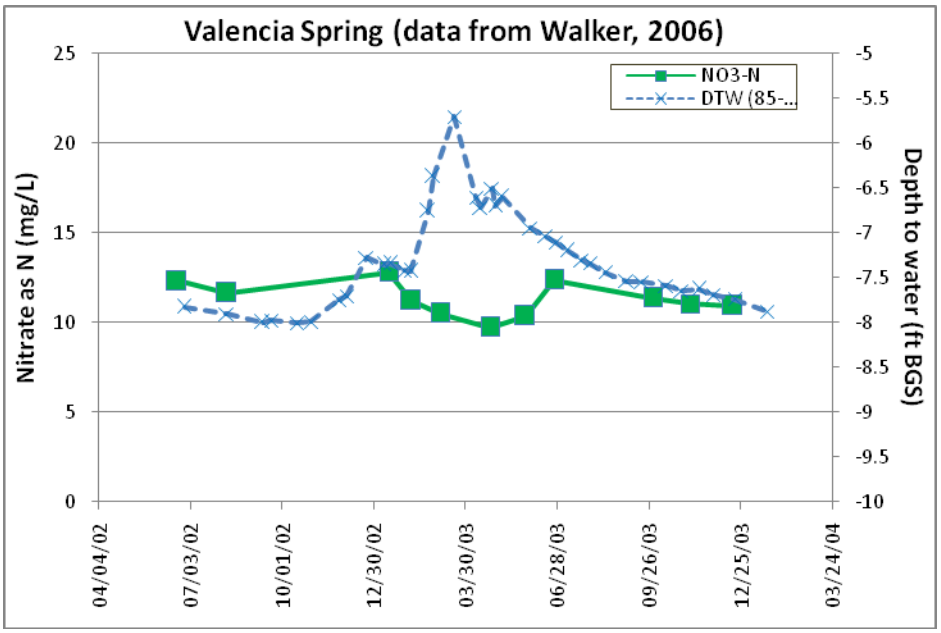

Como Yale Weephole
Dissolved Selenium (ug/L)
Depth to Water (ft. BGS)
Selenium
DTW (85-W)
30
25
20
15
10
5
0
-3
-3.5
-4
-4.5
-5
-5.5
-6
-6.5
-7
-7.5
-8
6/12/2006
8/11/2006
10/10/2006
12/9/2006
2/7/2007
4/8/2007
6/7/2007
8/6/2007

----------Wet-Year Data for Valencia Spring----------








Valencia Spring (data from Walker, 2006)
NO3-N
DTW (85-...
Nitrate as N (mg/L)
Depth to water (ft BGS)
25
20
15
10
5
0
-5
-5.5
-6
-6.5
-7
-7.5
-8
-8.5
-9
-9.5
-10
04/04/02
07/03/02
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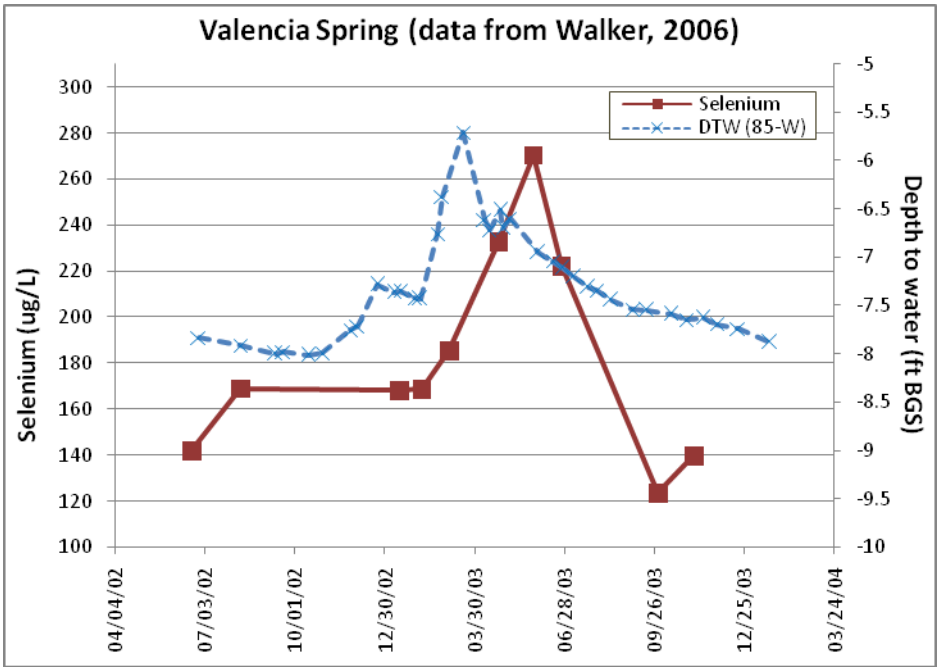
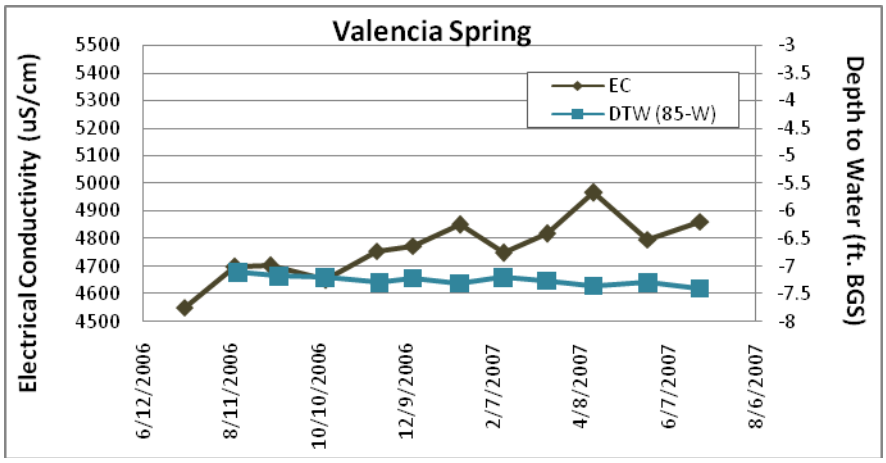
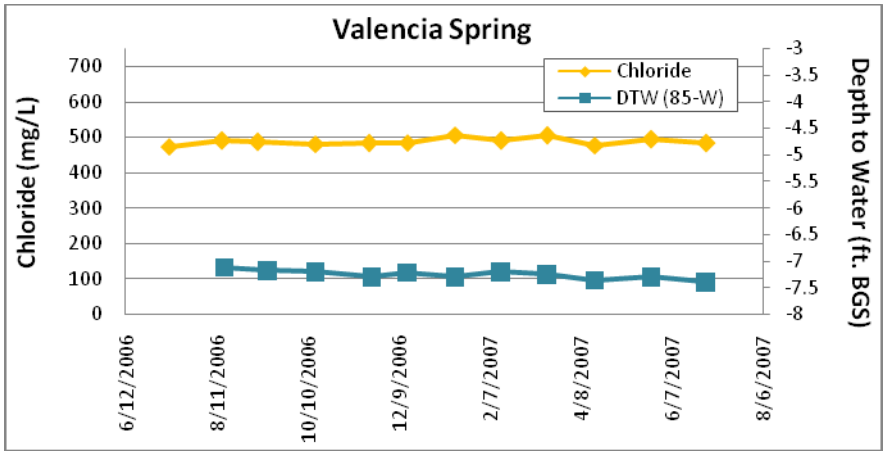
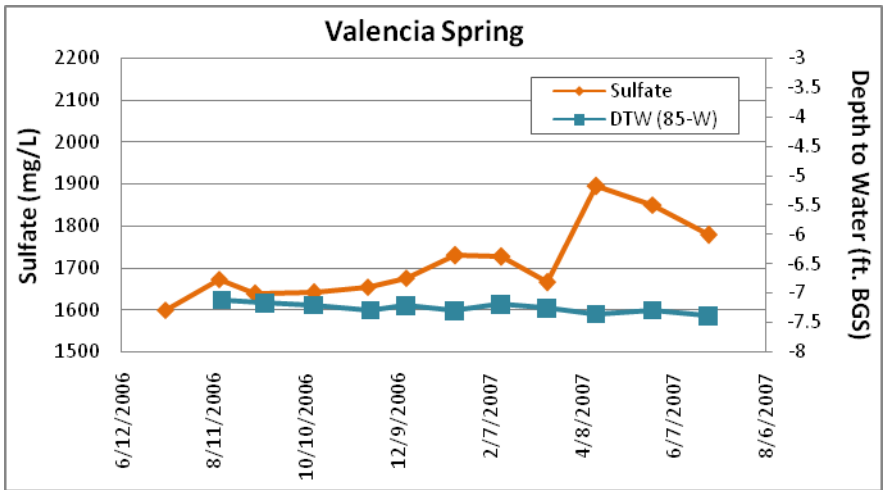
06/28/03
09/26/03
12/25/03
03/24/04

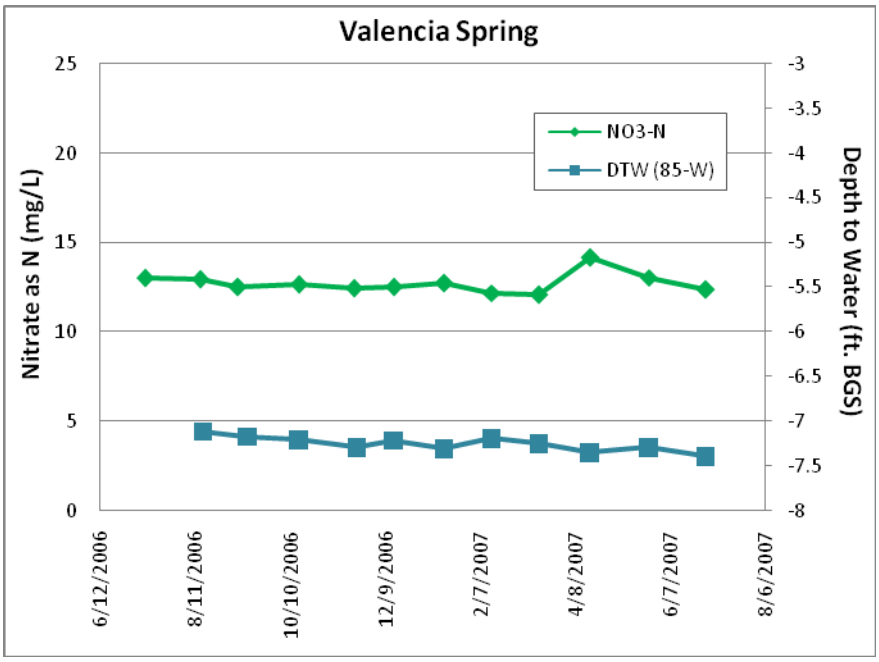

Valencia Spring (data from Walker, 2006)
Selenium
DTW (85-W)
Selenium (ug/L)
Depth to water (ft BGS)
300
280
260
240
220
200
180
160
140
120
100
-5
-5.5
-6
-6.5
-7
-7.5
-8
-8.5
-9
-9.5
-10
04/04/02
07/03/02
10/01/02
12/30/02
03/30/03
06/28/03
09/26/03
12/25/03
03/24/04

----------Drought-Year Data for Valencia Spring ----------








Valencia Spring
Nitrate as N (mg/L)
Depth to Water (ft. BGS)
NO3-N
DTW (85-W)
25
20
15
10
5
0
-3
-3.5
-4
-4.5
-5
-5.5
-6
-6.5
-7
-7.5
-8
6/12/2006
8/11/2006
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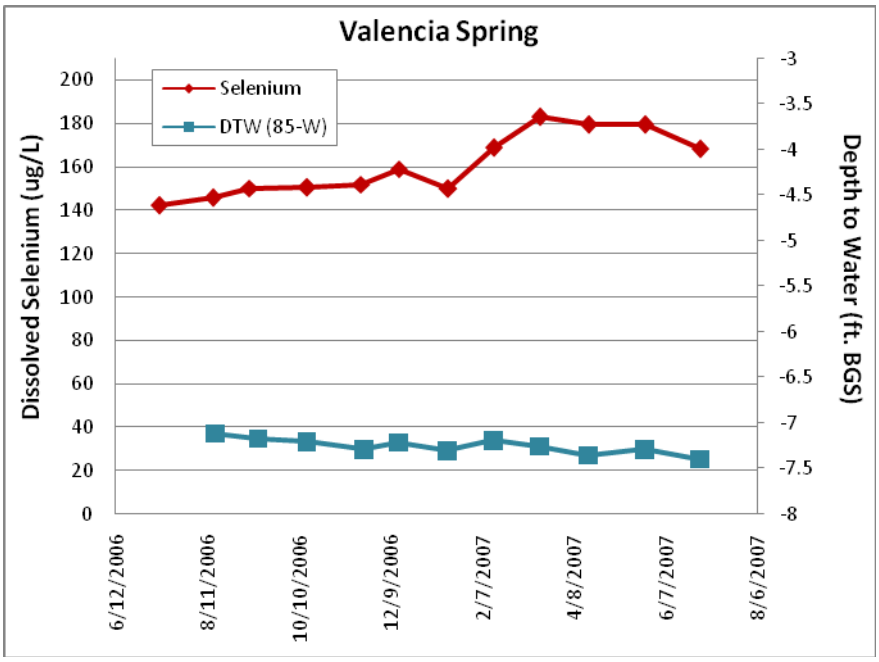
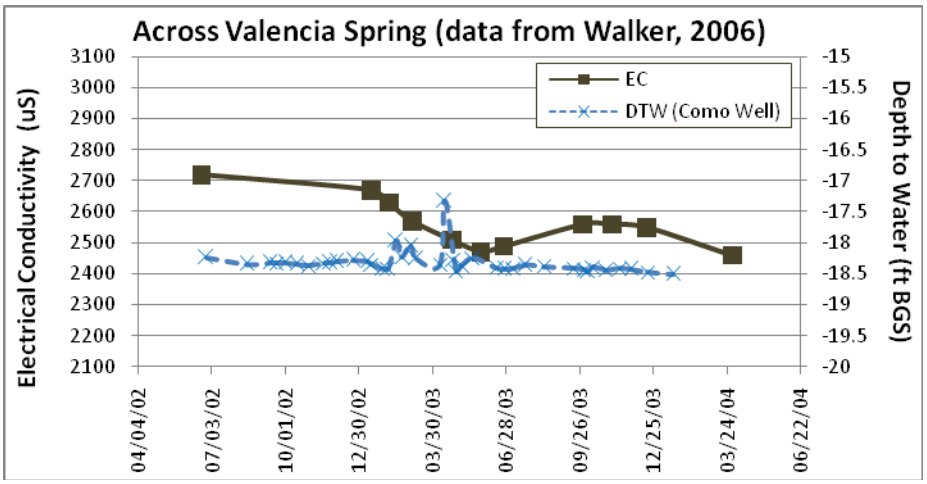
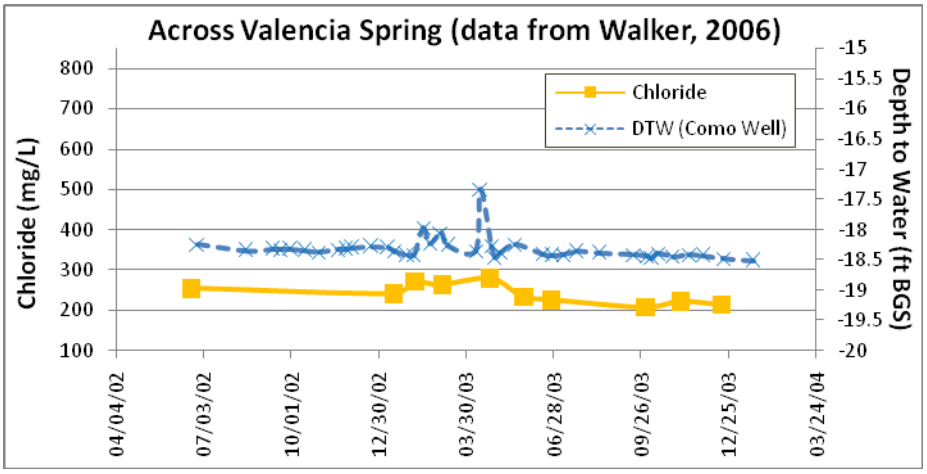
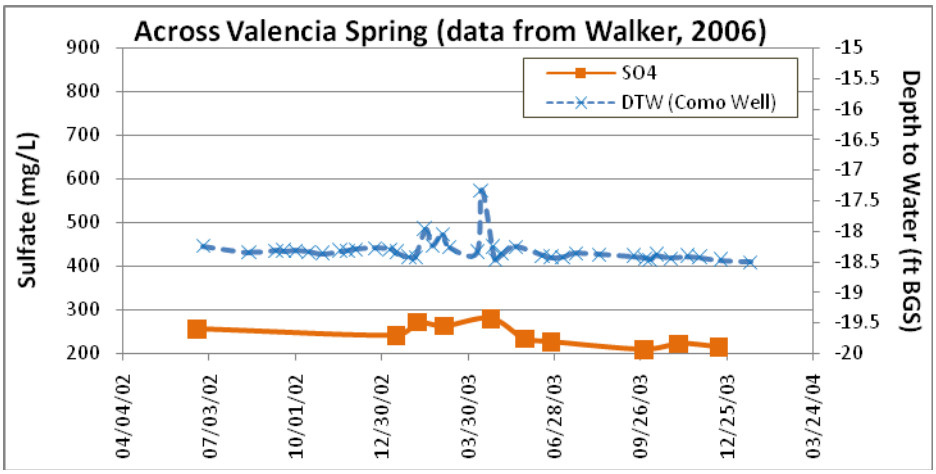
4/8/2007
6/7/2007
8/6/2007

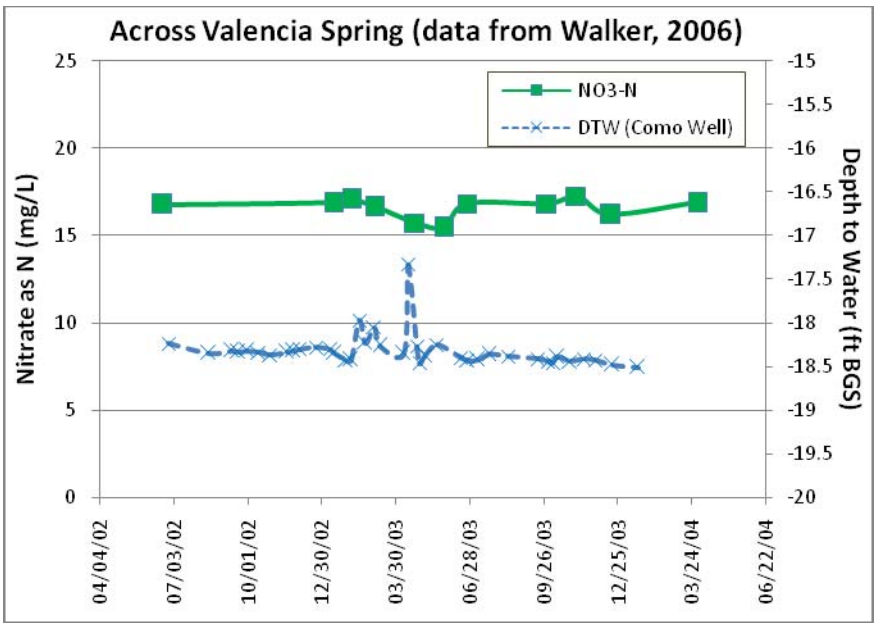

Valencia Spring
Dissolved Selenium (ug/L)
Depth to Water (ft. BGS)
Selenium
DTW (85-W)
200
180
160
140
120
100
80
60
40
20
0
-3
-3.5
-4
-4.5
-5
-5.5
-6
-6.5
-7
-7.5
-8
6/12/2006
8/11/2006
10/10/2006
12/9/2006
2/7/2007
4/8/2007
6/7/2007
8/6/2007

----------Wet-Year Data for Across Valencia Spring----------








Across Valencia Spring (data from Walker, 2006)
NO3-N
DTW (Como Well)
Nitrate as N (mg/L)
Depth to Water (ft BGS)
25
20
15
10
5
0
-15
-15.5
-16
-16.5
-17
-17.5
-18
-18.5
-19
-19.5
-20
04/04/02
07/03/02
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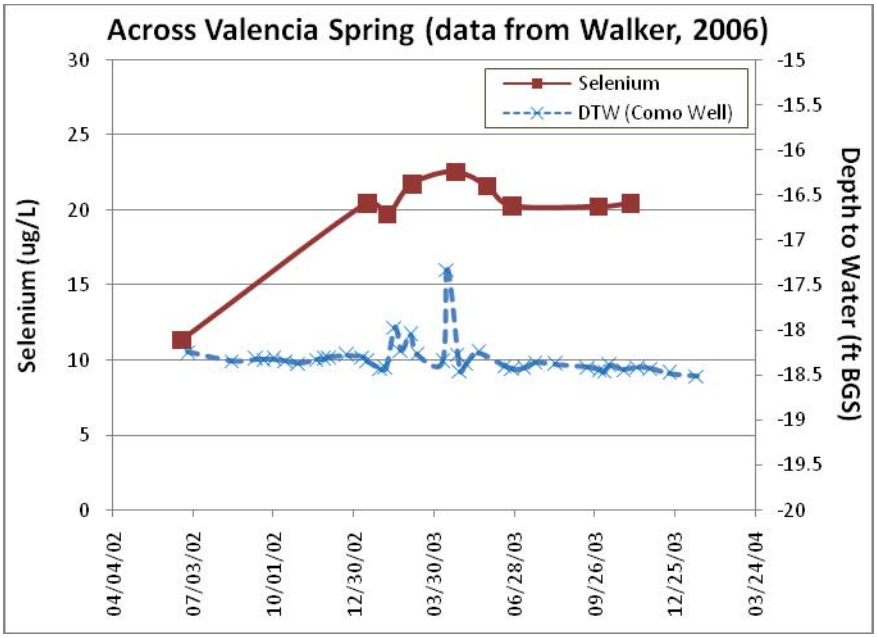
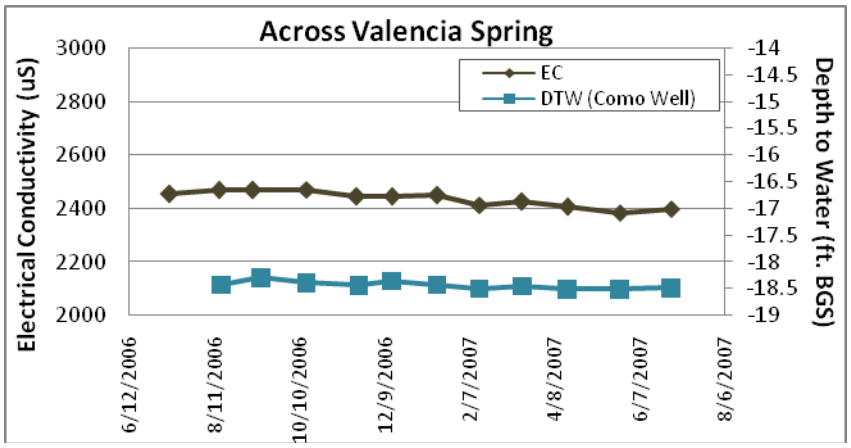
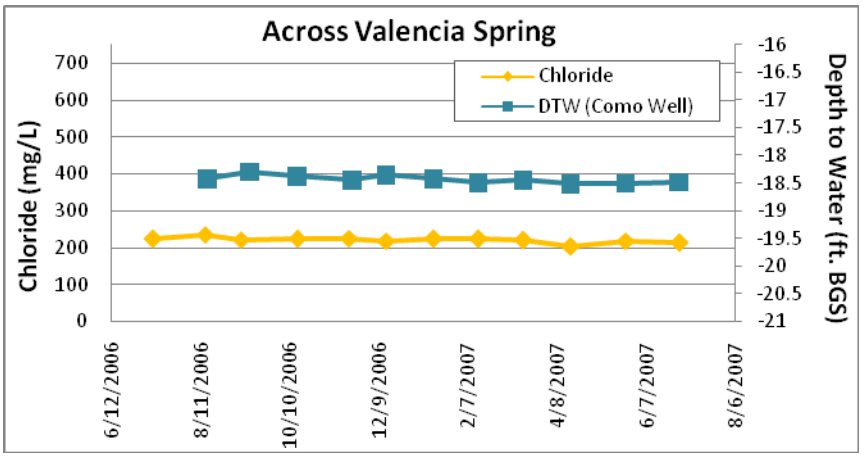
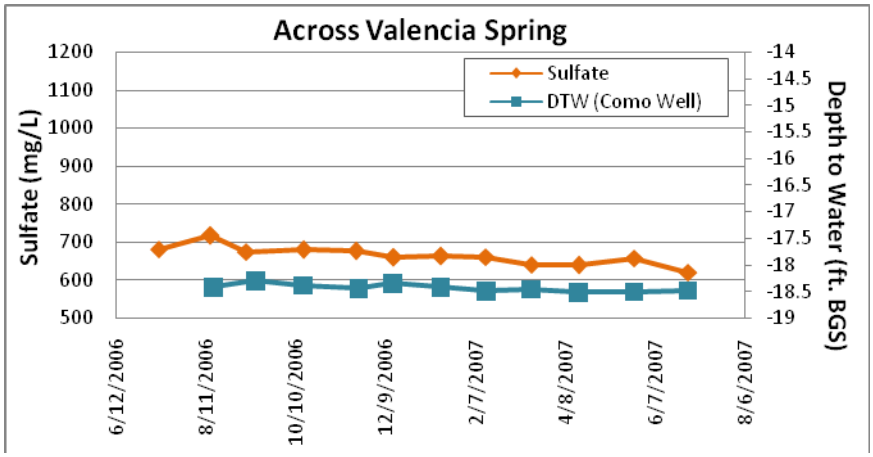
03/24/04
06/22/04

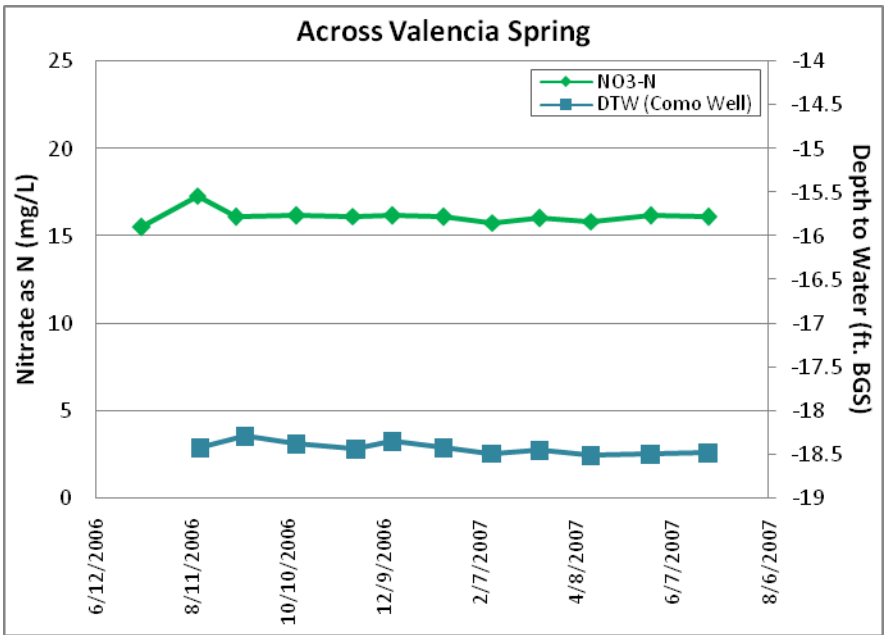

Across Valencia Spring (data from Walker, 2006)
Selenium
DTW (Como Well)
Selenium (ug/L)
Depth to Water (ft BGS)
30
25
20
15
10
5
0
-15
-15.5
-16
-16.5
-17
-17.5
-18
-18.5
-19
-19.5
-20
04/04/02
07/03/02
10/01/02
12/30/02
03/30/03
06/28/03
09/26/03
12/25/03
03/24/04

----------Drought-Year Data for Across Valencia Spring ----------








Across Valencia Spring
NO3-N
DTW (Como Well)
Nitrate as N (mg/L)
Depth to Water (ft. BGS)
25
20
15
10
5
0
-14
-14.5
-15
-15.5
-16
-16.5
-17
-17.5
-18
-18.5
-19
6/12/2006
8/11/2006
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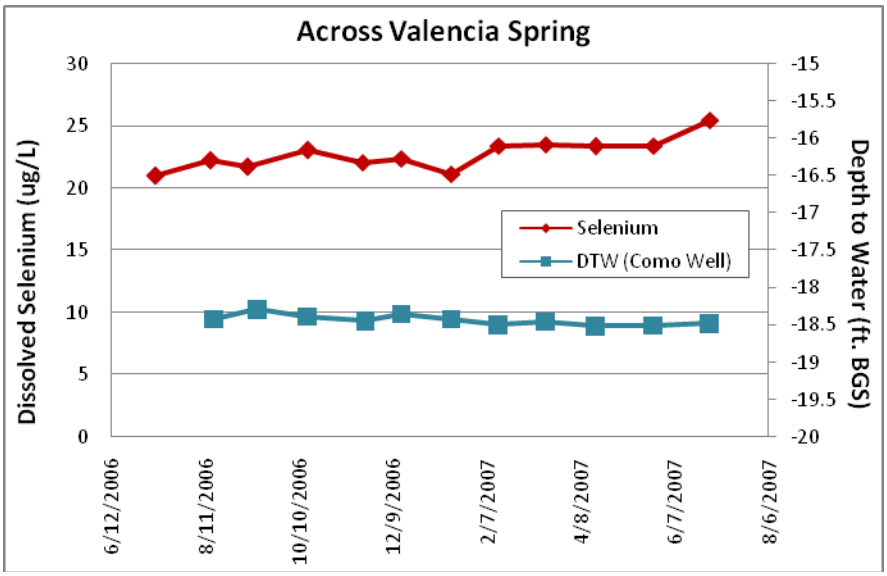
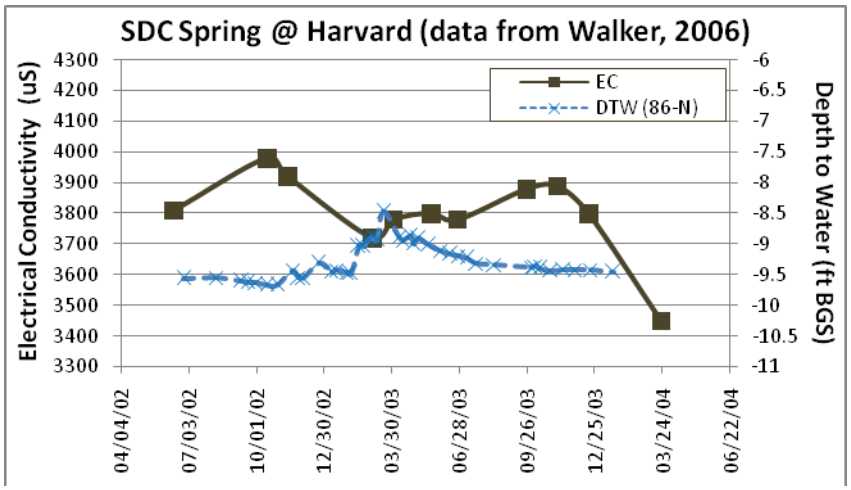
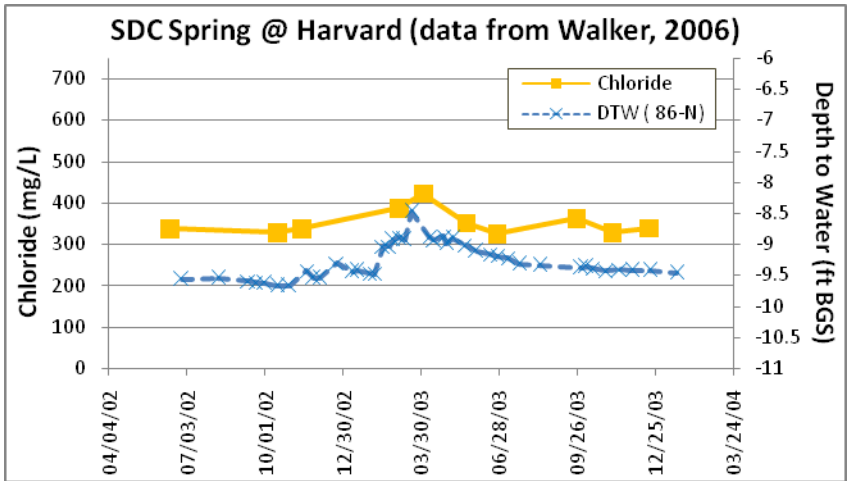
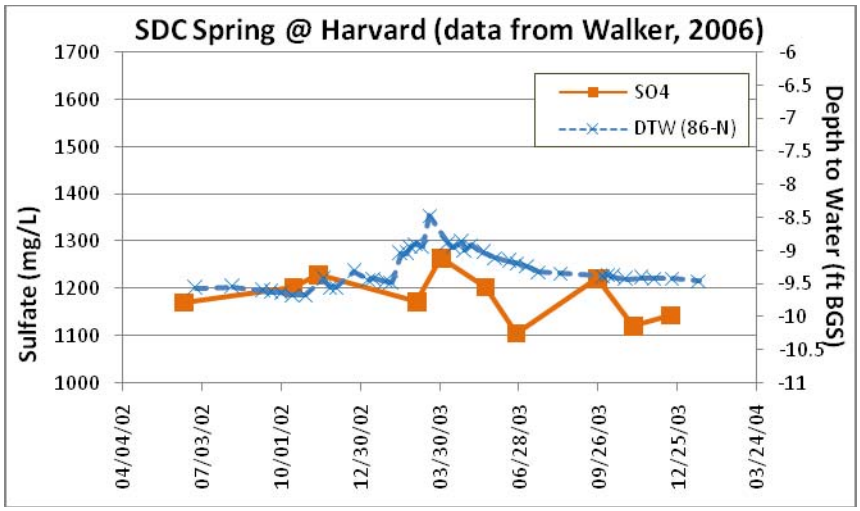
6/7/2007
8/6/2007

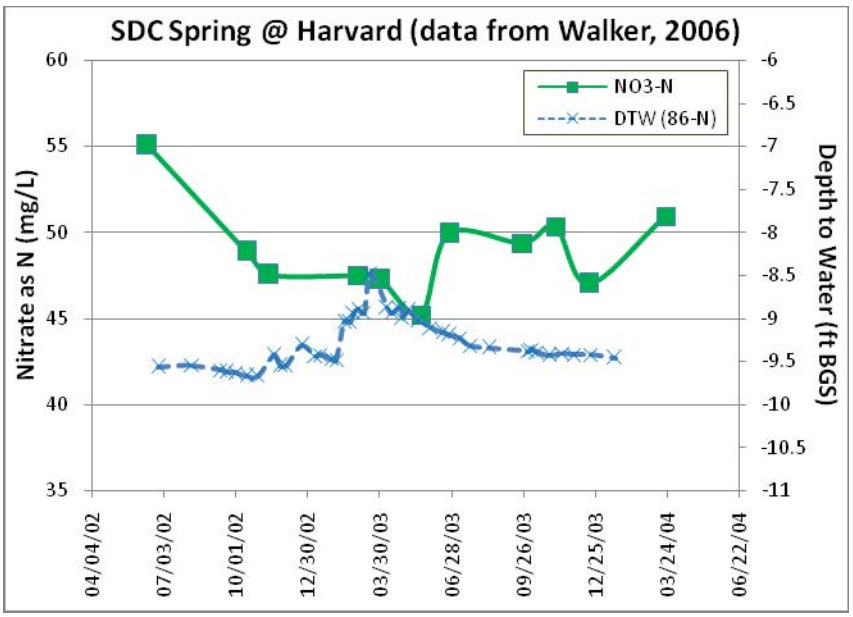

Across Valencia Spring
Selenium
DTW (Como Well)
Dissolved Selenium (ug/L)
Depth to Water (ft. BGS)
30
25
20
15
10
5
0
-15
-15.5
-16
-16.5
-17
-17.5
-18
-18.5
-19
-19.5
-20
6/12/2006
8/11/2006
10/10/2006
12/9/2006
2/7/2007
4/8/2007
6/7/2007
8/6/2007

----------Wet-Year Data for SDC Spring @ Harvard----------








SDC Spring @ Harvard (data from Walker, 2006)
NO3-N
DTW (86-N)
Nitrate as N (mg/L)
Depth to Water (ft BGS)
60
55
50
45
40
35
-6
-6.5
-7
-7.5
-8
-8.5
-9
-9.5
-10
-10.5
-11
04/04/02
07/03/02
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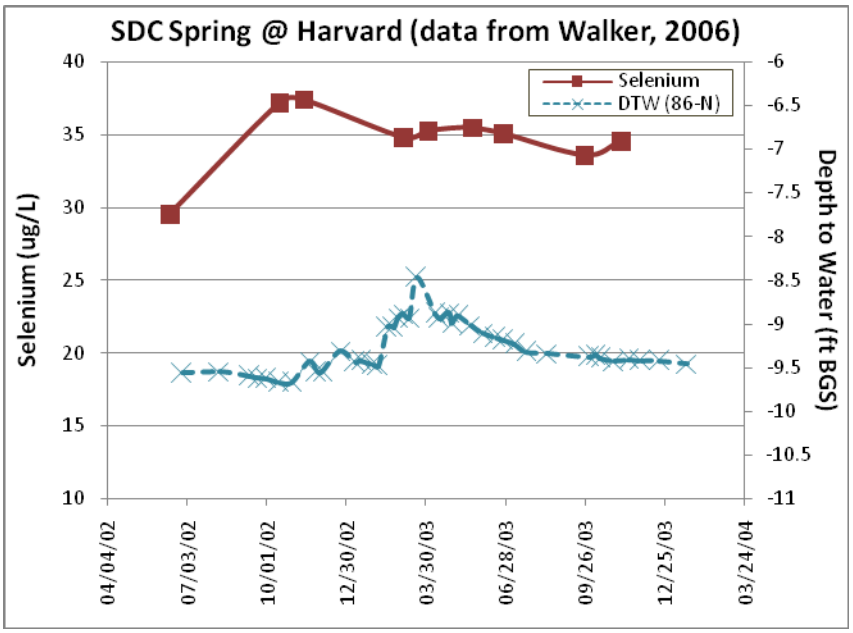
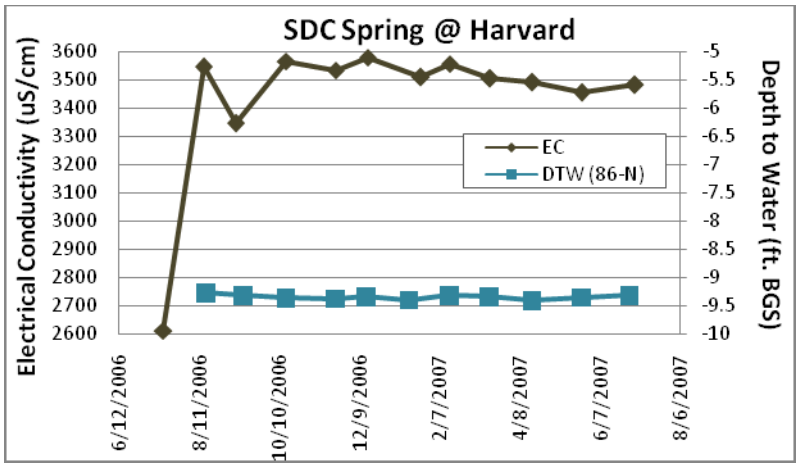
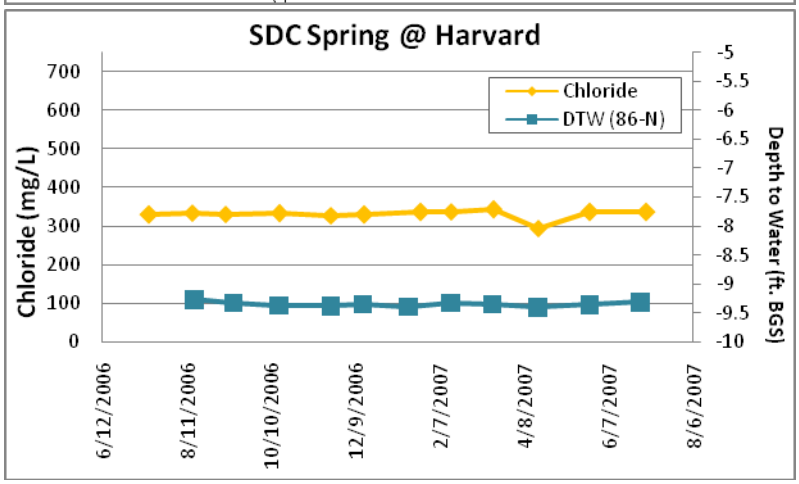
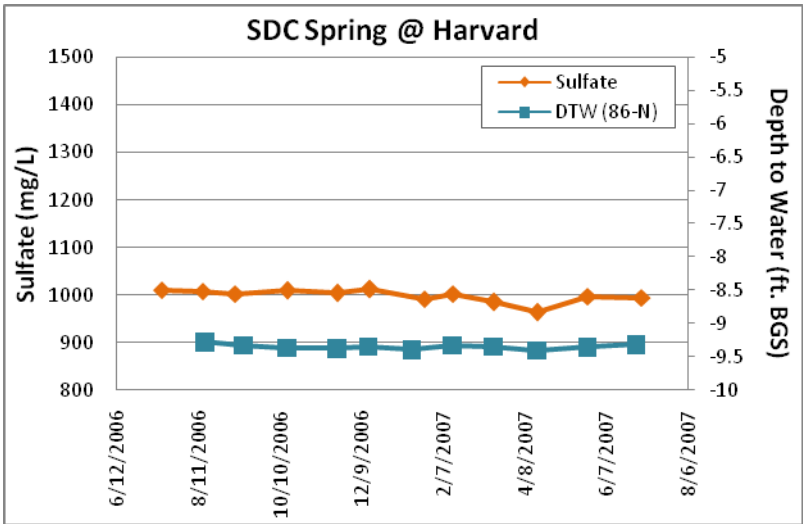
03/24/04
06/22/04

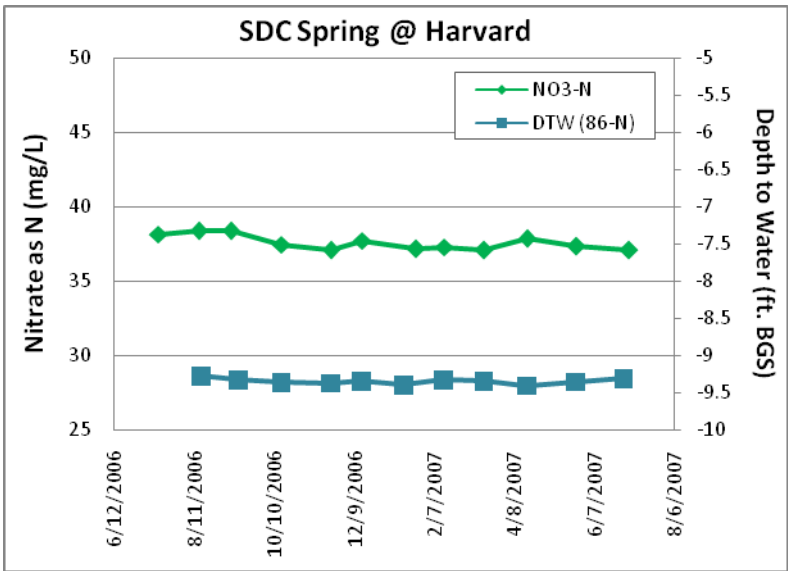

SDC Spring @ Harvard (data from Walker, 2006)
Selenium
DTW (86-N)
Selenium (ug/L)
Depth to Water (ft BGS)
40
35
30
25
20
15
10
-6
-6.5
-7
-7.5
-8
-8.5
-9
-9.5
-10
-10.5
-11
04/04/02
07/03/02
10/01/02
12/30/02
03/30/03
06/28/03
09/26/03
12/25/03
03/24/04

----------Drought-Year Data for SDC Spring @ Harvard ----------








SDC Spring @ Harvard
Nitrate as N (mg/L)
Depth to Water (ft. BGS)
NO3-N
DTW (86-N)
50
45
40
35
30
25
-5
-5.5
-6
-6.5
-7
-7.5
-8
-8.5
-9
-9.5
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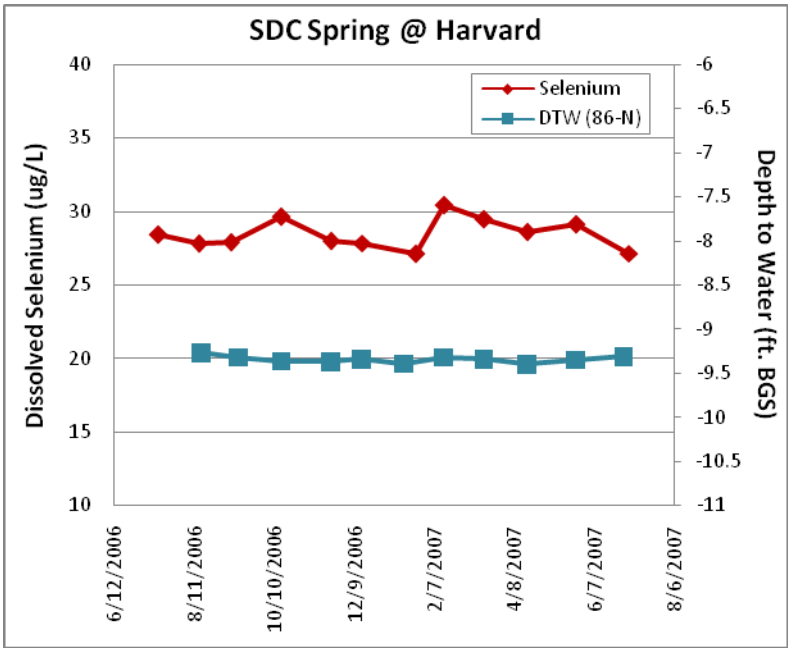
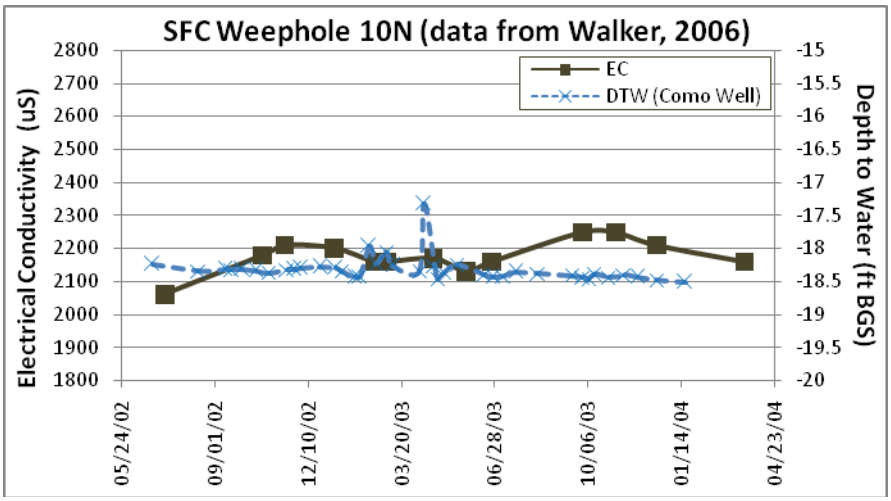
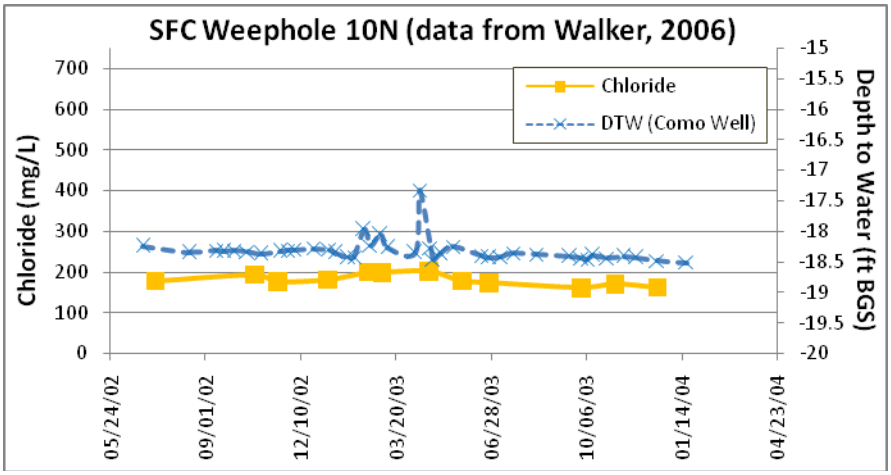
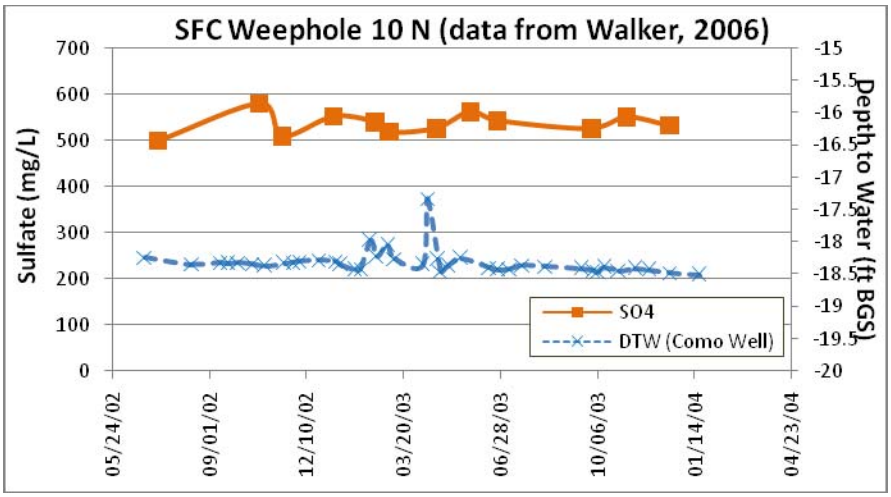
6/7/2007
8/6/2007

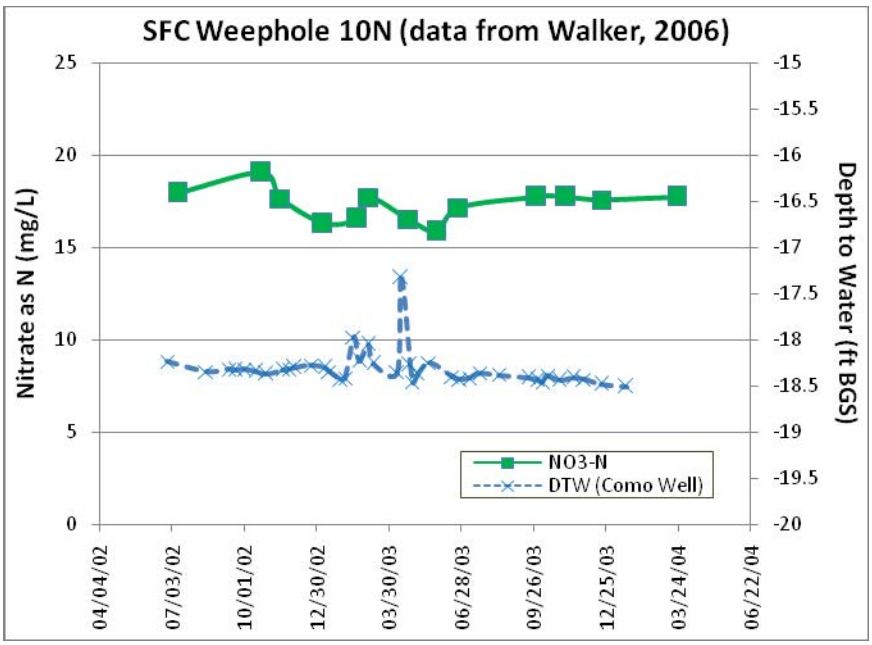

SDC Spring @ Harvard
Dissolved Selenium (ug/L)
Depth to Water (ft. BGS)
Selenium
DTW (86-N)
40
35
30
25
20
15
10
-6
-6.5
-7
-7.5
-8
-8.5
-9
-9.5
-10
-10.5
-11
6/12/2006
8/11/2006
10/10/2006
12/9/2006
2/7/2007
4/8/2007
6/7/2007
8/6/2007

----------Wet-Year Data for SFC Weephole 10N----------








SFC Weephole 10N (data from Walker, 2006)
Nitrate as N (mg/L)
Depth to Water (ft BGS)
NO3-N
DTW (Como Well)
25
20
15
10
5
0
-15
-15.5
-16
-16.5
-17
-17.5
-18
-18.5
-19
-19.5
-20
04/04/02
07/03/02
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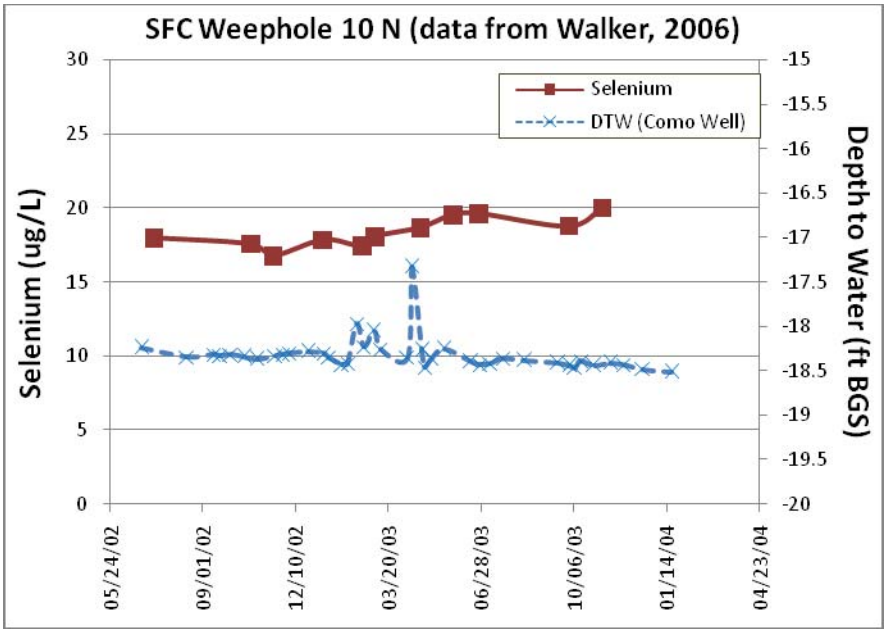
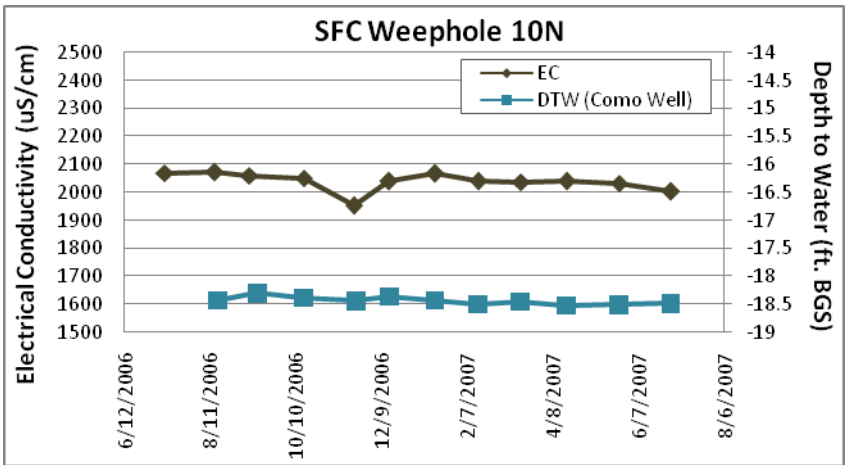
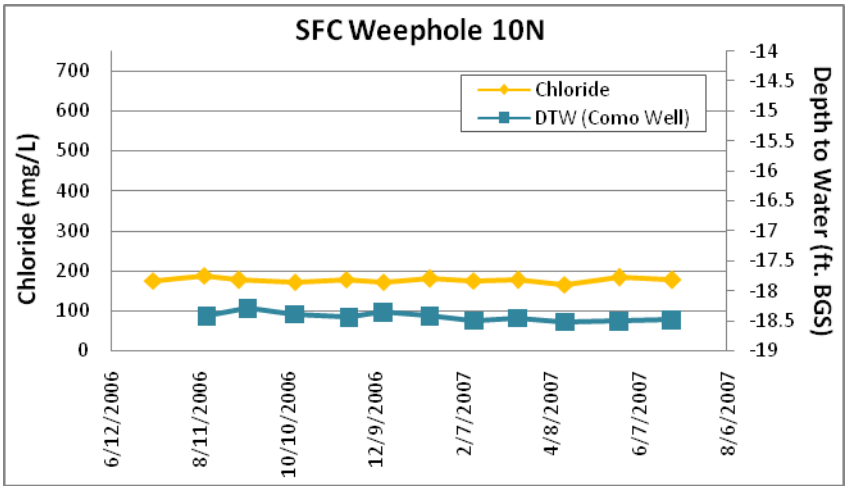
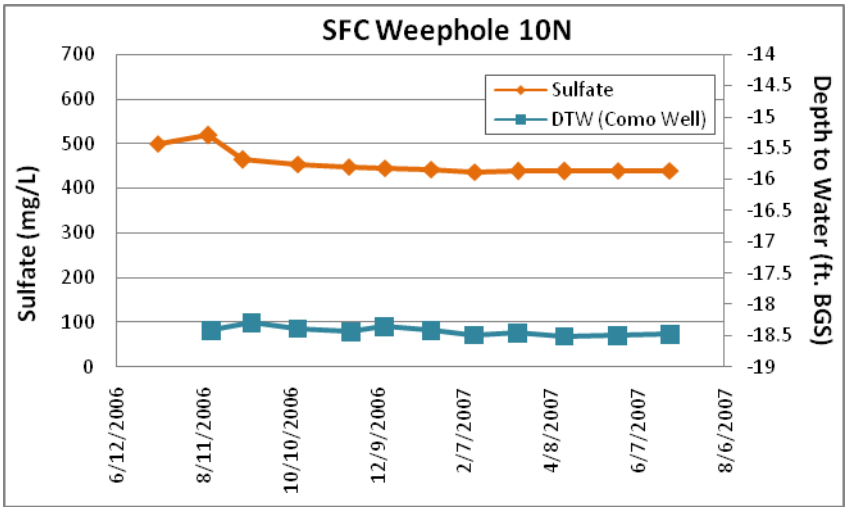
03/24/04
06/22/04

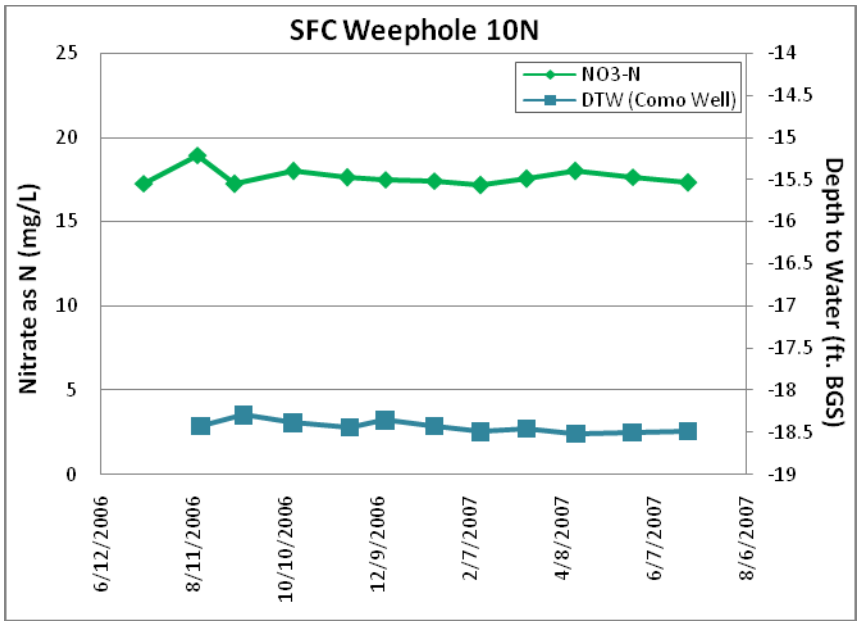

SFC Weephole 10 N (data from Walker, 2006)
Selenium (ug/L)
Depth to Water (ft BGS)
Selenium
DTW (Como Well)
30
25
20
15
10
5
0
-15
-15.5
-16
-16.5
-17
-17.5
-18
-18.5
-19
-19.5
-20
05/24/02
09/01/02
12/10/02
03/20/03
06/28/03
10/06/03
01/14/04
04/23/04

----------Drought-Year Data for SFC Weephole 10N ----------








SFC Weephole 10N
NO3-N
DTW (Como Well)
Nitrate as N (mg/L)
Depth to Water (ft. BGS)
25
20
15
10
5
0
-14
-14.5
-15
-15.5
-16
-16.5
-17
-17.5
-18
-18.5
-19
6/12/2006
8/11/2006
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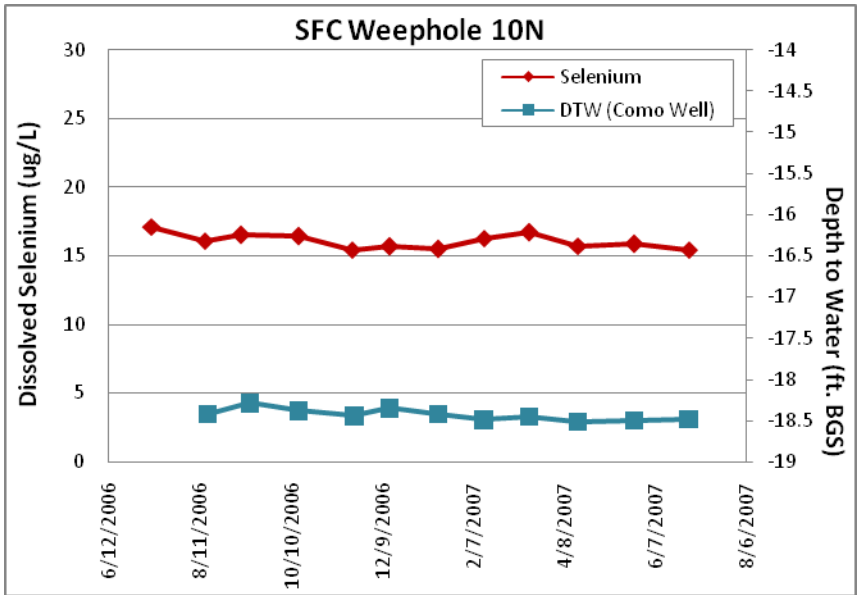
4/8/2007
6/7/2007
8/6/2007


SFC Weephole 10N
Selenium
DTW (Como Well)
Dissolved Selenium (ug/L)
Depth to Water (ft. BGS)
30
25
20
15
10
5
0
-14
-14.5
-15
-15.5
-16
-16.5
-17
-17.5
-18
-18.5
-19
6/12/2006
8/11/2006
10/10/2006
12/9/2006
2/7/2007
4/8/2007
6/7/2007
8/6/2007

Chapter 4

Selenium Dynamics in San Joaquin Marsh: San Diego Creek Watershed

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1 May 2008

Prepared for
Santa Ana Regional Water Quality Control Board

by

Barry Hibbs, and Mercedes Merino
Department of Geological Sciences
California State University, Los Angeles

INTRODUCTION

The Irvine Ranch Water District established freshwater ponds at San Joaquin Marsh for the specific purpose of naturally cleansing flows from the San Diego Creek Watershed before flows are routed back into Upper Newport Bay. Approximately 3.2 to 6.5 million gallons of water from San Diego Creek are diverted into the San Joaquin Marsh daily. The water circulates through a series of large freshwater ponds for 10 to 14 days, where microbes in the soil release nitrogen from the water before flows are routed back into San Diego Creek (IRWD 2002).

In this study, San Joaquin Marsh was analyzed for selenium and other hydrochemical and isotopic species to assess removal, uptake, and possible remobilization/immobilization occurring in the marsh. During the 1.5 years we monitored the marsh, there were periodic shutdowns of the marsh for channel and marsh maintenance. Total and dissolved selenium, index parameters, anions (sulfate, chloride) and select nutrients (nitrate, orthophosphate) were measured twice monthly when the marsh was circulating flows to and from San Diego Creek. Total and dissolved selenium was also measured every day for a two week period, and every hour during one twenty-four (24) hour period at the marsh inlet and outlet. Sediments were collected within the marsh and analyzed for selenium species.

At specific times, water column samples were collected from strategic stations in the marsh for selenium speciation analysis. These stations included inlet basins, mid-basins, and outlet basins in the marsh. Monitoring wells were also sampled to compare groundwater hydrochemistry to marsh hydrochemistry.

Study Area

The Newport Bay Watershed lies approximately 40 miles south of Los Angeles and 75 miles north of San Diego. It has been subdivided into the San Diego Creek Watershed and the (Lower) Newport Bay Watershed. Topographically, the watershed is bounded on the south side by the San Joaquin Hills and on the north side by Loma Ridge, a part of the Santiago Hills (Figure 4.1).

Encompassing approximately 154 mi^2, its major tributary San Diego Creek drains 122 mi^2 of the watershed into Upper Newport Bay, an estuary protected by the California Department of Fish and Game as an ecological preserve (Sevilla, 2003). Newport Bay is the abandoned mouth of the Santa Ana River that was closed by longshore drift and periodic flooding, and has been reopened by an artificial channel (Trinast, 1975). The treatment wetland at San Joaquin Marsh is located about 1.4 miles above Upper Newport Bay.

San Joaquin Marsh

The 538-acre San Joaquin Marsh (combined UCI San Joaquin Marsh and IRWD San Joaquin Marsh) is a remnant of a historical wetland ecosystem (Sevilla, 2003). For the past 200 years, wetlands were ditched and drained for the irrigation of crops and orchards, cattle and sheep were grazed on hills, and urban/industrial center were established. Numerous gun clubs obtained leases or bought wetlands from James Irvine in the early 1900s for the purposes of duck and geese hunting. The San Joaquin Gun Club constructed a system of dikes, pipes and ditches to divert water from San Diego Creek into the duck ponds (UCNRS 2002).

With the help of the Ford Foundation, the Regents of the University of California purchased the San Joaquin Marsh Reserve (hereafter called UCI-San Joaquin Marsh) in 1970 to become part of the UC Natural Reserve System (Sevilla, 2003). Located 1.25 miles upstream from Upper Newport Bay, the 202-acre UCI San Joaquin Marsh supports a variety of wetland habitats including shallow ponds, freshwater marshlands and channels that are confined by earthen dikes (Figure 4.2). San Diego Creek lie to the southeast of the Marsh's 18 ponds, while Campus Drive borders its northeastern edge and the UCI arboretum heads the marsh to the north (UCNRS 2002).

According to the ACOE (2001), the Irvine Ranch Water District own the 336-acre eastern portion of the San Joaquin Marsh, while the Sea and Sage Chapter of the National Audubon Society claims the other 29.5 acres (Figure 4.3) (Sevilla, 2003). As part of the San Joaquin Marsh Restoration Project with the Irvine Company, the Irvine Ranch Water District established freshwater wetlands for the specific purpose of naturally cleansing urban runoff from the San Diego Creek Watershed (wetlands hereafter called IRWD San Joaquin Marsh). These include six thorough-flowing water quality treatment ponds constructed in 1997 (GeoSyntec, 2003).

The water quality treatment ponds at IRWD San Joaquin Marsh include about 45 acres of open water and an additional 11 acres of vegetated marsh (Figure 4.3) (GeoSyntec, 2003). The treatment wetlands at IRWD San Joaquin Marsh divert flows from San Diego Creek for water quality treatment during dry weather/low flow regimes and during wet weather/low flow regimes, but not during larger storms and first flush storm events (GeoSyntec, 2003). Pumps for diversion of flows from San Diego Creek through IRWD San Joaquin Marsh are shut off during larger storm events to limit

sediment input to the water quality treatment ponds (Sevilla, 2003). During this study, an average of about 3.5 to 4.5 cfs was diverted from San Diego Creek into the IRWD San Joaquin Marsh.

Historical Assessment of Water Quality

The effectiveness of IRWD San Joaquin Marsh as a water quality treatment unit for nutrients is well documented (IRWD 2002):

> *"Approximately 3.25 to 6.5 million gallons of water from San Diego Creek are diverted into the San Joaquin Marsh daily. The water circulates through a series of large freshwater ponds for two weeks, where microbes in the soil release nitrogen from the water in a natural purifying process. By removing nutrients from the water before it reaches Upper Newport Bay, there are fewer algae blooms, which can impact water quality. Harmful bacteria are also naturally removed from the creek water, lowering the level of bacteria"*

According to IRWD (1999), three years of San Diego Creek water diversion had resulted in a 25 percent drop in bay algae growth associated with a drop in nitrogen levels. Other studies indicate that although the nitrate concentrations re-released into San Diego Creek are reduced by 90%, about one half of this nitrate is converted into organic nitrogen (OCPFRD, 1999).

Analysis of selenium data by GeoSyntec (2003), using IRWD acquired data, led to important observations and speculation on the fate of selenium at inlet and outlet flows at IRWD San Joaquin Marsh (GeoSyntec, 2003):

> *"Influent [inlet] and effluent [outlet] selenium loads to the existing IRWD WQT wetlands at the San Joaquin Marsh are plotted [Figure 4.4]. These plots reveal that daily effluent loads are for the most part below influent loads during the monitoring period…….. Selenium is mainly removed*

from water in the marsh by adsorption to organic rich wetland sediments under anoxic conditions. Since dissolved oxygen is present in the effluent from the Marsh, selenium will not tend to adsorb to the sediments in the effluent stream. Anoxic conditions will mainly be found in undisturbed sediments that have settled to the bottom of the Marsh, such as in areas with emergent vegetation. Based on the information from other surface flow wetlands, a fraction of the selenium in the sediments can be assimilated by the wetland vegetation, primarily in the root zone, whereupon a significant amount (10-30 percent) will be transferred to the atmosphere by volatilization (EPRI, 2000; Lin-Qing and Terry, 2003). The available sediment data from the Marsh were not sufficient to assess the current level of selenium accumulation in the Marsh sediment".

The data analysis indicated that about 30 percent of the influent selenium was impounded or lost in IRWD San Joaquin Marsh during the monitoring period shown in Figure 4.4 (GeoSyntec, 2003).

Purpose of Current Study

This project evaluates selenium in the water column and soils of IRWD San Joaquin Marsh. A percentage of the removal of selenium from the water column may be permanent due to volatilization of selenium associated with plant uptake; however, a percentage of selenium removal from the water column may not be permanent due to partitioning and re-partitioning across soil interfaces and biota. This project helps to evaluate water column removal and transfers across interfaces. Specific monitoring activities included:

- Specific areas of the marsh were analyzed for selenium species to assess removal, uptake, and possible remobilization/immobilization of selenium that may be occurring in the marsh.

- Total and dissolved selenium, dissolved oxygen, pH, specific conductance, turbidity, and temperature were measured at least twice monthly for a one (1) year period in water column samples collected from the marsh inlet and outlet.

- Total and dissolved selenium were measured every two (2) hours during a twenty-four (24) hour period at the marsh inlet and outlet.

- Sediment samples were collected from the marsh and analyzed for selenium species, once in the summer and once in the winter.

- Fifteen (15) water column samples were collected from strategic stations points in the marsh for selenium speciation analysis. Stations included inlet basins, mid-basins, and outlet basins in the Wildlife Sanctuary.

There were several interruptions that occurred during the expected one year study. IRWD shut down marsh inlet/outlet flows for several months during removal of sediment from Sediment Basin 3 in San Diego Creek. Another interruption occurred due to pump failure in San Joaquin Marsh. Accordingly, the study extended over a 19 month period, with about 13 months of cumulative monitoring.

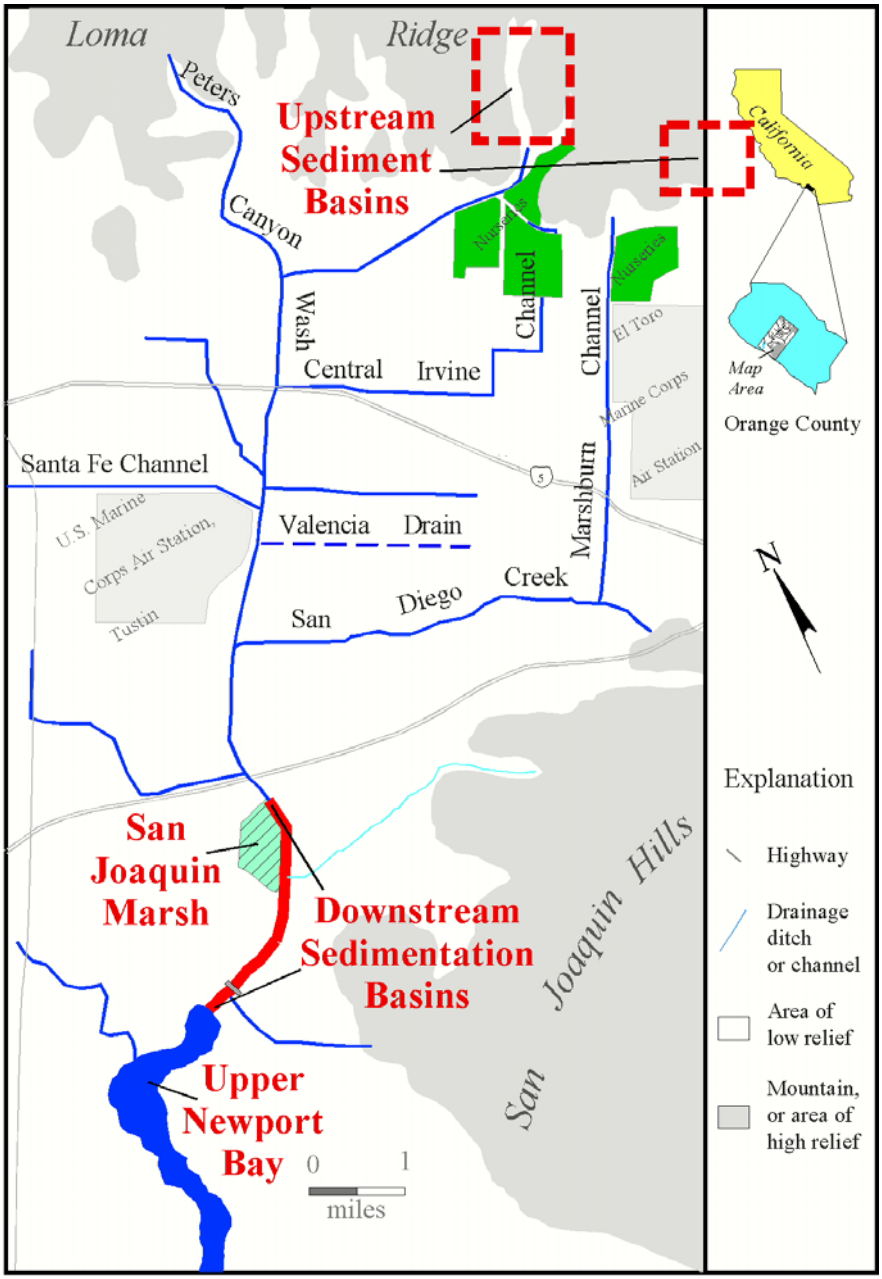

Figure 4.1. San Diego Creek Watershed showing location of San Joaquin Marsh.

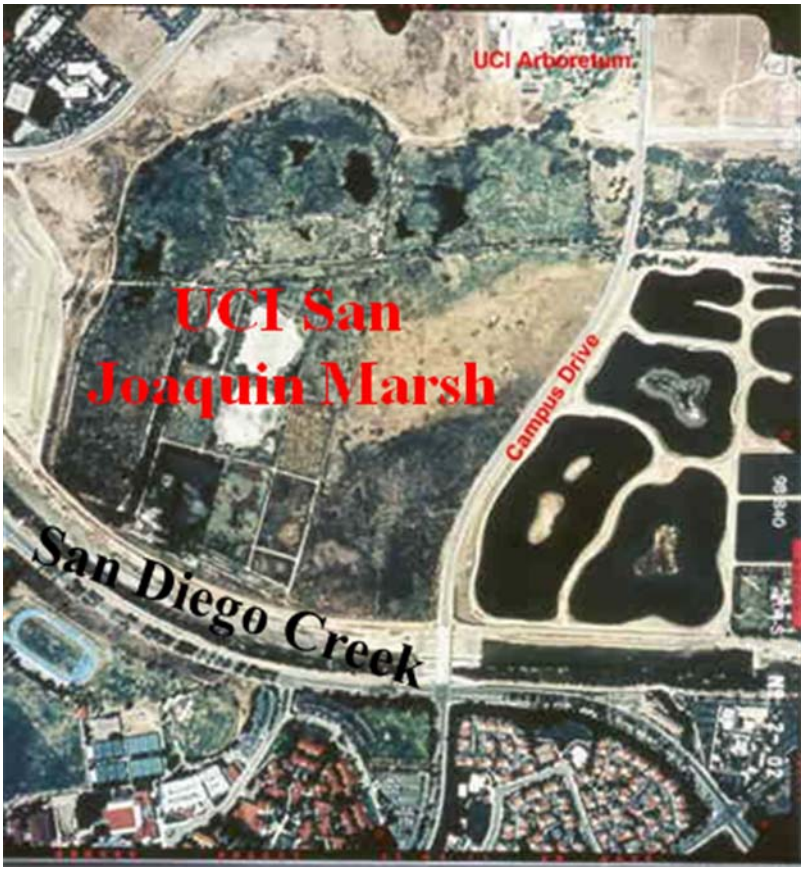

Figure 4.2. Aerial View of the UCI San Joaquin Marsh (UCNRS 2002).

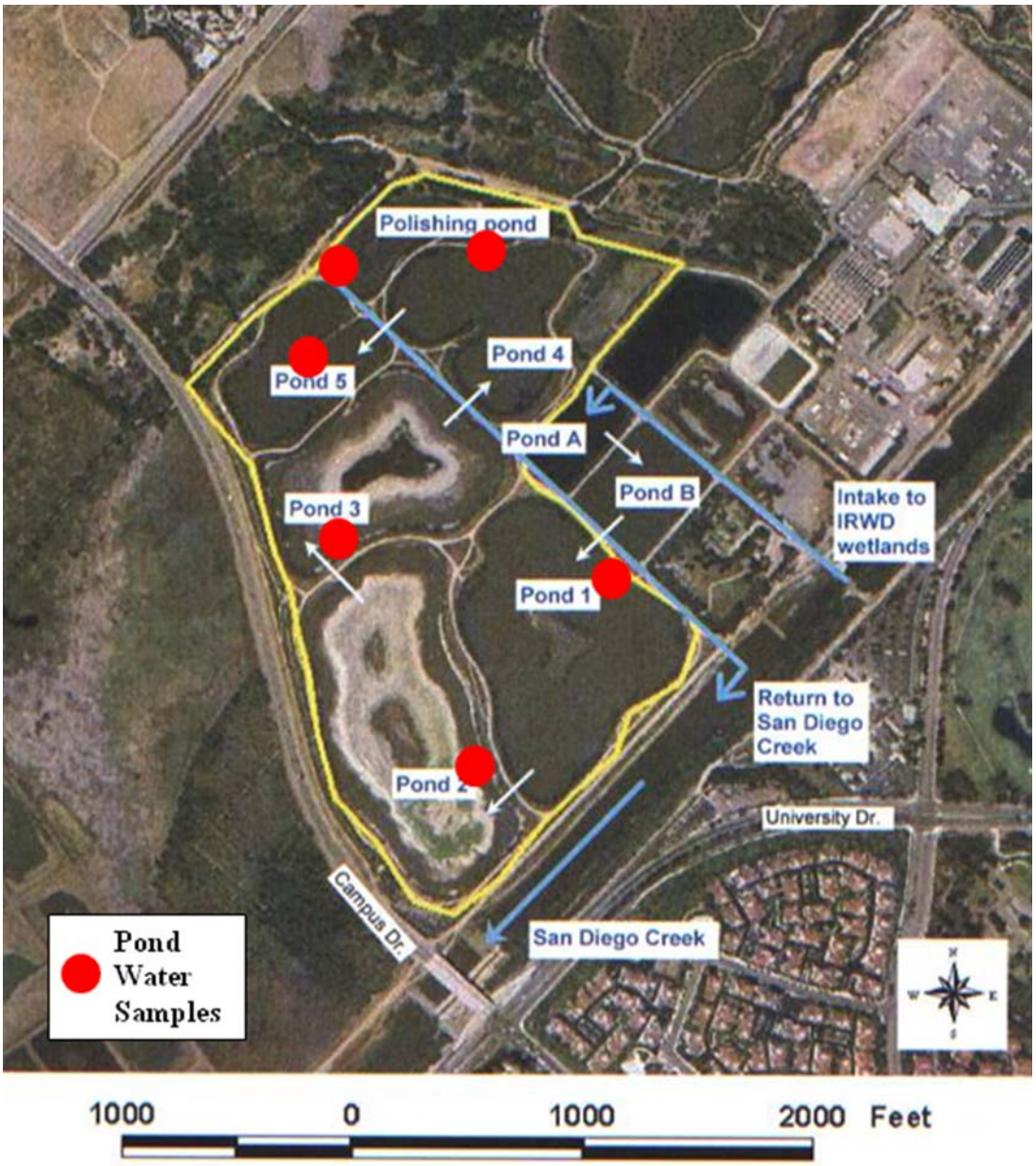

Figure 4.3. Aerial View of the IRWD San Joaquin Marsh, showing locations of water sampling sites at interior marsh ponds (modified from GeoSyntec, 2003).

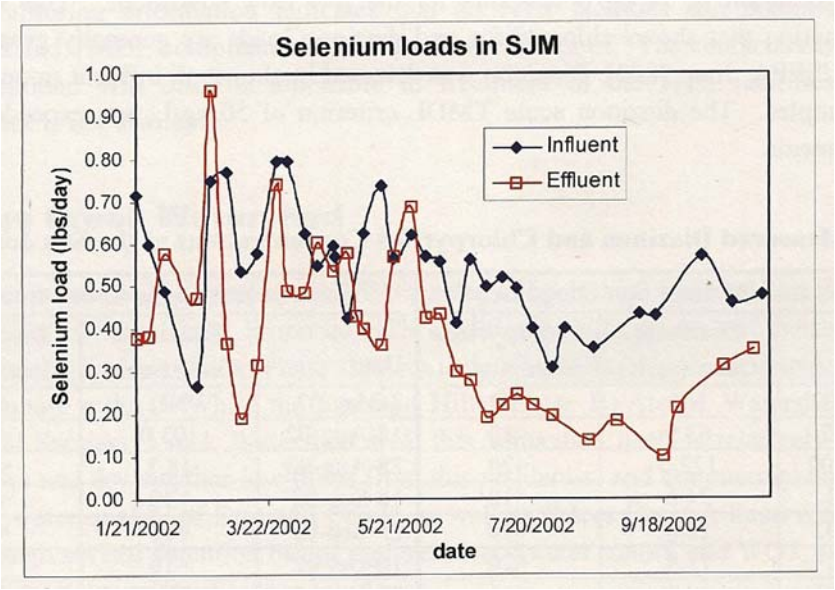

Figure 4.4. Selenium loads at the WQT Wetlands at the San Joaquin Marsh (from GeoSyntec, 2003).

METHODS

Field Sampling Methods

A variety of methods were used to collect samples from the diverse number of sites at the IRWD San Joaquin Marsh. These included marsh water and shallow groundwater samples and sediment samples collected from the marsh bottom. In general, water samples were collected at the marsh inlet and outlet, and from marsh Ponds 1, 2, 3, 4, and 5, plus the marsh Polishing Pond. Sediment samples were collected from most of these same locations.

Most field water samples were collected via pole-extended grab samplers in LDPE bottles. Sample bottles were soaked and triple rinsed in deionized water and inspected prior to field usage. Additionally all bottles were triple rinsed with the water being sampled in the field prior to filling. Aquatic and groundwater sampling sites included field-filtered and unfiltered samples. Filtered samples were obtained using 0.45 micrometer filters. Samples were stored on ice until returned to the lab. Sample preservation with acid was done in the field for those samples requiring it. All sites had conductivity, temperature, dissolved oxygen, and pH measured in the field using portable meters (YSI meters). Meters were calibrated according to manufacturer's guidelines.

Homogenization of samples was done with 1 gallon containers when water was collected from marsh ponds and marsh inlet and outlet. A one gallon container was filled, mixed, and used to breakout aliquots for the various sample matrices (different containers to different labs, or different containers for different preservation methods). Homogenization of groundwater was done when duplicates were taken but not during most other times. When groundwater was sampled from marsh observation wells,

samples were collected at the wellhead as quickly as containers could be reliably filled with groundwater. Filtering was done when necessary to satisfy matrix requirements (see Chapter 1 – Introduction and Methodology).

Surface water samples were taken several inches below the surface of the pond when depth of water was less than 1 foot. This was not the normal case for most conditions in the marsh. A bottle was inverted and then re-inverted to allow the container to fill up. When depth was greater than one foot, a pole-extended water sampler, which was extended by as much as 25 feet from the side of a pond out into the pond, was submerged at various depths to fill half-liter aliquots which were then used to fill up a one gallon homogenization container. An effort was made to do these as depth-integrated samples.

Monitoring well sampling was done with battery operated "whaler pumps." The pumps and pump tubing were rinsed first with a deionized water/phosphate-free laboratory detergent mixture and afterwards with a pure deionized water solution before they were used. This was done in the field between sampling events, and after returning from the field. Carboys filled with these solutions were used in the field to perform rinses.

Before sampling groundwater from monitoring wells, the wells were purged and stabilized. Well purging means the removal of a sufficient volume of groundwater in the well casing so that a representative water sample from the aquifer can be collected. When the well was pumped, it was necessary to set up a purge pump to extract stagnant water from the well bore. This was accomplished by setting up portable equipment and taking temperature, specific conductance, and pH readings at two minute intervals.

When the measurements stabilized, the wells were sampled. Checks for stabilization of index parameters was done after wells had been pumped long enough to purge at least three casing volumes of water from the well bore. After wells were pumped, samples were collected and preserved in accordance with methods described above for groundwater.

Sediment samples were collected using stainless steel hand augers, stainless steel shovels, and stainless steel spades. Auger samples were collected in properly identified (depth and location information) and wrapped plastic bags. The sediment sampling devices were cleaned first with a deionized water/phosphate-free laboratory detergent mixture and afterwards with a pure deionized water solution before the samplers were reused. This was done in the field between sampling events, and after returning from the field. Based on sample matrices, there were no byproducts of cleaning of sediment sampling apparatus that require special disposal procedures.

Laboratory Methods

Anion analysis was conducted by ion chromatography in the Hydrogeology Laboratory at California State University-Los Angeles. Analysis of total dissolved selenium and selenium speciation was conducted by hydride generation atomic absorption (HG-AA) following the method described by Zhang and others (1999) at the University of California-Riverside. Isotope ratios for common elements (H, O, and S) were analyzed by gas source ion ratio mass spectrometry (IRMS) at the Isotope Geochemistry Laboratory at the University of Arizona. Stable isotopes are reported in

"delta" notation as a per mille deviation from the accepted reference standard. Table 1.1 shows the standards and delta notation used in this study.

Table 4.1 Standards and Delta Notation Used for Stable Isotopes

Element	Notation	Standard
Hydrogen	δD or δ^2H	VSMOW (Vienna Standard Mean Ocean Water)
Oxygen	$\delta^{18}O$	VSMOW
Sulfur	$\delta^{34}S$	CDT (Canyon Diablo Troilite)

RESULTS

Preface

The original study plan required one year of water quality monitoring at the inlet and outlet of IRWD San Joaquin Marsh. Other contracted analysis included selenium speciation testing of marsh waters and sediments. Two major events did not allow us to complete one year of continuous monitoring of the marsh: (1) shut down of marsh flows from October 2004 to April, 2005, because of removal of sediments from in-channel sediment basin 3; and, (2) shut down of marsh flows from October 2005 to December 2005 due to pump failure. The study extended over a 19 month period, with about 15 months of cumulative monitoring.

Inflow and outflow data were collected during the 19 month monitoring period at IRWD San Joaquin Marsh (Figure 4.5). Selenium data were collected at the inlet and outlet of the marsh when flows were available to be sampled (Figure 4.6). Daily inlet flows, when available, usually varied from about 2.75 to 5.25 million gallons per day, while return flows from the marsh to San Diego Creek were typically slightly lower and much more variable (Figure 4.5).

During the entire study approximately 20 to 35% of the selenium in the inlet was removed as it traveled through San Joaquin Marsh to the marsh outlet (Figure 4.6). Moderate decrease in selenium between the inlet and the outlet indicates that selenium is being sequestered or lost somewhere in the marsh. This pattern was relatively stable throughout the monitoring period (Figure 4.6).

Variations in flow conditions in San Joaquin Marsh during the 19 month period provided logical breaks when different monitoring programs could be carried out. The remaining sections of this chapter correspond to time periods when marsh flows were either cycling into and out of San Diego Creek, or when they were not. Other sections of this chapter cover specialized surveys, such as the results of groundwater sampling beneath IRWD San Joaquin Marsh. The remaining sections of this chapter include:

1. **June 2004 to October 2004, Continuous Inlet-Outlet Flows**
2. **October 2004 to April 2005, Marsh Shutdown Period and Miscellaneous Monitoring**
3. **Additional Groundwater Studies**
4. **April 2005 to September 2005, Nearly Continuous Inlet-Outlet Flows**
5. **Recycling Flow Period, October 2005 to Study Completion**
6. **Selenium Analysis of Marsh Sediments**

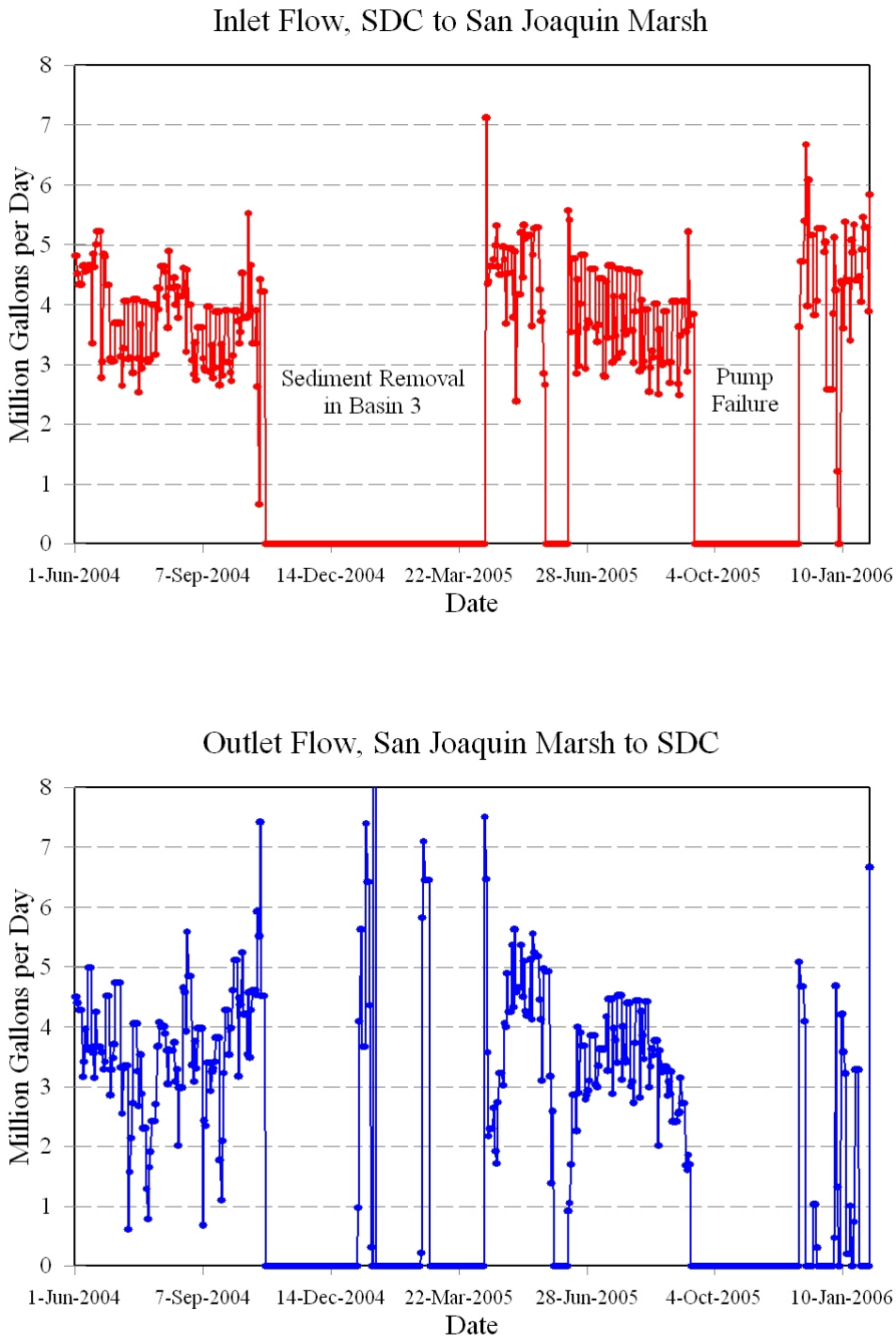

Figure 4.5. Inlet and outlet flows between San Diego Creek and IRWD San Joaquin Marsh, covering the monitoring interval in this study of IRWD San Joaquin Marsh (data provided courtesy of IRWD).

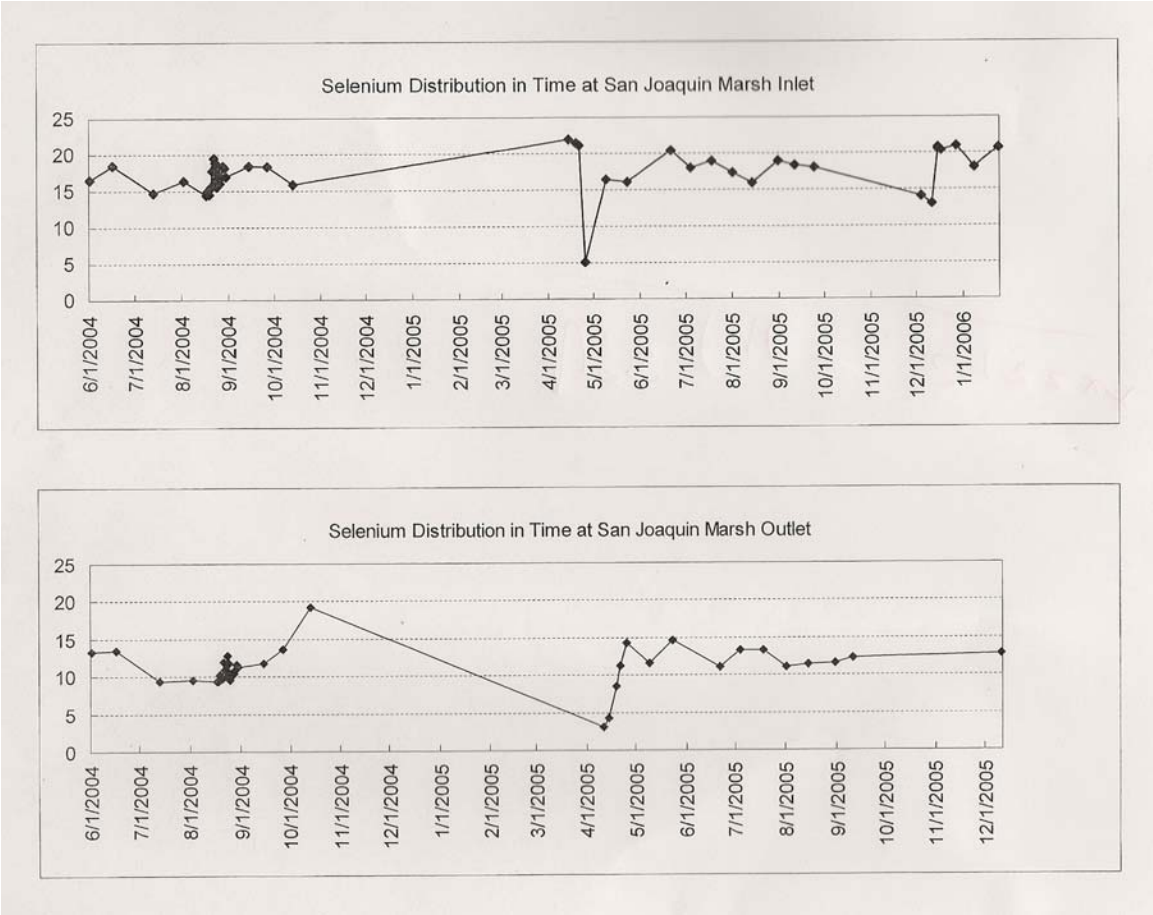

Figure 4.6. Selenium in IRWD San Joaquin Marsh inlet and outlet, covering the monitoring intervals when flows were available to be sampled at the inlet and outlet.

1. June 2004 to October 2004, Continuous Inlet-Outlet Flows

Monitoring during this time period began in early June 2004 and continued until late October 2004. In late October 2004, the Irvine Ranch Water District discontinued inflow/outflow in the IRWD San Joaquin Marsh due to a sediment removal project from the sediment basins adjacent to the marsh. Therefore, monitoring of the inlet and outlet stopped temporarily.

Monitoring of the inlet and outlet from mid-June 2004 to late October 2004 included a series of daily measurements at the inlet and outlet for two weeks (Aug 17 – Aug 30, 2004), and a diurnal measurement cycle in late August when samples were collected every two hours for 24 hours (Figure 4.3). Measurements at the site included temperature, pH, specific conductance, and dissolved oxygen. Laboratory analysis by the contract UC-Riverside Laboratory, which ended December 1, 2004 due to departure of co-principal investigator Tom Meixner, included total and dissolved selenium, dissolved arsenic, nitrate, and orthophosphate. Most of the data collected through December 2004 was analyzed and reported by the UC-Riverside contracting laboratory. However, a small number of arsenic measurements were not provided. Since arsenic analysis was not required in the contract with SWRCB, the omission is primarily a scientific issue and not a contract issue.

Approximately 20 to 35% of the selenium in the inlet is removed as it travels through the marsh and is not appearing at the outlet (Figures 4.7 and 4.9). Moderate decrease in selenium between the inlet and the outlet indicates that selenium is being sequestered or lost somewhere in the marsh. This pattern was relatively stable throughout the monitoring period.

Arsenic shows a small net change as it moves through the marsh and in fact at times the marsh appears to be a slight source of arsenic to the water column (Figures 4.8 and 4.10). Nearly all of the inlet and outlet differences are within the analytical uncertainty level which is plus or minus 1 ug/L. With respect to this data set, it does not appear that arsenic loss or mobilization is of much concern as regards the operation and management of the IRWD San Joaquin Marsh.

Slight jump in arsenic concentration of about 2 to 3 ug/L at the inlet and outlet during late August 2004 is interesting, but the cause of the jump is unknown (Figure 4.8 and Figure 4.10). Data showing a fairly rapid and simultaneous jump in arsenic concentrations at both the inlet and outlet in late August may be suspect, as the marsh residence period for water to move from inlet to outlet is reported to be 10 to 14 days. We are unsure what environmental factor could cause arsenic concentrations to jump simultaneously at the inlet and outlet of the marsh. Residence times in the marsh are calculated based on total inflow/outflow rates versus total water storage in the marsh, which can be an oversimplification. Stagnant waters can stand quietly on the margins of pools while internal waters recalculate more efficiently in the pools.

Selenium data collected daily at the inlet and outlet of the marsh for two weeks shows an oscillatory pattern that repeats itself every 7 days (Figure 4.9). The two peaks occur on Sunday August 22 and Sunday August 29 2004. It is likely that the absence of nursery flows and smaller amounts of urban runoff during the weekend allowed selenium-laden baseflows from groundwater to become a more important component of the flows in San Diego Creek. A greater *relative* percentage of baseflow probably causes the oscillatory pattern and selenium peaks on two successive Sundays (Figure 4.9).

Twenty-four hour monitoring of selenium and arsenic did not show any diurnal pattern of note, other than a gradual and very small decrease in the concentration of selenium and arsenic (Figures 4.11 and 4.12). This is probably due to upstream factors and not due to any change in selenium or arsenic redox conditions during the early morning hours.

Finally, total and dissolved selenium concentrations are approximately equal at the marsh inlet and at the marsh outlet (Figures 4.13 and 4.14). Due to the prevalence of groundwater baseflows as the source of most of the selenium in San Diego Creek Watershed, and tendency for selenium to exist mostly in soluble forms in groundwater, it was already expected that selenium at the inlet would be mostly dissolved selenium. We were initially unsure how much of the selenium would be in particulate form at the marsh outlet. Our results suggest that most of the selenium at the marsh outlet is dissolved selenium.

Insofar as it is impossible for total selenium to be present in lower concentrations than dissolved selenium, the few instances where total selenium is slightly lower than dissolved selenium indicates some form of analytical laboratory error or sample interference (Figure 4.13 and 4.14). This inaccuracy may be due to an unidentified organic agent in the unfiltered marsh water that interferes with selenium analyses.

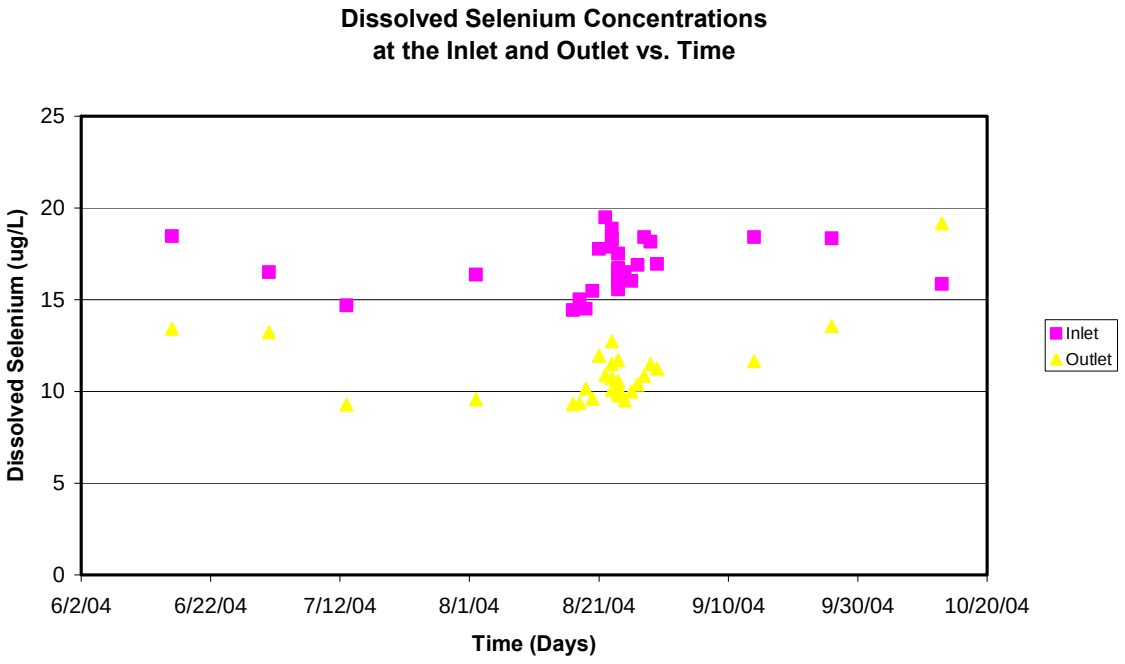

Figure 4.7. Results of dissolved selenium sampling at IRWD San Joaquin Marsh inlet and outlet, June 2004 to October 2004.

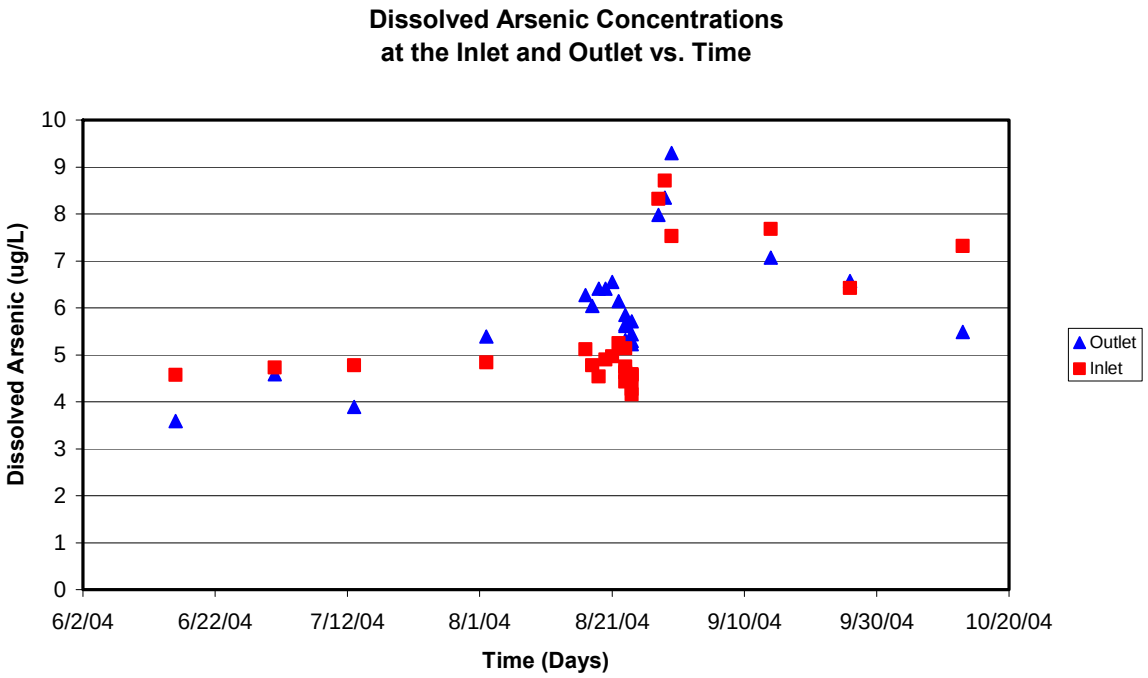

Figure 4.8. Results of dissolved arsenic sampling at IRWD San Joaquin Marsh inlet and outlet, June 2004 to October 2004.

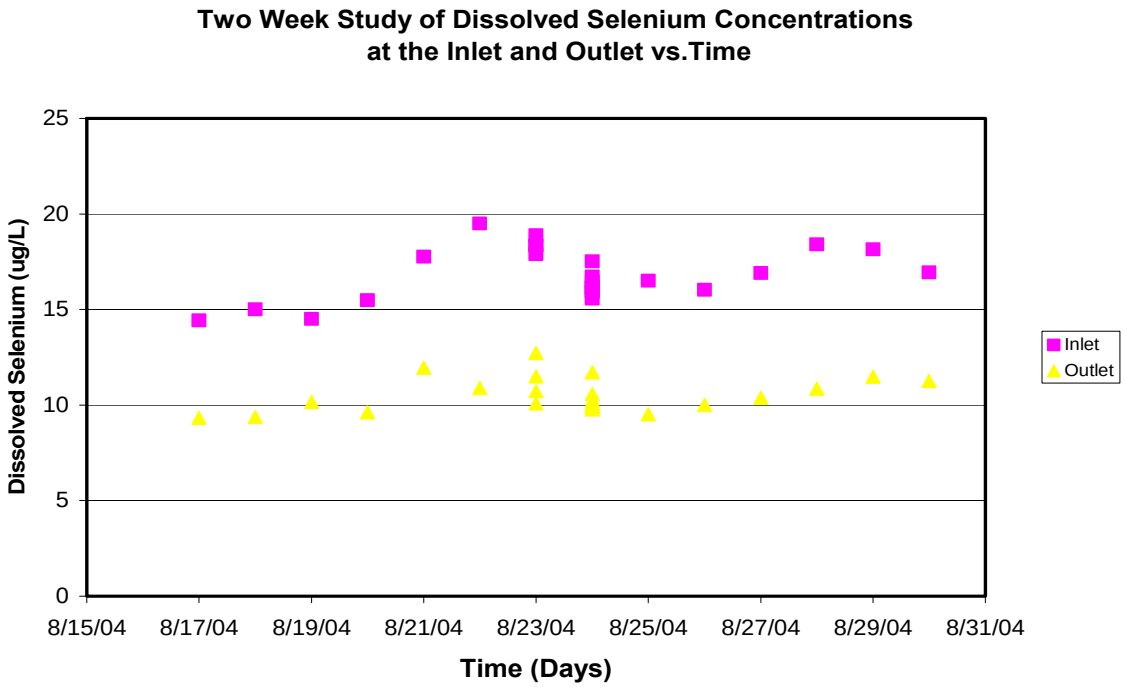

Figure 4.9. Results of daily dissolved selenium sampling at IRWD San Joaquin Marsh inlet and outlet, August 17 2004 to August 30 2004.

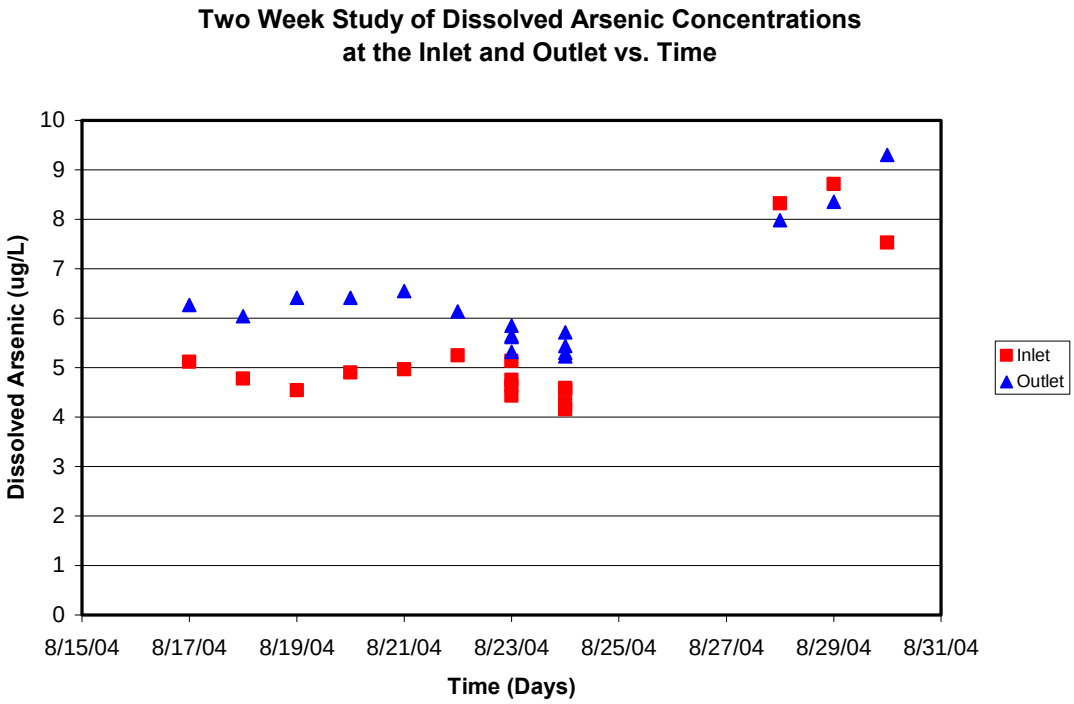

Figure 4.10. Results of daily dissolved arsenic sampling at IRWD San Joaquin Marsh inlet and outlet, August 17 2004 to August 30 2004.

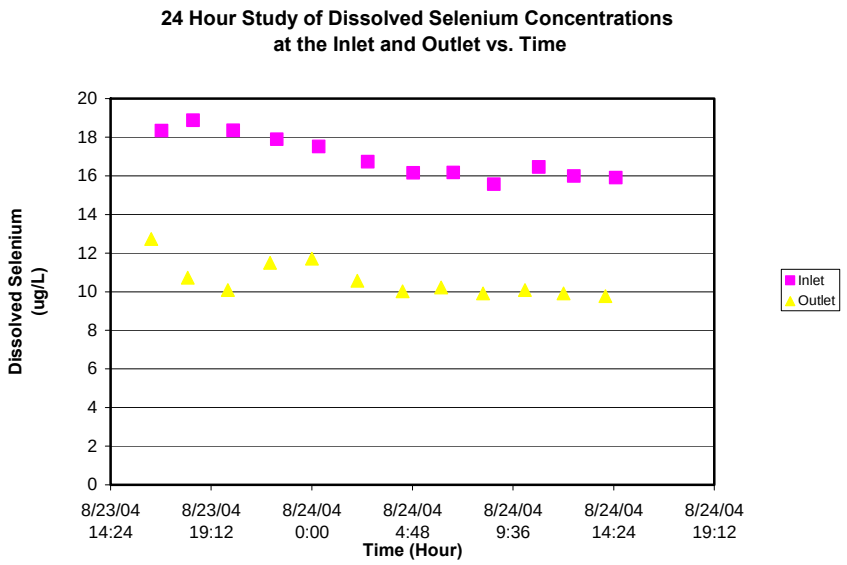

Figure 4.11. Results of 24 hour dissolved selenium sampling at IRWD San Joaquin Marsh inlet and outlet, August 23 2004 to August 24 2004.

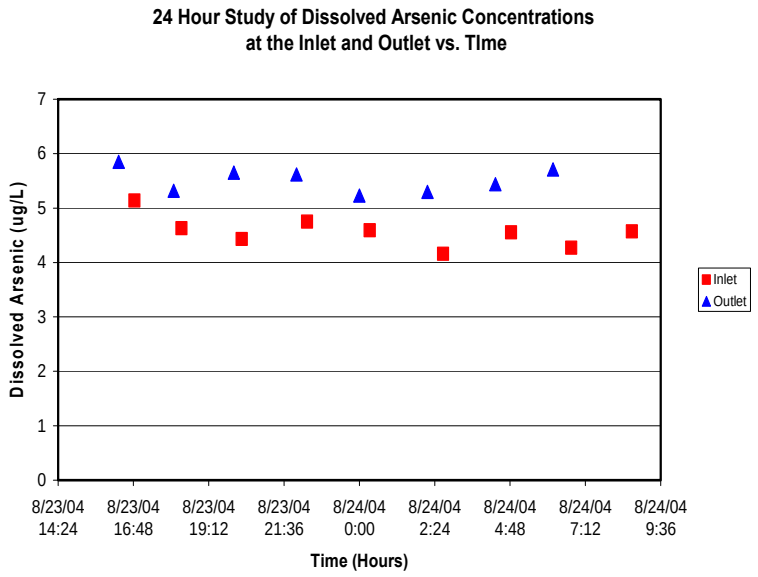

Figure 4.12. Results of 24 hour dissolved arsenic sampling at IRWD San Joaquin Marsh inlet and outlet, August 23 2004 to August 24 2004.

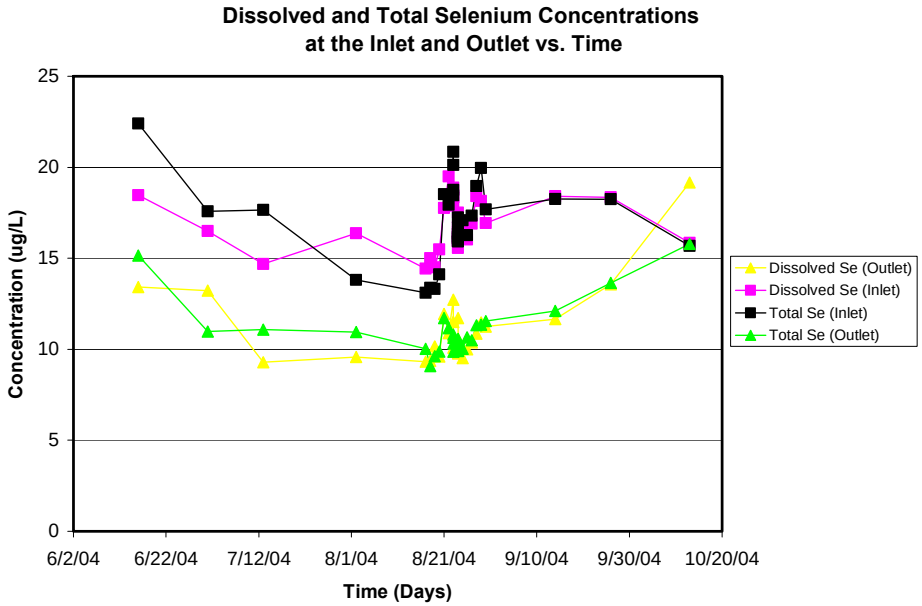

Figure 4.13. Comparison of total and dissolved selenium concentrations at IRWD San Joaquin Marsh inlet and outlet, for samples collected June 2004 to October 2004.

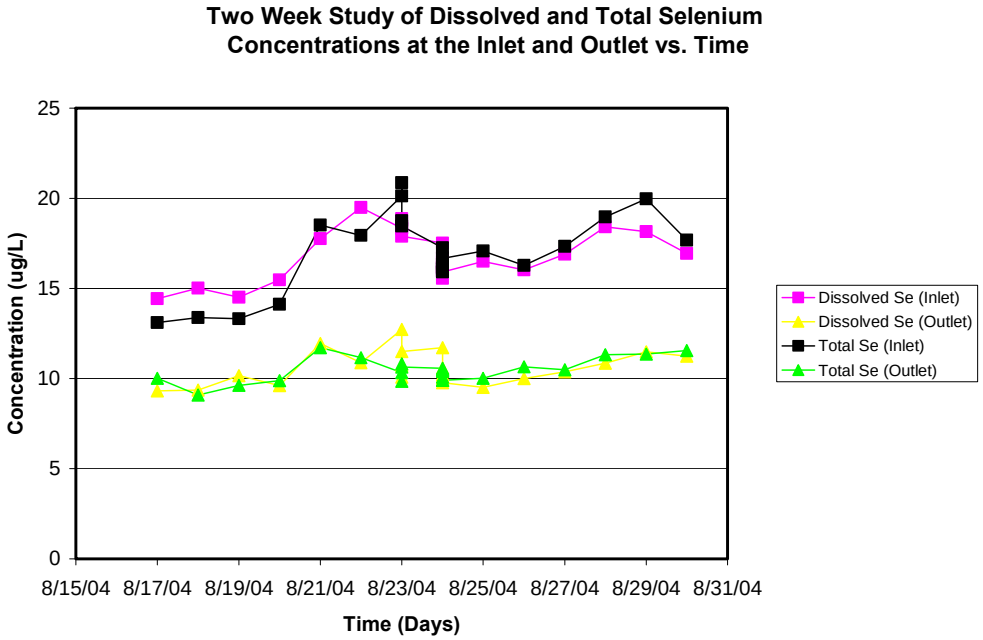

Figure 4.14. Comparison of total and dissolved selenium concentrations at IRWD San Joaquin Marsh inlet and outlet, for samples collected August 17 2004 to August 30 2004.

2. October 2004 to April 2005, Marsh Shutdown Period and Miscellaneous Monitoring

When the Irvine Ranch Water District discontinued inflow/outflow in the San Joaquin Marsh in October 2004, no monitoring of inlet and outlet flows was possible. Accordingly, we used this opportunity to sample water wells and surface water ponds within the interior of the marsh (Figure 4.15).

In the first stage of this sub-investigation, we collected surface water and groundwater data within IRWD San Joaquin Marsh in late December, 2004 (Figures 4.3 and 4.15). At that time, the specific conductance of surface water in the marsh was only about 1900 uS/cm. This was down from 2800 uS/cm in late October when the marsh stopped cycling water in and out of San Diego Creek. Dilution of water in the marsh occurred due to inflows from urban runoff during heavy storms in November, 2004. By calculating dilution with specific conductance values, combined with the assumption of relatively small amounts of evapotranspiration losses since October 2004 (e.g., less than 5% ET loss), the dilution of pond water by urban runoff was about 40%.

When pond water was sampled in December 2004 (Figure 4.3), the total dissolved selenium concentration was only 3.5 to 4 ug/L Se (Table 4.2). This is lower than the normal 12 to 15 ug/L selenium concentration at the marsh outlet by a factor of about 3 (see Figures 4.6 and 4.7). With only 40% dilution by urban runoff, the low selenium concentration in December 2004 implies that a large fraction of selenium was lost from the water column in the marsh when the marsh was not cycling water from San Diego Creek.

One of the ways for selenium to be lost in the marsh is by sorption on marsh organic-sediments due to reducing conditions. Marsh waters were already predominantly

selenium-IV (selenite) in December 2004 (Table 4.2). Selenium-IV has a tendency to sorb onto bottom sediments in marshes (Zhang and Moore, 1997a, 1997b, 1997c). Also, some of the selenium in the marsh was apparently transformed into organic selenium forms via biogeochemical cycling and/or algal uptake, as shown by the presence of organic selenium in the pond (Table 4.2). Finally, some of the selenium is probably lost to the atmosphere by conversion of selenium into dimethyl selenide gas (Figures 4.16 and 4.17).

Prior to this study, it was unknown if surface water percolates downward into groundwater beneath the marsh. San Diego Creek is at a lower elevation than the water level in IRWD San Joaquin Marsh, which could create a condition of seepage of marsh water downward into groundwater ("losing marsh" condition). If marsh water is recharging groundwater beneath the marsh, some selenium is probably lost in the interstitial sediments beneath the marsh. Lower concentrations of selenium in groundwater, most of it being selenium-IV, suggest that selenium is reduced and lost in interstitial sediments by sorption, precipitation, and/or biological uptake (Table 4.2).

Stable isotopes of oxygen and hydrogen confirm that the marsh is replenishing the aquifer beneath the marsh (Figure 4.18 and Table 4.3). Water collected at the inlet of the marsh during Summer 2004 falls right on the shallow aquifer evaporation line determined by Hibbs and others (2008) (Figure 4.18). This is expected because dry weather flows in San Diego Creek are sourced mostly from groundwater baseflows from upstream areas. Water flowing from the outlet of IRWD Marsh is even more evaporated because of a 11-to-14 day residence time of surface water in the marsh. The outlet samples are shifted slightly above the groundwater evaporation line. This slight shift above the evaporation

line may be due to plant fractionation processes in the wetland that modifies isotopic evaporation trends. Isotopic data trace surface flows into groundwater during the main re-circulating period, which occurs during most of a normal year. Percolation of marsh water downward into groundwater is probably not a very fast process, so the bulk isotopic signature of the groundwater determined during this sampling event probably represents a composite isotopic signature of the water in the marsh ponds over a period of time, perhaps well over a year.

Monitoring Well 1 is located near the inlet pond closest to San Diego Creek (Figure 4.15). This well produces water that is isotopically similar to inlet flows (Figure 4.18). Monitoring Well 9 is located closer to the outlet pond at IRWD San Joaquin Marsh. Well 9 produces water that is evaporated and isotopically similar to water flowing from the outlet of the marsh (Figures 4.15 and 4.18). This is exactly the relationship that is expected if the ponds recharge the shallow aquifer beneath the wetland. Keep in mind that groundwater beneath the marsh probably represents a long term composite isotopic signature of the water in the marsh ponds.

These data seem to confirm a source of recharge from the ponds to the shallow aquifer beneath the marsh wetlands. Flow relationships between surface water and groundwater could indicate selenium immobilization in the wetland sediments, because surface water moves down through organic rich and suboxic/anoxic sediments at the bottom of the ponds. In reducing sediments, selenium precipitation and sorption is likely to occur (Zhang and Moore, 1997a, 1997b, 1997c).

Other data collected within the marsh during its inactive period indicated that selenium was relatively low in water wells and surface ponds (Tables 4.4 and 4.5). An

exception was the February 7 sampling period when selenium reached a concentration of 12.5 ug/L in Well 9 (Figure 4.15 and Table 4.4). We do not know why selenium was much lower in Well 9 on March 9, 2005 (compare Tables 4.4 and 4.5). It is possible that selenium was diluted by percolating storm runoff waters that partly filled the marsh after cycling of water from San Diego Creek was temporarily stopped.

Arsenic concentrations are moderately low to very low, except in Well 1 where a large amount of arsenic (~43 ug/L) was detected when samples were collected in February and March 2005 (Tables 4.4 and 4.5). Intermediate redox conditions in the aquifer near this well may account for the large amount of arsenic detected in Well 1. Intermediate redox conditions in the aquifer would predictably decrease selenium concentrations in shallow groundwater beneath the marsh.

Table 4.2: Selenium Speciation Data in San Joaquin Marsh Area, Collected December 20, 2004*

Sample ID	Se VI (ug/L)	Se IV (ug/L)	Organic Se	Total Dissolved Se (ug/L)
San Joaquin Marsh Polishing Pond	0.48	2.77	0.69	3.94
San Joaquin Marsh Pond 1	0.50	2.14	0.85	3.49
San Joaquin Marsh Well 1	0.085	1.75	<0.2	1.84
San Joaquin Marsh Well 9	0.18	0.85	<0.2	1.03

*Ponds are surface water and wells are groundwater

Table 4.3: Isotope Data for the San Joaquin Marsh Area*

Sample ID	Date	$\delta^{18}O$ ‰	δD ‰
Inlet	6/16/04	-5.6	-45
Outlet	6/16/04	-4.2	-37
Inlet	7/1/04	-5.7	-45
Outlet	7/1/04	-4.1	-37
Well 1	12/20/04	-5.8	-44
Well 9	12/20/04	-4.6	-39
Well 1	2/7/05	-5.6	-47
Well 9	2/7/05	-4.6	-39

*Inlet and outlet are surface water and wells are groundwater

Table 4.4: Selenium and Arsenic Data in San Joaquin Marsh, Collected February 7, 2005*

Sample ID	Total Dissolved Se (ug/L)	Total Dissolved As (ug/L)
San Joaquin Marsh Polishing Pond	3.1	1.8
San Joaquin Marsh Pond 1	3.3	1.8
San Joaquin Marsh Well 1	2.3	42.9
San Joaquin Marsh Well 9	12.5	5.6

*Ponds are surface water and wells are groundwater

Table 4.5: Selenium and Arsenic Data in San Joaquin Marsh, Collected March 9, 2005*

Sample ID	Total Dissolved Se (ug/L)	Total Dissolved As (ug/L)
San Joaquin Marsh Polishing Pond	3.3	2.2
San Joaquin Marsh Pond 1	3.3	2.5
San Joaquin Marsh Well 1	1.9	42.5
San Joaquin Marsh Well 9	3.3	9.4

*Ponds are surface water and wells are groundwater

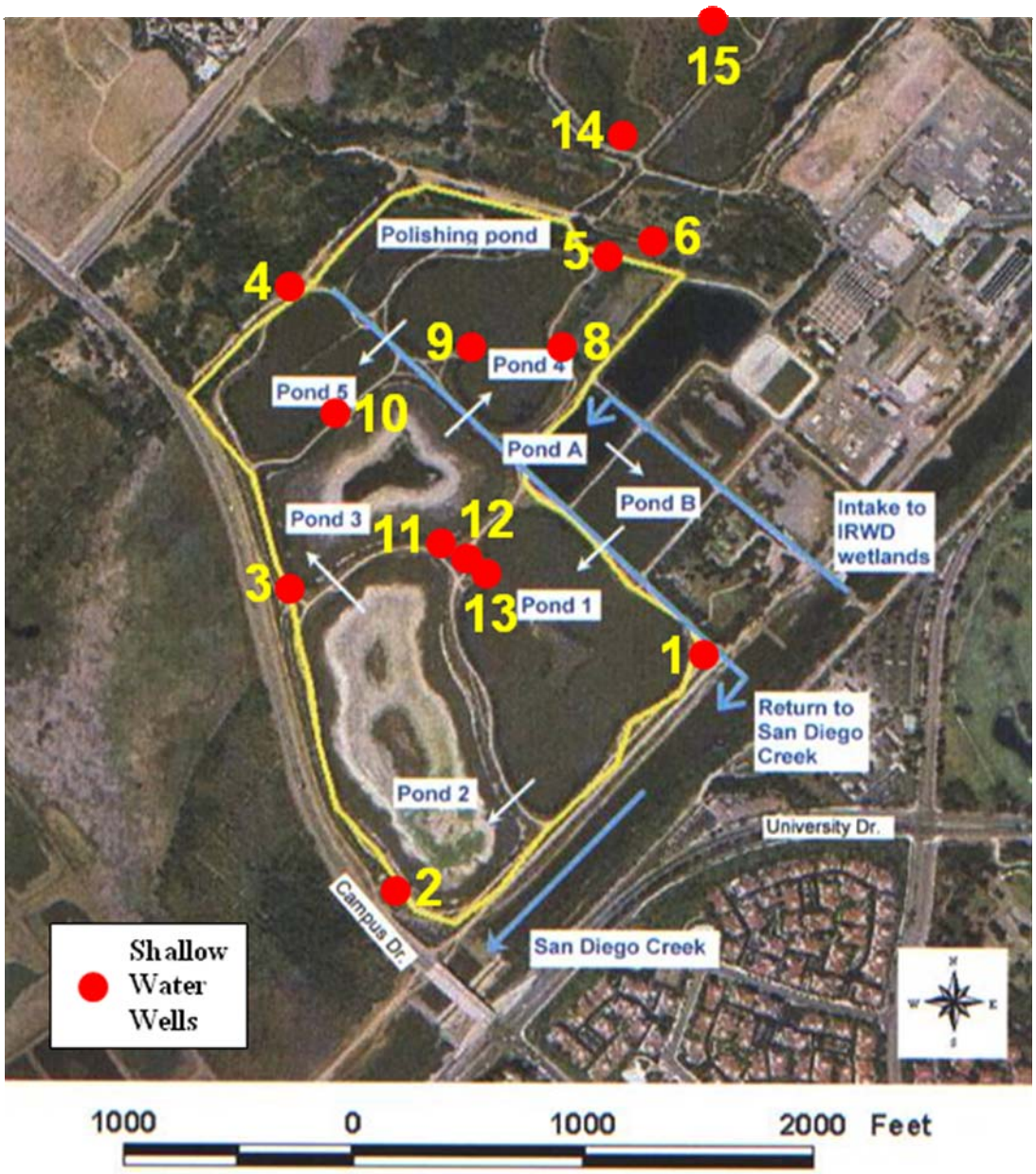

Figure 4.15. IRWD San Joaquin Marsh diagram showing locations of shallow groundwater monitoring wells.

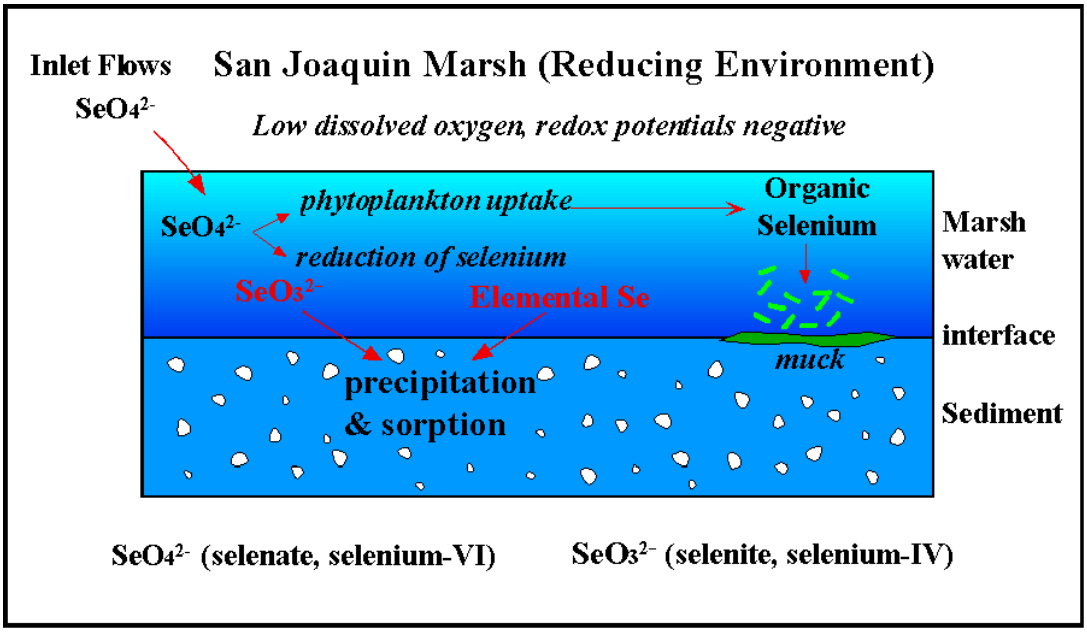

Figure 4.16. Selenium entering the IRWD San Joaquin Marsh is mostly selenate (selenium-VI). Selenate is very soluble and tends to exist in the dissolved phase. Once selenate enters the marsh, it encounters reducing conditions at the marsh/sediment interface and in the bottom waters of the marsh. This might lead to reduction of selenium to form selenite (selenium-IV) and elemental selenium, which are lost from the water column by sorption and precipitation onto bed sediments. Another portion of the selenium in solution may cycle biochemically into phytoplankton, algae, and other plants. Organic detritus containing organic selenium may then settle onto the top of streambed sediments as organic muck. There the organic selenium may become bioavailable to life forms.

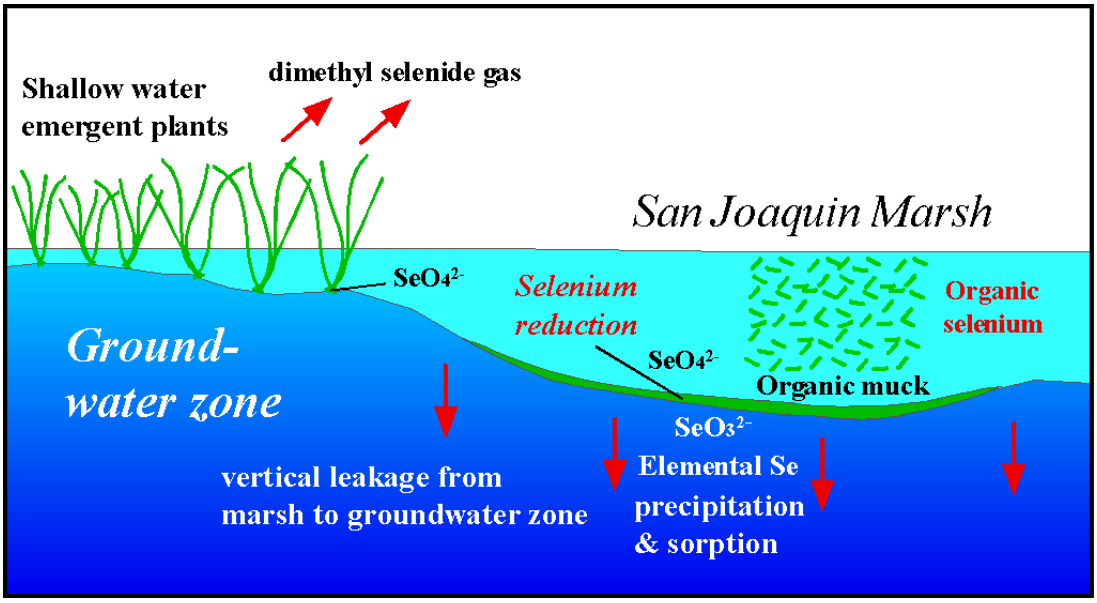

Figure 4.17. Conceptual diagram showing loss of selenium by plant uptake along with a possible relationship between marsh water and groundwater beneath IRWD San Joaquin Marsh. Leakage of marsh water into the groundwater zone beneath the marsh may result in accumulation of selenium at the marsh/ground water interface in anoxic sediments and organic muck. Reducing conditions at the sediment/water interface may cause selenium speciation and loss of selenium due to reduction of Se to lower solubility forms. Another possible loss mechanism is by uptake of selenium by plants and emission into the atmosphere as selenium gas.

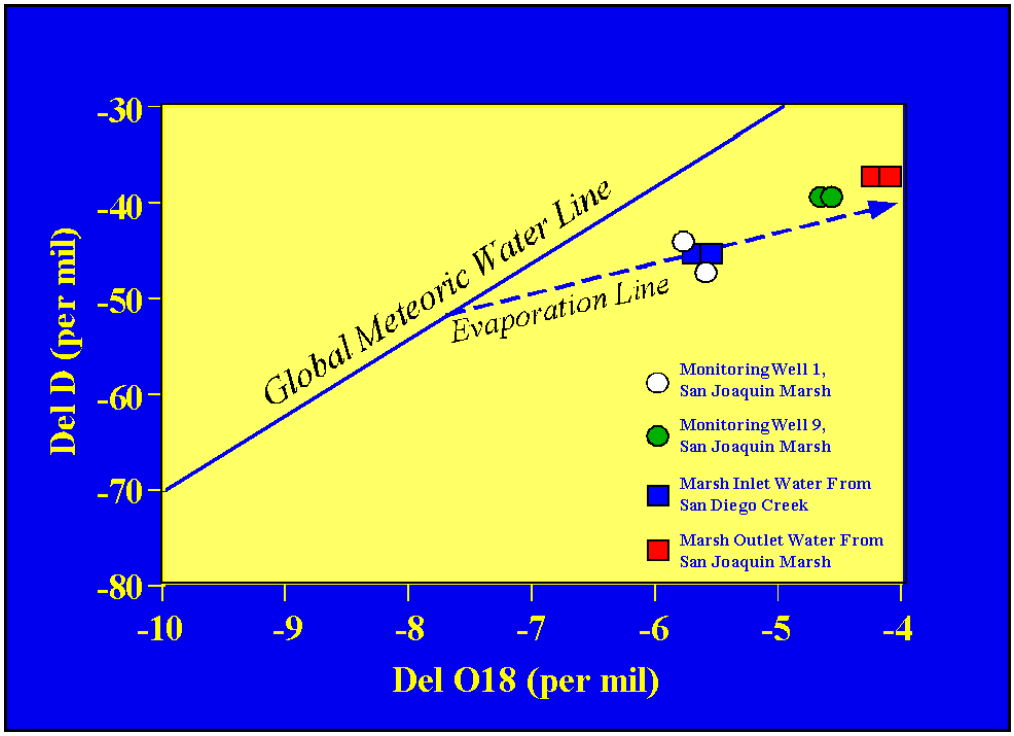

Figure 4.18. Stable isotope data for IRWD San Joaquin Marsh inlet and outlet, and for select monitoring wells in the marsh (see Figure 4.15 for well locations).

3. Additional Groundwater Studies

The last section showed that marsh water percolates downward into groundwater beneath the marsh. A flux of selenium-laden water moving through the organic-rich marsh sediments into groundwater beneath the marsh could lead to selenium reduction in marsh bottom-sediments (Figures 4.16 and 4.17). This would lead to a net accumulation of selenium in the marsh sediments. Therefore, 14 shallow groundwater monitoring wells were sampled in IRWD San Joaquin Marsh in July 2005 to expand upon the analysis done in the last section (Figure 4.15). Flows had been ongoing for several months when additional groundwater sampling was done in July 2005.

Groundwater samples were tested for selenium species and stable isotopes of oxygen and hydrogen (Table 4.6 and Figure 4.19). Groundwater data indicate that wells contain very little selenium, and that species are reduced, with most wells containing selenium-IV as the dominant selenium species (Table 4.6). Depending on the rate of seepage to groundwater beneath the marsh, this could indicate minimal-to-substantial accumulation of selenium in marsh bottom-sediments, as shown in Figures 4.16 and 4.17. The role of plant uptake and selenium removal as a gas is another factor that could contribute to selenium removal, and neither process has been quantified.

An expanded suite of stable isotopes of oxygen and hydrogen in water from the June 2005 period indicates that shallow groundwater beneath IRWD Marsh is recharged over a large area by percolation at the marsh ponds (Figure 4.19). The mixing region for groundwater defined by bounding marsh inlet and outlet stable isotopes confirms recharge from the ponds. Groundwater samples show no isotopic relationship to marsh water where wells are not located in the vicinity of marsh ponds (Figure 4.19).

In summary, where groundwater is recharged by marsh water, selenium is partially lost from percolating pond water by reduction at the organic rich sediment/water interface (Figures 4.16 and 4.17). This model explains why groundwater selenium concentrations are so low (Table 4.6). Selenium could also be converted into organic particulate forms. Loss by plant uptake and conversion into dimethyl selenide gas is another possible loss mechanism.

Table 4.6: Selenium Speciation Results from San Joaquin Marsh Monitoring Wells

Well ID	Se VI (ug/L)	Se IV (ug/L)	Organic Se (ug/L)	Total Dissolved Se (ug/L)
Well 1	0.27	0.86	<0.2	1.13
Well 2	0.67	1.48	<0.2	2.16
Well 3	0.12	0.26	<0.2	0.38
Well 4	0.45	0.12	<0.2	0.57
Well 5	0.28	0.09	<0.2	0.37
Well 6	0.33	0.18	<0.2	0.51
Well 8	0.01	0.52	<0.2	0.53
Well 9	0.30	0.28	<0.2	0.58
Well 10	0.59	0.93	<0.2	1.52
Well 11	0.69	0.39	<0.2	1.08
Well 12	0.73	1.41	<0.2	2.14
Well 13	1.68	5.95	<0.2	7.63
Well 14	0.19	0.09	<0.2	0.28
Well 15	0.61	0.40	<0.2	1.01

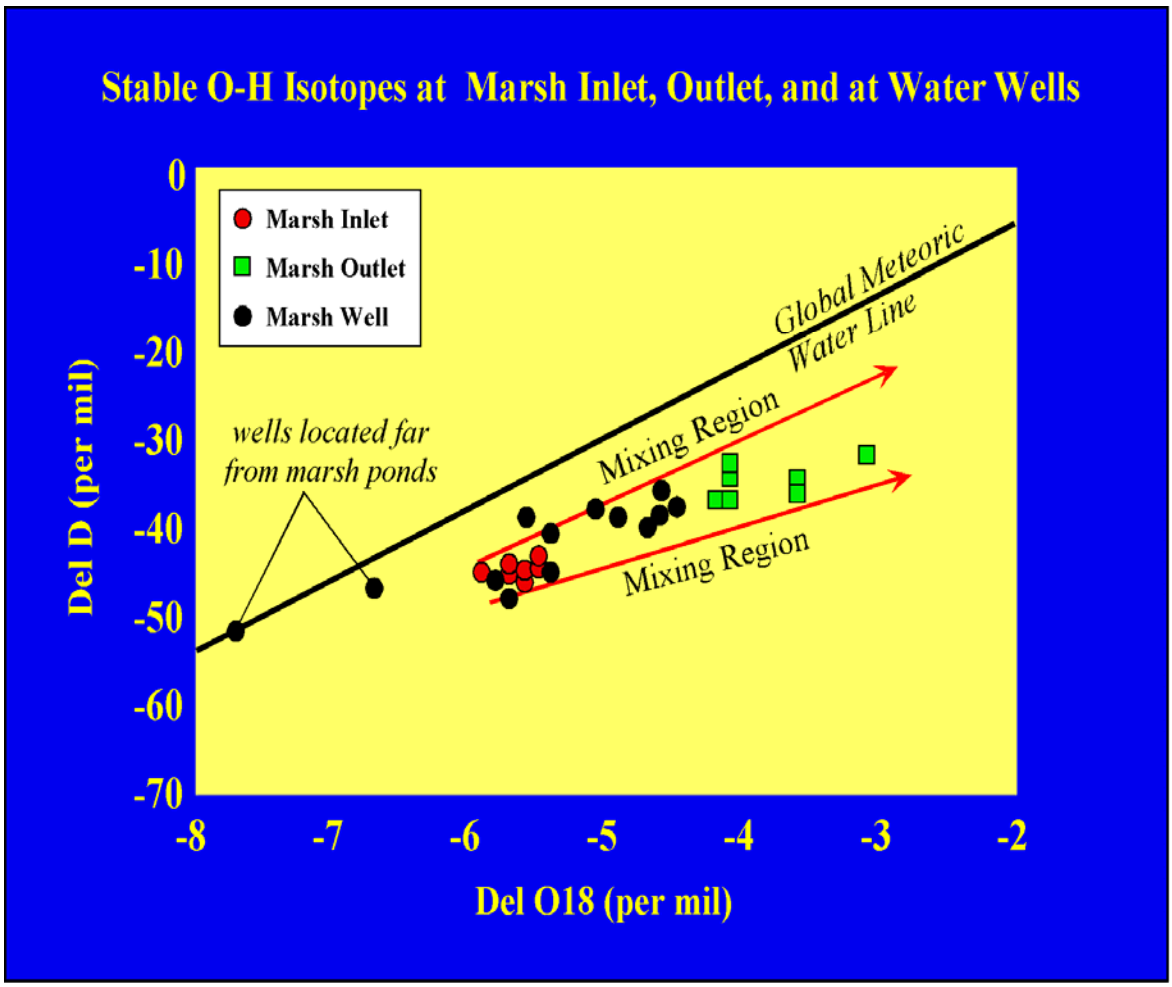

Figure 4.19. Stable isotopes of oxygen and hydrogen indicate that shallow groundwater beneath IRWD San Joaquin Marsh is recharged by percolation at the marsh ponds. The mixing region for groundwater defined by bounding marsh inlet and outlet stable isotopes confirms recharge from the ponds. When groundwater is recharged by pond water, selenium is probably lost by reduction at the organic rich sediment/water interface. The model explains why groundwater selenium concentrations are so low (Table 4.6). Selenium could also be converted into particulate forms. Loss by plant uptake and conversion into dimethyl selenide gas is another possible loss mechanism. Figures 4.16 and 4.17 show the complete model for selenium loss in the marsh.

4. April 2005 to September 2005, Nearly Continuous Inlet-Outlet Flows

Short term monitoring results after marsh re-startup

IRWD San Joaquin Marsh flows resumed mid-April 2005 after dredging operations in adjacent sediment basins were completed. We collected inlet and outlet samples frequently after flows resumed. Initially, selenium and salinity concentrations were very low because much of the water storage in the marsh was derived from urban stormwater runoff (Table 4.7). Selenium and salinity concentrations at the outlet of San Joaquin Marsh began to increase as flows from San Diego Creek began to displace the dilute waters in the marsh. After two weeks of continuous cycling (April 11 to April 25, 2005), concentrations of selenium at the inlet and outlet reached concentrations that were observed before dredging operations shut down operations in the marsh. There was little difference between total dissolved selenium and total (unfiltered) selenium at the inlet or the outlet (Table 4.7).

On April 25, the inlet flows from San Diego Creek had very low selenium and low salinity concentrations (Table 4.7). It doesn't appear that these dilute waters were due to precipitation. Dilute water in San Diego Creek was due to some upstream operations that put relatively dilute waters into the creek (e.g., irrigation runoff).

Based on our work and on IRWD work, it is well known that selenium is lost somewhere in the San Joaquin Marsh. To help determine how and where selenium is lost from the marsh, we collected water samples from the marsh ponds in July 2005 (Figure 4.3). Ponds 1, 2, 3, 4, and 5 plus the Polishing Pond were sampled and analyzed for selenium species (Table 4.8). All samples were filtered.

Flow outlets lead from Pond 4 into Pond 5 and into the Polishing Pond. This is not shown in Figure 4.3, which shows flow from Pond 4 into Pond 5. While sampling the ponds it was discovered that most of the flows from Pond 4 cycled into the Polishing Pond, bypassing Pond 5. We do not know if this was a temporary or normal configuration of flows in the marsh. The salinity in Pond 5 was about 10% higher than the salinity of the other ponds during the sampling period, suggesting that Pond 5 was not an active part of the circulation of the marsh during the July 2005 sampling event.

Selenium speciation data from July 2005 indicates that total selenium declines steadily between Pond 1 and the Polishing Pond (Table 4.8). Pond 5 had the lowest selenium concentration because water in this pond was not an active part of the circulation of the marsh. Longer residence time in Pond 5 probably led to greater selenium removal there (Table 4.8).

In all ponds, selenium IV was a significant percentage of the total selenium. Selenium IV remained relatively steady in all ponds while selenium VI decreased about 25% between Pond 1 and the Polishing Pond (Table 4.8). Organic selenium increased slightly from about 0.3 to 0.6 ug/L. This suggests that selenium speciates and is converted slightly to organic forms in the marsh while total dissolved selenium gradually decreases (Table 4.8).

Possible loss mechanisms that may be consistent with the data includes reduction of selenium VI into reduced forms (selenium IV and elemental selenium), along with some uptake and conversion of an unknown amount of selenium into organic forms (Figure 4.16). Our speciation analysis was done on filtered samples only, and some selenium could be converted into particulate forms. However, the small difference

between filtered and unfiltered selenium at the marsh inlet and outlet suggests that little selenium exists in *suspended* particulate form (Table 4.7). We do not know how much particulate selenium is settling out on the marsh bottom (Figure 4.16).

Full term monitoring results after marsh re-startup

Longer term data sets for samples collected from April 2005 to September 2005 at the marsh inlet and outlet continued to show selenium and nitrate removal in IRWD Marsh (Figures 4.20 and 4.21). A new observation showed that arsenic was being removed between inlet and outlet after April 11, 2005 (Figure 4.22). In earlier monitoring (pre-2005) we observed similar concentrations of arsenic at marsh inlet and outlet (Figures 4.8 and 4.10). The change in arsenic concentrations at the marsh inlet and outlet may indicate that redox or other hydrochemical conditions changed in the marsh when water was not being continually cycled into and out of the marsh from San Diego Creek. This brings up the interesting idea that optimal use of the marsh for water quality treatment might involve periods of inactive cycling from San Diego Creek.

Table 4.7: Total (unfiltered) Selenium, Total Dissolved Selenium and Salinity Data in San Joaquin Marsh Area for Re-Start of Marsh Flows after April 11, 2005

Sample ID	Total Selenium	Total Dissolved Selenium	Specific Conductance
Marsh Outlet, 4/11/05	3.0	3.0	1509
Marsh Flows Resume			
Marsh Outlet, 4/14/05	4.3	4.3	1569
Marsh Outlet, 4/19/05	8.4	8.3	1909
Marsh Outlet, 4/21/05	11.2	10.7	2154
Marsh Outlet, 4/25/05	14.2	14.1	2440
Marsh Inlet, 4/14/05	22.0	22.0	2973
Marsh Inlet, 4/19/05	21.5	21.3	2340
Marsh Inlet, 4/21/05	21.1	21.1	3055
Marsh Inlet, 4/25/05	5.1	4.9	1097

Table 4.8: Selenium Speciation Data for San Joaquin Marsh, Collected July 10, 2005

Sample ID	Se VI (ug/L)	Se IV (ug/L)	Organic Se (ug/L)	Total Dissolved Se (ug/L)
San Joaquin Marsh Pond 1	13.5	3.5	0.28	17.3
San Joaquin Marsh Pond 2	12.2	3.9	0.27	16.3
San Joaquin Marsh Pond 3	11.3	4.0	0.23	15.5
San Joaquin Marsh Pond 4	10.4	4.2	0.54	15.1
San Joaquin Marsh Pond 5	3.5	3.6	0.51	7.6
San J. Marsh Polishing Pond	10.3	3.7	0.61	14.6

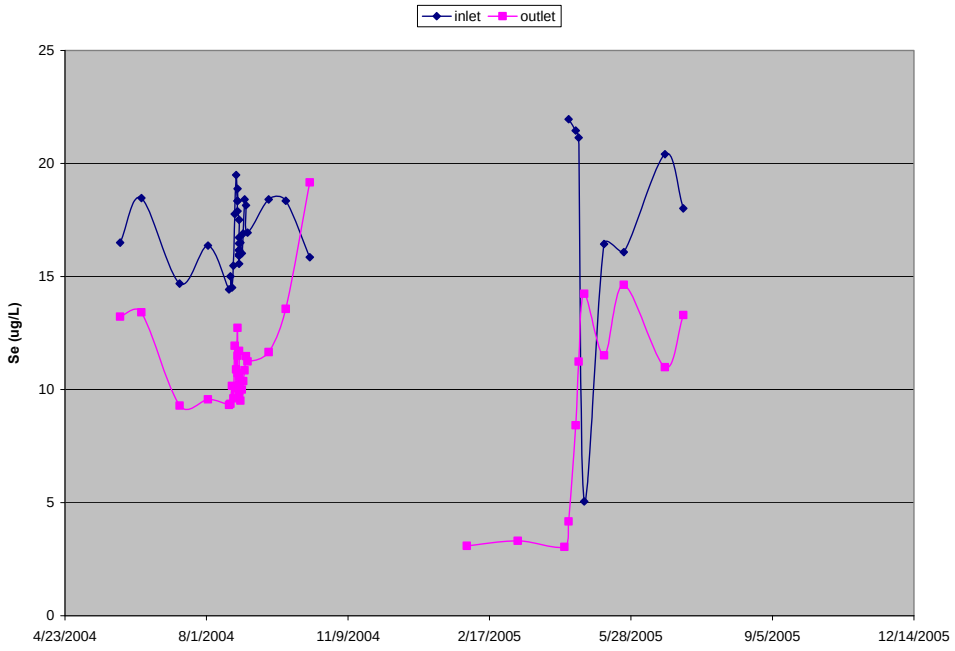

Figure 4.20. Dissolved selenium concentrations at the inlet and outlet of IRWD San Joaquin Marsh; collected while the marsh cycled water into and out of San Diego Creek.

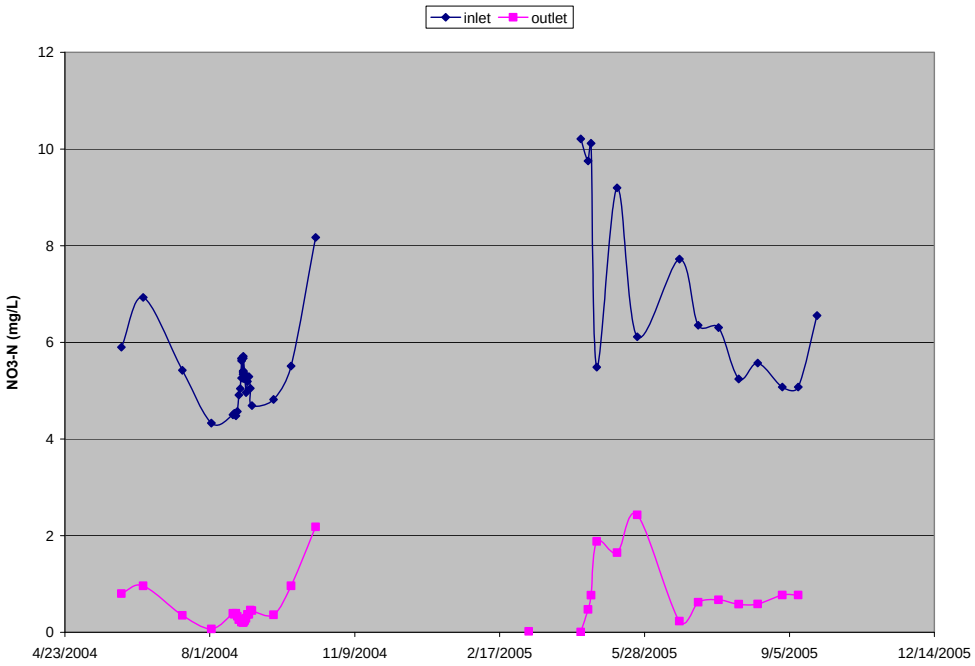

Figure 4.21. Nitrate-nitrogen concentrations at the inlet and outlet of IRWD San Joaquin Marsh; collected while the marsh cycled water into and out of San Diego Creek.

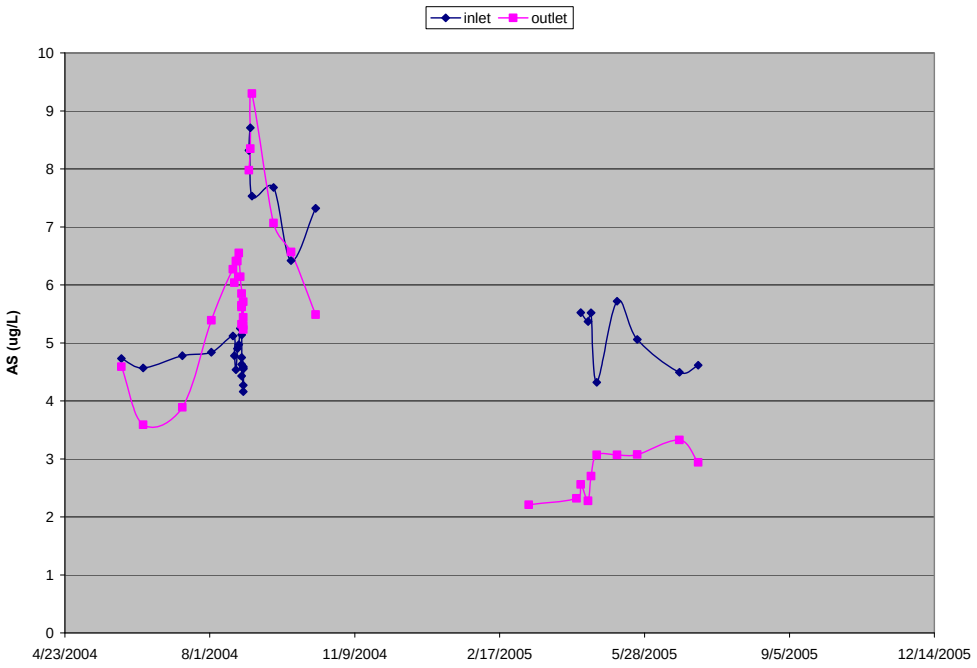

Figure 4.22. Dissolved arsenic concentrations at the inlet and outlet of IRWD San Joaquin Marsh; collected while the marsh cycled water into and out of San Diego Creek.

5. Recycling Flow Period, September 2005 to Study Completion

In mid-September 2005, the Irvine Ranch Water District discontinued inflow/outflow in the San Joaquin Marsh due to repair work of pumps and pipelines adjacent to the marsh. No monitoring of inlet and outlet flows was possible when water was not cycling in and out of San Diego Creek. San Joaquin Marsh flows through inlet and outlet resumed sporadically after December 2005.

We used this opportunity to collect selenium speciation data at ponds while water in the ponds recirculated internally. With only one rain shower recorded during the six week intensive monitoring period, this investigation provided a rare opportunity to assess selenium removal and speciation processes in the marsh during internal recirculation with limited net addition of water.

Based on our work and on IRWD work, it is well known that selenium is lost in the IRWD San Joaquin Marsh. To assess removal during internal recirculation of marsh water, we collected water samples from Ponds 1, 2, 3, 4, and 5 plus the Polishing Pond. These were sampled and analyzed for selenium species (Table 4.9). All samples for speciation analysis were filtered. When inlet/outlet flows were discontinued in mid September, the IRWD cycled existing stored water through the ponds in the marsh (Figure 4.3). Flow outlets lead from Pond 4 into Pond 5 and into the Polishing Pond. This is not shown in Figure 4.3, which shows flow only from Pond 4 into Pond 5. While sampling the ponds it was discovered that most of the flows from Pond 4 cycled into the Polishing Pond, bypassing Pond 5.

Selenium speciation data indicate that total selenium declines steadily between Pond 1 and the Polishing Pond (Table 4.9). Pond 5 had the lowest selenium

concentration because water in this pond was not an active part of the circulation of the marsh. Longer residence time in Pond 5 probably led to greater selenium removal there (Table 4.9). Also, there was a steady decline in selenium concentrations through time, and by November 20 none of the ponds had more than 5 ug/L Se.

In all ponds, selenium IV and organic selenium became a more significant percentage of the total selenium through time. Selenium VI decreased noticeably during the monitoring period, and was a small percentage of the total selenium at the end of the monitoring period (Table 4.9). Organic selenium increased slightly at most ponds from about 0.3 to 0.9 ug/L and then began to decrease slightly as total selenium continued its decline. This suggests that selenium speciated into reduced forms and was converted to organic forms in the marsh as total dissolved selenium was gradually removed (Table 4.9). These trends are shown graphically in Pond 4 in time series (Figure 4.23).

Probable loss mechanisms during the internal recirculation period that are consistent with the data (Table 4.9) includes reduction of selenium VI into reduced forms (selenium IV and elemental selenium), along with some uptake and conversion of an unknown amount of selenium into organic forms (Figures 4.16 and 4.17). Our speciation analysis was done on filtered samples only, and some selenium could be converted into particulate forms (Figure 4.16). We did collect filtered and unfiltered samples in the ponds for analysis of total dissolved selenium and total (unfiltered) selenium. As has often been the case during marsh monitoring, filtered selenium analyses are often slightly higher than unfiltered selenium analysis (Table 4.10); an inaccurate analytical result.

Previously we speculated that this inaccurate result was due to an unidentified organic agent in the unfiltered marsh water that interferes with selenium analyses.

Because results have been very close, we assumed that total dissolved selenium and total (unfiltered) selenium were approximately equal in the marsh waters. The small difference between filtered and unfiltered selenium in the marsh suggests that little selenium exists in *suspended* particulate form. However, a curious observation came out of the recent data; namely, that the total dissolved selenium became somewhat less than the total selenium during the monitoring period (Table 4.10 and Figure 4.24). This either means that the presumed organic interfering agent was removed during internal marsh recirculation or that suspended particulate material, bearing selenium, became a greater percentage of the analytical measurement of selenium during analysis of total selenium. If the latter is true, this means that selenium was accumulating and retained in suspended particulate matter (e.g., phytoplankton) during continuous internal recirculation of marsh water (closed system). During normal times, when the marsh circulates between inlet and outlet, this mass of suspended particulate matter would be removed at the marsh outlet as marsh water flows back into San Diego Creek. In other words, during normal circulation, suspended material (bearing selenium) does not accumulate in marsh water as a significant percentage of selenium bearing suspended solids in the marsh water (open system conditions).

These results became known when the selenium analyses were completed after the end of the closed system monitoring. We did not collect and analyze marsh samples for total suspended solids or other useful indicators of particulate selenium (except filtered and unfiltered selenium in water) through time. It would have been useful to do this had we had the *apriori* understanding of the need, as well as the additional financial resources needed to complete the work.

Table 4.9: Selenium Speciation Data for San Joaquin Marsh (Internal recirculation with no San Diego Creek inlet/outlet flows)

Sample ID	Se VI (ug/L)	Se IV (ug/L)	Organic Se (ug/L)	Total Dissolved Se (ug/L)
October 2, 2005				
Pond 1	7.23	4.96	0.54	12.73
Pond 2	7.45	5.43	0.45	13.33
Pond 3	6.97	5.33	0.49	12.80
Pond 4	6.57	4.91	0.45	11.93
Pond 5	1.91	3.15	0.29	5.36
Polishing Pond	6.18	4.59	0.34	11.12
October 8, 2005				
Pond 1	4.77	4.79	0.78	10.35
Pond 2	4.75	5.16	0.73	10.65
Pond 3	4.02	4.62	0.86	9.50
Pond 4	4.04	5.29	0.83	10.17
Pond 5	1.37	3.71	0.61	5.70
Polishing Pond	3.39	4.07	0.76	8.22
October 22, 2005				
Pond 1	1.02	3.08	1.12	5.23
Pond 2	1.19	3.33	0.88	5.41
Pond 3	0.61	2.45	1.13	4.20
Pond 4	0.93	3.27	0.91	5.12
Pond 5	0.25	2.51	0.58	3.32
Polishing Pond	0.38	2.97	0.80	4.16
November 7, 2005				
Pond 1	2.16	3.09	0.78	6.03
Pond 2	1.44	3.27	0.65	5.35
Pond 3	1.77	2.65	0.72	5.14
Pond 4	1.13	3.93	0.93	6.00
Pond 5	1.65	2.97	0.24	4.86
Polishing Pond	1.13	2.78	0.51	4.43
November 20, 2005				
Pond 1	1.24	2.84	0.84	4.93
Pond 2	1.46	3.05	0.38	4.89
Pond 3	1.77	2.61	0.29	4.69
Pond 4	1.18	2.97	0.49	4.65
Pond 5	0.65	2.43	0.54	3.63
Polishing Pond	0.50	2.62	0.85	3.97

Table 4.10: Total Selenium and Total Dissolved Selenium in San Joaquin Marsh (Internal recirculation with no San Diego Creek inlet/outlet flows)

Sample ID	Total (unfiltered) Se	Total Dissolved (filtered) Se
October 2, 2005		
Pond 1	12.76	12.73
Pond 2	12.82	13.33
Pond 3	12.32	12.80
Pond 4	11.63	11.93
Pond 5	4.18	5.36
Polishing Pond	10.43	11.12
October 8, 2005		
Pond 1	9.90	10.35
Pond 2	10.29	10.65
Pond 3	9.35	9.50
Pond 4	9.49	10.17
Pond 5	4.75	5.70
Polishing Pond	8.13	8.22
October 22, 2005		
Pond 1	5.11	5.23
Pond 2	5.33	5.41
Pond 3	4.38	4.20
Pond 4	5.71	5.12
Pond 5	2.65	3.32
Polishing Pond	4.60	4.16
November 7, 2005		
Pond 1	5.52	6.03
Pond 2	5.22	5.35
Pond 3	4.62	5.14
Pond 4	6.41	6.00
Pond 5	4.85	4.86
Polishing Pond	5.36	6.16
November 20, 2005		
Pond 1	5.47	4.93
Pond 2	5.51	4.89
Pond 3	4.78	4.69
Pond 4	5.59	4.65
Pond 5	3.93	3.63
Polishing Pond	4.71	3.97

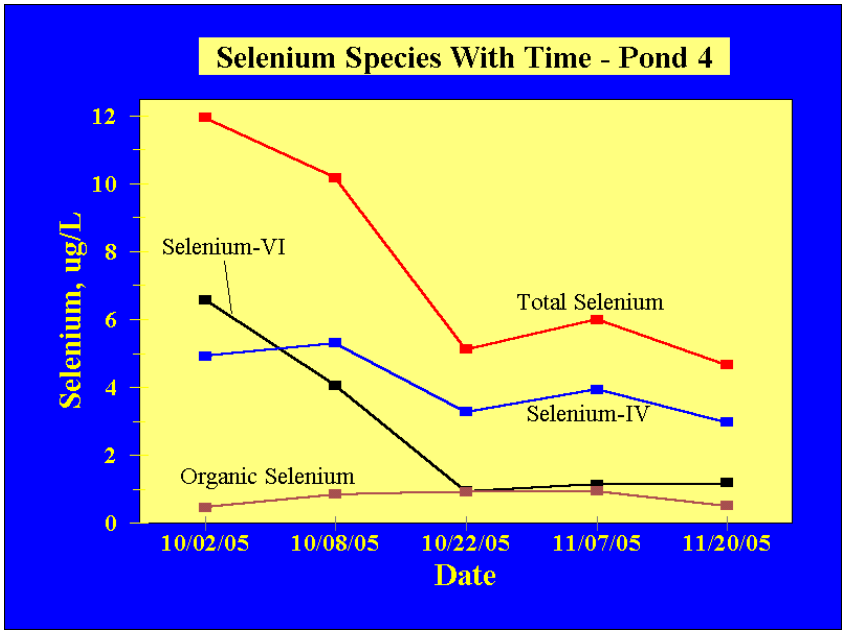

Figure 4.23. Speciation of pond 4 water through time, showing net removal of total dissolved selenium and substantial decrease in selenium-VI.

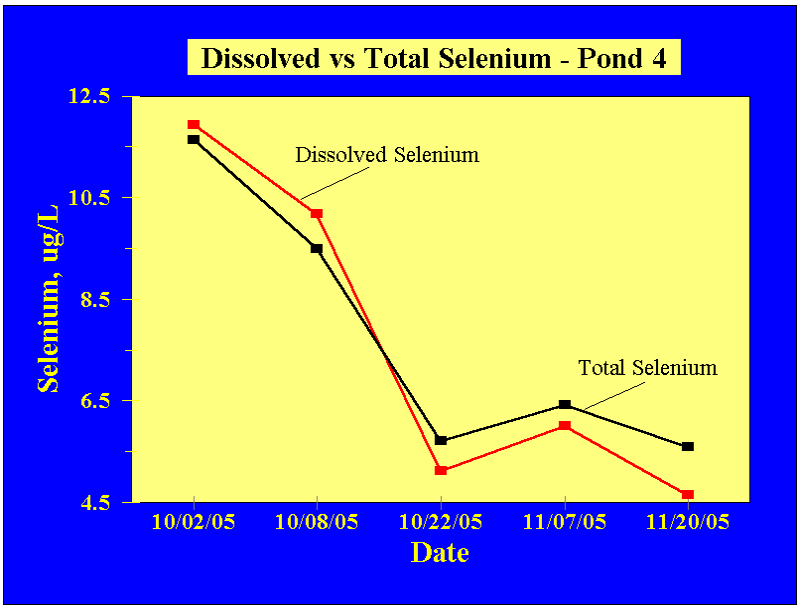

Figure 4.24. Comparison of total and dissolved selenium in pond 4 water through time. Dissolved selenium is initially higher due to presumed analytical interference by unidentified organic agent. Later, total selenium is higher than dissolved selenium.

6. Selenium Analysis of Marsh Sediments

Sediment samples collected from the IRWD San Joaquin Marsh in early 2008 were analyzed for selenium species (Figure 4.25). Wet and dry weight results are presented in Table 4.11. The highest dry weight selenium concentration for both total selenium and selenium-IV was measured in the sediments collected from Pond 4 (1.517 mg/kg and 0.229 mg/kg respectively). The lowest dry weight selenium concentration for total selenium and selenium-IV was measured in sediments collected from Pond 1 (0.180 mg/kg and 0.032 mg/kg respectively) (Table 4.11). The range of total dry weight selenium concentrations from the sediments from the marsh was not highly variable (0.180 mg/kg to 1.517 mg/kg), while the highest concentration of dry weight selenium from the marsh sediment was not especially concentrated (1.517 mg/kg) (Table 4.11). Selenium-IV plus Selenium VI in sediments is only 7% to 25% of the total selenium in the marsh sediments; the remaining selenium is probably mostly elemental selenium. Organic selenium in marsh sediments was not analyzed by the contract laboratory.

Comparisons between selenium concentrations in sediments collected from IRWD Marsh and from soils collected within the Historic Swamp of the Frogs Marsh region, near Peters Canyon Wash and Barranca Channel show notable differences (compare Tables 4.11 and 4.12). Different fractional distributions of selenium species were measured in the soils from the historic swamp, along with a wider range of selenium concentrations. Notably, the “blue clay” collected within the Historic Swamp of the Frogs Marsh region has a much higher concentration than marsh sediments, 13.96 mg/kg dry weight selenium (Table 4.12).

Based on the concentrations observed, the limited sediment data collected from the IRWD Marsh suggest that there is moderately-low risk of selenium toxicity associated with this pathway, where selenium levels in sediments of the marsh are below recommended limits (Presser and Luoma, 2004). Background concentration for total selenium in soils not impacted by selenium is approximately 0.4 mg/kg whereas soils derived from Cretaceous rocks have higher total selenium in the range of 5 mg/kg (Thomas et al, 1998). Based on these values, the selenium data for marsh soils at these locations probably indicates that the IRWD marsh sediments were not heavily impacted by selenium when samples were collected in early 2008.

As noted earlier, speciation data for the sediments show that sediments collected from the marsh have non-detectable concentrations of selenium-VI, while selenium-IV makes up 7% to 25% of total selenium in sediments collected from the marsh ponds. Selenium-IV tends to adsorb to mineral surfaces and organic matter (Ellis et al., 2003). Adsorption on sediments removes dissolved selenium from marsh water (Zhang and Moore, 1997a, 1997b, 1997c).

Based on the available data, it is difficult to say if much of this fraction of selenium enters the marsh already associated with suspended solids (herein called "process 1"), or as a dissolved phase that subsequently is reduced in bottom sediments and adsorbs to available surfaces or precipitates as elemental selenium (herein called "process 2"). Process 2 occurs to some extent as a result of percolation of marsh water downward into groundwater, as described in earlier sections of this report. The pre-settling ponds at the IRWD Marsh (Ponds A, B, and C) remove a major portion of the suspended solids in the marsh before marsh waters are eventually routed into Pond 1.

Consequently, pre-settling processes in these ponds removes bound forms of selenium from the water column before flows are routed to the larger ponds in the marsh (Figure 4.3).

Even though the pre-settling ponds effectively remove suspended solids from the water column, some of the smaller colloids and other suspended solids are passed on to the main ponds. Therefore, it is very likely that process 1 and process 2 operate simultaneously in IRWD Marsh. More focused work is needed to quantify the relative importance of these two processes.

Table 4.11: Selenium in Sediments of Upper Newport Bay

	Wet-weight (mg/kg)			%TS	Dry-weight (mg/kg)		
Station	**Se (IV)**	**Se (VI)**	**Total Se**		**Se (IV)**	**Se (VI)**	**Total Se**
Pond 1	0.027	ND (< 0.046)	0.152	84.27	0.032	ND	0.180
Pond 2	0.027	ND (< 0.046)	0.248	80.00	0.032	ND	0.310
Pond 3	0.047	ND (< 0.046)	0.617	70.74	0.066	ND	0.872
Pond 4	0.162	ND (< 0.046)	1.073	70.73	0.229	ND	1.517
Pond 5	0.103	ND (< 0.046)	0.631	62.49	0.163	ND	1.009
Polish Pond	0.100	ND (< 0.046)	0.387	68.40	0.146	ND	0.566

Table 4.12: Selenium in Sediments of Historic Swamp of Frogs Marsh Area

	Wet-weight (mg/kg)			%TS	Dry-weight (mg/kg)		
Station	**Se (IV)**	**Se (VI)**	**Total Se**		**Se (IV)**	**Se (VI)**	**Total Se**
Barranca Upper Clay	ND (< 0.046)	0.155	0.383	78.21	ND	0.198	0.490
Barranca Blue Clay	2.98	1.27	10.40	74.51	3.99	1.70	13.96

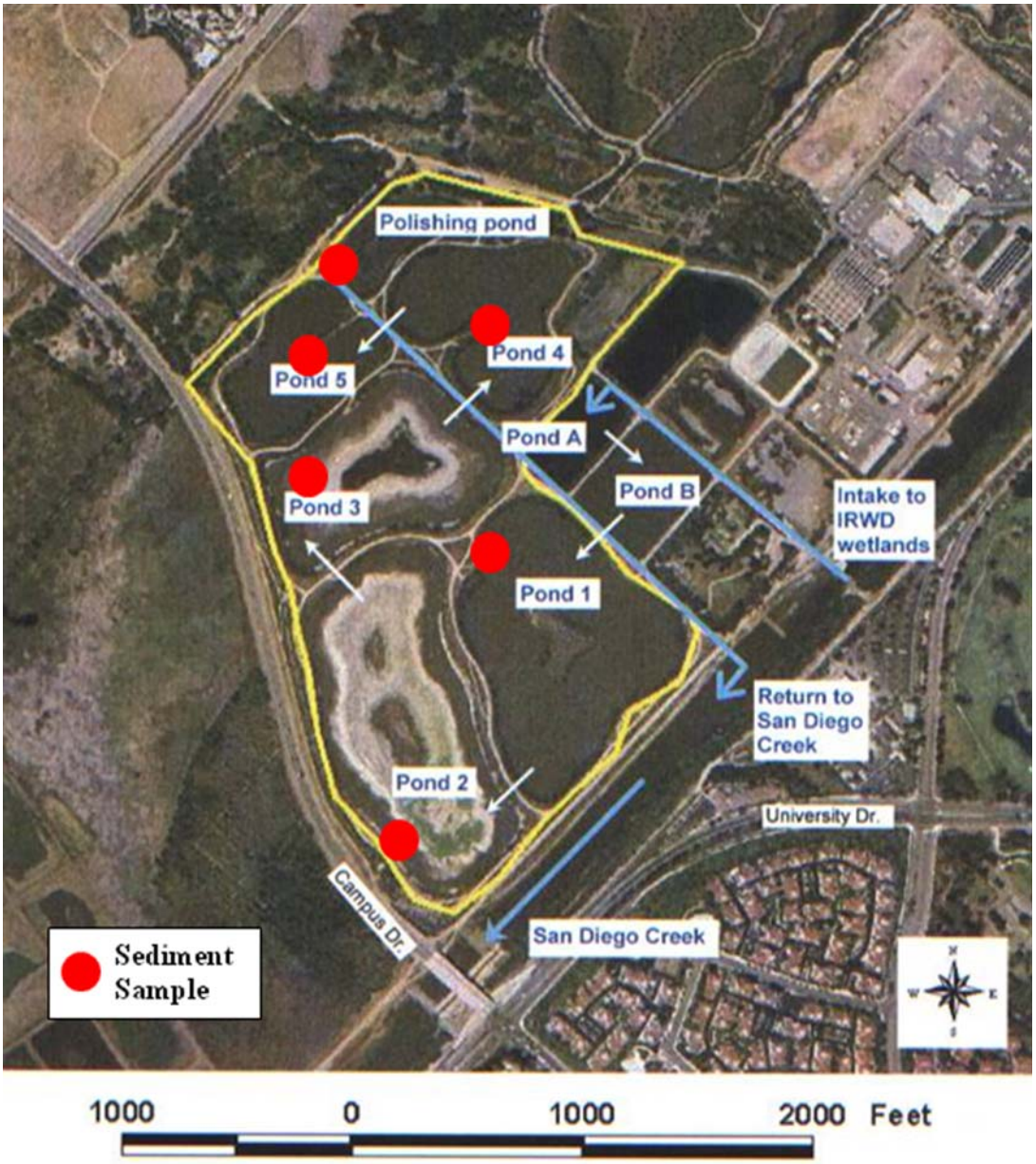

Figure 4.25. Aerial View of the IRWD San Joaquin Marsh showing locations where sediment samples were collected from the marsh for selenium analysis (modified from GeoSyntec, 2003).

SUMMARY CONCLUSIONS AND DATA RECONCILIATION

In this study, San Joaquin Marsh was analyzed for selenium and other hydrochemical and isotopic species to assess removal, uptake, and possible remobilization/immobilization occurring in the marsh. During the 1.5 years we monitored the marsh, there were periodic shutdowns of the marsh for channel and marsh maintenance. Total and dissolved selenium, index parameters, anions, and select nutrients were measured when the marsh was circulating flows to and from San Diego Creek.

A variety of methods were used to collect samples from the diverse number of sites at the IRWD San Joaquin Marsh. These included marsh water and shallow groundwater samples and sediment samples collected from the marsh bottom. In general, water samples were collected at the marsh inlet and outlet, and from marsh Ponds 1, 2, 3, 4, and 5, plus the marsh Polishing Pond. Sediment samples were collected from most of these same locations. Monitoring wells were also sampled to compare groundwater hydrochemistry to marsh hydrochemistry.

The original study plan required one year of water quality monitoring at the inlet and outlet of IRWD San Joaquin Marsh. Other contracted analysis included selenium speciation testing of marsh waters and sediments. Two major events did not allow us to complete one year of <u>continuous</u> monitoring of the marsh: (1) shut down of marsh flows from October 2004 to April, 2005, because of removal of sediments from in-channel sediment basin 3; and, (2) shut down of marsh flows from October 2005 to December 2005 due to pump failure. The study extended over a 19 month period, with about 15 months of cumulative monitoring. Variations in flow conditions in San Joaquin Marsh

during the 19 month period provided logical breaks when different monitoring programs could be carried out. Major findings for the different sub-study "break" periods are summarized:

June 2004 to October 2004, Continuous Inlet-Outlet Flows

Monitoring of the inlet and outlet from mid-June 2004 to late October 2004 included a series of daily measurements at the inlet and outlet for two weeks (Aug 17 – Aug 30, 2004), and a diurnal measurement cycle in late August when samples were collected every two hours for 24 hours. During this period, approximately 20 to 35% of the selenium in the inlet is removed as it travels through the marsh and is not appearing at the outlet. Moderate decrease in selenium between the inlet and the outlet indicates that selenium is being sequestered or lost somewhere in the marsh. This pattern was relatively stable throughout the monitoring period.

October 2004 to April 2005, Marsh Shutdown Period and Miscellaneous Monitoring

The Irvine Ranch Water District discontinued inflow/outflow in the San Joaquin Marsh in October 2004. No monitoring of inlet and outlet flows was possible during this time. Accordingly, we used this opportunity to sample water wells and surface water ponds within the interior of the marsh. Prior to this study, it was unknown if surface water percolates downward into groundwater beneath the marsh. San Diego Creek is at a lower elevation than the water level in IRWD San Joaquin Marsh, which could create a condition of seepage of marsh water downward into groundwater ("losing marsh"

condition). If marsh water is recharging groundwater beneath the marsh, some selenium is probably lost in the interstitial sediments beneath the marsh.

Stable isotopes of oxygen and hydrogen confirm that the marsh is replenishing the aquifer beneath the marsh. Percolation of marsh water downward into groundwater is probably not a very fast process, so the bulk isotopic signature of the groundwater determined during this sampling event probably represents a composite isotopic signature of the water in the marsh ponds over a period of time, perhaps well over a year.

These data confirmed a source of recharge from the ponds to the shallow aquifer beneath the marsh wetlands. Flow relationships between surface water and groundwater could indicate selenium immobilization in the wetland sediments, because surface water moves down through organic rich and suboxic/anoxic sediments at the bottom of the ponds. In reducing sediments, selenium precipitation and sorption is likely to occur.

Additional Groundwater Studies

Many additional groundwater monitoring wells were sampled in IRWD San Joaquin Marsh in July 2005 to expand upon our earlier analysis. Groundwater samples were tested for selenium species and stable isotopes of oxygen and hydrogen. Groundwater data indicate that wells contain very little selenium, and that species are reduced, with most wells containing selenium-IV as the dominant selenium species.

Depending on the rate of seepage to groundwater beneath the marsh, this could indicate minimal-to-substantial accumulation of selenium in marsh bottom-sediments. The role of plant uptake and selenium removal as a gas is another factor that could contribute to selenium removal, and neither process has been quantified. Where

groundwater is recharged by marsh water, selenium is partially lost from percolating pond water by reduction at the organic rich sediment/water interface. This model would explain why groundwater selenium concentrations are so low beneath IRWD Marsh.

April 2005 to September 2005, Nearly Continuous Inlet-Outlet Flows

Based on earlier work, it became well known that selenium is lost somewhere in the San Joaquin Marsh. To help determine how and where selenium is lost from the marsh, we collected water samples from the marsh ponds in July 2005. Selenium speciation data from July 2005 indicates that total selenium declines steadily between Pond 1 and the Polishing Pond. In all ponds, selenium IV was a significant percentage of the total selenium. Selenium IV remained relatively steady in all ponds while selenium VI decreased about 25% between Pond 1 and the Polishing Pond. Organic selenium increased slightly from about 0.3 to 0.6 ug/L. This suggests that selenium speciates and is converted slightly to organic forms in the marsh while total dissolved selenium gradually decreases. Possible loss mechanisms that may be consistent with the data includes reduction of selenium VI into reduced forms (selenium IV and elemental selenium), along with some uptake and conversion of an unknown amount of selenium into organic forms.

Recycling Flow Period, September 2005 to Study Completion

In mid-September 2005, the Irvine Ranch Water District discontinued inflow/outflow in the San Joaquin Marsh due to repair work of pumps and pipelines adjacent to the marsh. No monitoring of inlet and outlet flows was possible when water

was not cycling in and out of San Diego Creek. San Joaquin Marsh flows through inlet and outlet resumed sporadically after December 2005. We used this opportunity to collect selenium speciation data at ponds while water in the ponds recirculated internally.

Selenium speciation data indicate that total selenium declines steadily between Pond 1 and the Polishing Pond during this "internal recycling" sub-study. There was a steady decline in selenium concentrations through time, and by November 20 none of the ponds had more than 5 ug/L Se. In all ponds, selenium IV and organic selenium became a more significant percentage of the total selenium through time. Selenium VI decreased noticeably during the monitoring period, and was a small percentage of the total selenium at the end of the monitoring period. Organic selenium increased slightly at most ponds from about 0.3 to 0.9 ug/L and then began to decrease slightly as total selenium continued its decline. This suggests that selenium speciated into reduced forms and was converted to organic forms in the marsh as total dissolved selenium was gradually removed.

Selenium Analysis of Marsh Sediments

Sediment samples collected from the IRWD San Joaquin Marsh in early 2008 were analyzed for selenium species. The highest dry weight selenium concentration for both total selenium and selenium-IV was measured in the sediments collected from Pond 4 (1.517 mg/kg and 0.229 mg/kg respectively). The lowest dry weight selenium concentration for total selenium and selenium-IV was measured in sediments collected from Pond 1 (0.180 mg/kg and 0.032 mg/kg respectively). The range of total dry weight selenium concentrations from the sediments from the marsh was not highly variable

(0.180 mg/kg to 1.517 mg/kg), while the highest concentration of dry weight selenium from the marsh sediment was not especially concentrated (1.517 mg/kg). Selenium-IV plus Selenium VI in sediments is only 7% to 25% of the total selenium in the marsh sediments.

Based on the concentrations observed, the limited sediment data collected from the IRWD Marsh suggest that there is moderately-low risk of selenium toxicity associated with this pathway, where selenium levels in sediments of the marsh are below recommended limits. Background concentration for total selenium in soils not impacted by selenium is approximately 0.4 mg/kg whereas soils derived from Cretaceous rocks have higher total selenium in the range of 5 mg/kg. Based on these values, the selenium data for marsh soils at these locations probably indicates that the IRWD marsh sediments were not heavily impacted by selenium when samples were collected in early 2008.

Data Reconciliation

This study indicated that approximately 20 to 35% of the selenium is removed as water travels through the IRWD Marsh from the marsh inlet to the marsh outlet. Moderate decrease in selenium between the inlet and the outlet indicates that selenium is being sequestered or lost somewhere in the marsh. Our groundwater investigations in IRWD Marsh indicated that percolating marsh waters recharge the shallow aquifer beneath the marsh, allowing selenium to be lost as the recharge waters pass through organic rich bed-sediments. We postulate that much of the selenium lost in the recharge waters develops as a result of reduction of highly soluble selenium oxyanions to lower solubility forms (selenite and elemental selenium) in the sediments of the marsh.

Contrary to these interpretations, sediments collected from the marsh do not appear to contain particularly elevated levels of selenium. Apparent inconsistencies in the data sets can be explained, potentially. First, the IRWD San Joaquin Marsh has been in operation for little more than a decade. If selenium is accumulating in sediments beneath the marsh, it may take much more time for the element to accumulate to potentially harmful or elevated levels. Occasional sediment dredging and sediment removal from the marsh may have removed bound and precipitated forms of selenium. Likewise, occasional dewatering of marsh ponds might have oxidized and remobilized selenium from reduced forms, allowing mobilized Se to be leached out of bed-sediments when the ponds were rewetted. Finally, the few sediment samples we collected and analyzed for selenium may have provided inadequate representation of selenium levels in the marsh sediments, particularly if selenium reduction is limited to spatially restricted micro reducing-environments in the marsh. Previous analysis of sediment collected from IRWD Marsh showed similarly modest concentrations of selenium however (Lou Denger, IRWD staff, personal communication).

Regarding apparent contradictions between the water column, sediment, and groundwater quality data, we simply do not have enough information at this time to take our interpretations any further. Even so, we have advanced the conceptual understanding of the dynamics of selenium in IRWD San Joaquin Marsh. An attendant data base has been developed that should help guide future investigations of the marsh.

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Chapter 5

Time Series Analysis of Nitrate and Selenium in Downstream Sedimentation Basins: San Diego Creek

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INTRODUCTION

The main purpose of this study is to observe the water quality characteristics of the San Diego Creek estuarine interface (prebasin) and in-channel sedimentation basins above the Upper Newport Bay Ecological Reserve. As a transitional zone for terrestrial (dilute) freshwater and marine (saline) water, conditions in the sedimentation basins and mixing basin alter water quality and sediment dynamics. Tracing hydrologic fluxes through depth dependent conductivity/salinity, temperature, and dissolved oxygen measurements indicates mixing or stratification schemes that occur in the in-channel sedimentation basins and the mixing prebasin above Upper Newport Bay. An analysis of the water column interface provides a look at potential processes that contribute to mixing and chemical transformations in the basins. Water samples of nutrients (various nitrogen and phosphorous species), selenium, and soluble major ions were taken.

Study Area

The study area includes a 0.40-mile long estuarine mixing basin (also known as the prebasin) located between Upper Newport Bay, and three in-channel sedimentation basins in San Diego Creek that are adjacent to the San Joaquin Marsh (Figure 5.1). Acting as a transitional area between the Upper Newport Bay ecological reserve and the county owned (Irvine Ranch Water District managed) sedimentation basins, the prebasin begins at Jamboree Road Bridge and extends to the southern border of in-channel basin 1 at MacArthur Boulevard (Figure 5.1). In-channel sediment basin 1 is the southernmost basin, located between Campus Drive and MacArthur Boulevard, while in-channel sediment basin 2 is located about a quarter-mile upstream of the confluence of San Diego

Creek and Sand Canyon Channel. In-channel sediment basin 3 is the northernmost basin, located between in-channel sediment basin 2 and the confluence of San Joaquin Channel (OCPFRD 2000).

The San Diego Creek Sedimentation Basins

In 1982, the Southern California Association of Governments completed the San Diego Creek Comprehensive Stormwater Sedimentation Control Plan, which led to the implementation of best management practices for construction and agricultural sites within the watershed. This plan included the construction of foothill basins, in-channel basins to trap coarse-grained sediment, and two in-Bay basins to settle out the fine sediments (mostly silts and clays) through flocculation of the particles as sediment comes into contact with saline waters (ACOE 2001). Two of the sediment trapping basins were built in 1997, and the third basin was completed in 1999 (IRWD 2002). These basins are located within San Diego Creek and act as "traps" to retard the flow of water coming through the Creek prior to its discharge into Newport Bay (Figure 5.1). By slowing down the velocity of the water, sediment is able to drop out of suspension and deposit in the basins rather than being carried to the Bay (OCPFRD 2000).

According to San Diego Creek Sediment Monitoring Program report by the Orange County Public Facilities and Resources Department (OCPFRD 2000), the in-channel basins capture a percentage (varies from 23% during the 1986-1997 period to 1% during the 1997-1998 record El Nino flow season) of the sediment load from upstream sources. Sedimentation process also can trap phosphorous, a key nutrient for algae growth because of its affinity for sediment. As of 1999, the design capacity of Basin 1

was 218,000 cubic yards, design capacity of Basin 2 was 64,000 cubic yards, and design capacity of Basin 3 was 90,833 cubic yards for a total of 372,833 cubic yards. These numbers have increased slightly due to some recent modifications to deepen the channels to trap more sediment, and to allow higher flood discharge capacity. IRWD indicated that "over 130,000 cubic yards or 13,000 dump-truck loads of sand and silt were prevented from entering the Bay since 1997" (IRWD 2002).

Downstream Sedimentation Basins and Relationship to Upper Newport Bay

As one of only a few remaining estuaries in Southern California, Newport Bay provides wildlife habitat and cultural benefits (recreation, science/education, and aesthetic value); the associated wetlands contribute to filtration, flood control, erosion prevention and shoreline stabilization. Current pollutants of high priority for the Upper Newport Bay Ecological Reserve include trace elements such as selenium, nutrients, pathogens, pesticides and sediment (siltation). Sources for these pollutants include agriculture, urban runoff (storm sewers and channels), groundwater loading, construction, land development and channel erosion. Most of these pollutant loads are predominantly from San Diego Creek, which is the largest contributor of freshwater flows to Newport Bay. The sedimentation basins are a key interface between Upper Newport Bay and the San Diego Creek Watershed. Intensive study of the dynamics of the downstream sedimentation basins contributes to our understanding of pollutant loads, fate, and transport to Upper Newport Bay.

METHODS

To characterize the sedimentation basins and the mixing prebasin, a suite of chemical parameters were tested (Table 5.1). Monitoring and sampling sites were selected and written descriptions of the sites were developed. Multiple stations were established in each of the in-channel sedimentation basins and the prebasin (Figure 5.2). With the exception of basin 3, each monitoring station was sampled from a boat. Water-column data were collected from November, 2005 to February, 2007 (Table 5.2).

Table 5.1: Summary of Sampling Protocol and Laboratories

Water Samples			
Parameter	Preservative	Method	Container
Orthophosphate, Nitrate, Sulfate, Chloride	Cool to 4° C, filter with 0.45 micron filter	IC-CSULA	1 Liter High Density Polyethylene (HDPE)
Selenium (total)	Cool to 4° C	AA-Hydride Generation-UC-Riverside	250 Milliliter HDPE
Selenium (dissolved)	Cool to 4° C, filter with 0.45 micron filter	AA-Hydride Generation-UC-Riverside	250 Milliliter HDPE
Selenium Speciation	Cool to 4° C, filter with 0.45 micron filter	AA-Hydride Generation-UC-Riverside (Zhang Method)	250 Milliliter HDPE
Turbidity	Cool to 4° C	Turbidimeter-CSULA	250 Milliliter HDPE
Ammonium	Cool to 4° C	Ion Selective Electrode-CSULA	500 Milliliter HDPE

Depth dependent water column measurements (one-half or one-foot intervals depending on total depth) for specific conductance/salinity, temperature, pH, and dissolved oxygen were taken with two Yellow Springs Instruments (YSI) water quality meters. At each site, water-column samples were collected through grab sampling to observe any vertical water-quality gradients. Sampling runs rotated between the three upstream in-channel sedimentation basins and the mixing prebasin above Upper Newport

Bay. Each sample was collected, preserved and analyzed using different procedures depending on the parameter being tested (Table 5.1).

Table 5.2 Water Column Sampling Dates in Downstream Sedimentation Basins

Basin 3	Basin 2	Basin 1	Prebasin
01-08-06	11-20-05	11-27-05	12-15-05
02-16-06	01-08-06	01-19-06	02-02-06
03-23-06	02-16-06	03-02-06	03-16-06
04-18-06	03-23-06	03-30-06	04-11-06
05-18-06	04-18-06	05-02-06	05-09-06
06-12-06	05-18-06	05-31-06	06-08-06
07-27-06	06-12-06	07-05-06	07-15-06
08-29-06	07-27-06	07-20-06	08-17-06
09-19-06	08-17-06	08-29-06	09-13-06
10-11-06	09-13-06	09-19-06	10-29-06
12-12-06	11-15-06	10-11-06	12-07-06
01-18-07	12-12-06	12-06-06	01-18-07
		02-01-07	

Water column samples were collected from the top portion of the water column (approximately 6 inches from the surface) and from the deep section located 7.5 inches above the riverbed (Figure 5.3). Shallow samples were collected by submerging a one gallon plastic bottle into the creek, and then manually shaking the sample to homogenize the liquid before it was transferred into pre-cleaned sample containers. Deep samples were collected using a telescopic sub-surface grab sampler equipped with 32-oz glass jars. Water samples collected with the grab sampler were poured into the one gallon homogenization bottle, thoroughly shaken, then decanted into the laboratory sample containers.

RESULTS AND DISCUSSION

Complete water quality data collected during investigations of the downstream sediment basins are presented in Appendix 5.0 and in the Excel File for downstream sedimentation basins. For the convenience of the users of this report, an abbreviated set of data containing selenium and nitrate information is presented in text (Table 5.3). Study findings are discussed in several topical areas:

1. Water Column Salinity Dynamics and Relationship to Water Quality Issues

2. Longitudinal Trends in Selenium and Nitrate

3. Time Series Analysis of Nitrate, Selenium, and Chloride in Downstream Sedimentation Basins

4. Selenium Speciation Data in Water Column in Downstream Sedimentation Basins

5. Water Column Dissolved Oxygen Profiles

6. Nutrient Biogeochemical Cycling Processes in Mixing Prebasin

7. Basin No. 2 Site Specific Analysis of Hyporheic Zones

Results and discussion are integrated in each section, providing a modular framework to the text.

1. Water Column Salinity Dynamics and Relationship to Water Quality Issues

A. Salinity Dynamics

A convenient way to measure salinity is to measure the electrical conductivity (specific conductance) of a water sample. As the concentration of salts in the water increases, so does the electrical conductivity. Since dissolved ions increase salinity as

well as specific conductance, the two measures are related. Specific conductance (measured in siemens, and here reported as milli-siemens, or mS) is the reciprocal of electrical resistivity, and measures the ability of water to pass an electrical current. It is affected by the presence of inorganic dissolved solids such as chloride, sulfate, bicarbonate, nitrate, and phosphate anions (ions that carry a negative charge) or sodium, magnesium, calcium, potassium, iron, and aluminum cations (ions that carry a positive charge). Precise conversion to salinity requires information on the available proportions of the different ions contributing to the specific conductance (Drever 1988), but in general TDS can be determined by multiplying specific conductance in millisiemens by 650. Specific conductance varies with water source (groundwater, surface water, and seawater).

Graphical examples of specific conductance profiles are shown in Figures 5.4 to 5.7, while Appendix 5.0 contains detailed salinity measurements for each sedimentation basin monitoring station data sheet. Summer and winter specific conductance profiles are prepared for select stations (Figures 5.4 to 5.7). Salinity profiles vary with tidal and freshwater influences, dilution, mixing of the water by wind, storms, seasonal changes and channel morphology. Monitoring station profiles are shaped differently due to the varying amounts of salinity found at depth, which determines the degree of vertical stratification. Sediment basins 2 and 3, which are located upstream of basin 1 and Newport Bay, do not exhibit a vertical stratification scenario with respect to specific conductance/salinity (Figures 5.4 and 5.5). Specific conductance measurements are all in the 2 to 3 mS range at sedimentation basins 3 and 2 (Figures 5.4 and 5.5), with no strong differences from top to bottom of the water column.

Unlike upstream basins 2 and 3, which have virtually no water column stratification in regards to specific conductance, sediment basin 1 shows marine water advancing up to station 1 near Campus Drive during the winter (Figure 5.6). This happens when the tidal fluctuations are peaking, and when the volume of terrestrial freshwater flowing downstream from San Diego Creek is low.

The mixing prebasin usually shows a mixed freshwater/marine water profile, indicating stratification of terrestrial freshwater and marine water (Figure 5.7). There are three scenarios that develop as the freshwater from San Diego Creek interacts with the tidally forced bay water in the mixing basin (Figures 5.8 to 5.10). Most of the time, a thin layer of relatively dilute freshwater overlies the entire mixing basin and flows into Newport Bay, much like a sheet flow effect (Figures 5.8). In general, a dilute freshwater lens up to 3.5 feet thick floats above a denser saltwater layer, which varies up to 10 feet thick. Typically, dilute freshwater flows are small, and the tide fluctuates in normal cyclic patterns. When freshwater inputs are high after heavy urban runoff (dry weather) or storm events, or when neap tides are in occurrence, the saltwater that usually sinks to the deeper parts of the channel is flushed out of the mixing prebasin, and the dilute freshwater lens becomes thicker (Figure 5.9). On the other hand, if the tidal fluctuations are more dramatic, with higher highs and lower lows, and freshwater inputs are low, the occurrence of the dilute freshwater lens is much diminished (Figure 5.10).

In most scenarios, the dilute freshwater overrides the heavier saltwater that sinks to the bottom of the mixing prebasin (Figure 5.8). The dilute freshwater-saltwater interface of the mixing basin is not a stagnant mass, but a dynamic system that varies in area and salinity throughout the day. Dilute water movement tends to be unidirectional

toward Newport Bay with some instances of bilateral flow. Partial reversal in flow direction of the dilute freshwater does occur during dramatic flood tides (Tillis, 2000). We do not know for sure what happens to the freshwater/saltwater interface in the mixing basin during terrestrial flood stages. However, it is likely that the mixing prebasin is flushed almost completely, if not entirely, of marine water during storm events of long duration. Limited rain and hazardous monitoring conditions precludes analysis of salinity profiles during floods.

B. Flocculation and Sedimentation Effects

Colloids and other particles remain suspended in water because of the random movement of particles arising from turbulence (Exhibit 1). However, individual particles in suspension can form aggregates, which eventually settle out by gravity through a process termed flocculation (McBride 1994). A clay is dispersed or flocculated depending on how far the individual clay particles are separated from each other by the double layer, or the thickness of the layer of adsorbed cations surrounding each particle (Bouwer, 1978). In the mixing prebasin, the salt concentration of the water can promote flocculation when the water column is well mixed because of the high ionic strength of the sodium chloride (NaCl) concentrations (Figure 5.11). By compressing the double layer, the clay particles are close enough to each other for the van der Waals forces to be dominant (Bouwer, 1978). Exhibit 1 shows the stages of flocculation as NaCl concentrations increase.

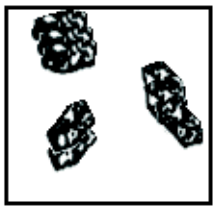
By studying the extent of tidal influence in San Diego Creek, it was observed that the upstream migration of saltwater is able to traverse above the upper reaches of the

mixing prebasin as far as Campus Drive. However, the marine waters and dilute freshwaters are usually not well mixed in the prebasin and in sediment basin 1. Inadequate mixing of higher salinity water (higher NaCl concentrations) with dilute terrestrial water may increase the probability of fine sediments and colloids being transported into Upper Newport Bay because of limited flocculation.

Stage 1: At NaCl concentrations less than 0.001 molar (M), the individual platelets do not interact (i.e., are dispersed) unless the clay concentration is high enough to force overlap between the co-volumes of the particles.

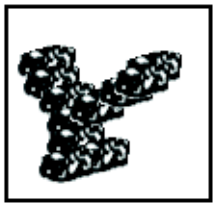
STAGE 1: Dispersion

Stage 2: At NaCl concentrations greater than 0.001 M, clay platelets may begin to approach closely enough to form tactoids, groups of aligned platelets.



STAGE 2: Aggregation

Stage 3: At NaCl concentrations greater than 0.01 M, interlayer spacings diminish even further and extensive flocculated structures build up, which increases the settling capacity of the particles.



STAGE 3: Aggregation and Flocculation

Exhibit 1: Stages of Flocculation in Increasingly Saline Environments (adapted from McBride 1994).

Aggregation will causes some of the particles to have sufficient mass to sink to the bottom of the mixing prebasin (sedimentation) before reaching Upper Newport Bay (Figure 5.11). After the sediment is deposited, the organic matter and pollutants entrained in the clays may decay, or may be removed by sediment dredging. Such a process will reduce delivery of sediment-entrained pesticides, phosphates, and toxic

metals to Upper Newport Bay. At this time, these processes have not been evaluated sufficiently. Further study of the salinity and mixing dynamics of the prebasin combined with flocculation and sedimentation studies, will provide a better understanding of these important processes.

2. Longitudinal Trends in Selenium and Nitrate

Figure 5.12 provides a representative longitudinal section of nitrate and selenium concentrations along the downstream sediment basins. Nitrate and selenium values are concentrated at the most upstream sample station in sediment basin 3, exceeding 28 mg/L total NO3 and 16 ug/L dissolved Se. Dilution of nitrate and selenium occurs downstream in sediment basin 2, most likely due to inflows of more dilute water from Sand Canyon Channel and San Joaquin Marsh.

Concentrations of nitrate and selenium at top and bottom stations are not very different in sediment basins 3, 2, and 1 (Figure 5.12). This suggests that there is little removal of nitrate or selenium in the water column. Removal could conceivably occur as a result of anoxia in the bottom sediments. The data do not suggest that any significant removal occurs in the upper three basins; otherwise we would expect to see lower values of selenium and nitrate at the bottom of the water column.

Differences between concentrations of nitrate and selenium at top and bottom stations are clearly seen in the prebasin however. Bottom samples have very dilute concentrations of nitrate and selenium compared to the concentrations of these constituents at the top of the water column (Figure 5.12). Dilution of nitrate and selenium at the bottom of the water column is not by anoxia-related removal processes.

Instead, dilution is by influx of marine water. This process is shown by noting the chloride concentrations at the top and bottom of the water column in the prebasin (Figure 5.13). The data clearly show a marine influence in the bottom samples collected in the prebasin, where the chloride concentration approaches marine salinity (Figure 5.13).

Chloride data indicates that marine water advances into the prebasin due to tidally-forced fluctuations in Upper Newport Bay (Figure 5.13). Very little selenium and nitrate is present in marine water in Upper Newport Bay (see Chapter 6). The top samples in the prebasin primarily show a terrestrial freshwatersalinity signature and are enriched in nitrate and selenium. This suggests that a lens of terrestrial freshwater, sourced from San Diego Creek, "rides" on top of the marine layer and flows directly into Upper Newport Bay. This process delivers nutrients and selenium directly to the bay, as shown schematically in Figure 5.14.

Table 5.3: Total and Dissolved Selenium and Total Nitrate at Top and Bottom of the Water Column in Downstream Sedimentation Basins

Location	Date	Station	Depth (ft)	Diss. Se (µg/L)	Total Se (µg/L)	NO_3 (mg/L)
SDC-Basin 2-Station 1 (0.5ft)	11/20/2005	1	0.5	21.621	21.054	46.3601
SDC-Basin 2-Station 1 (2.8ft)	11/20/2005		2.8	21.525	21.257	46.3904
SDC-Basin 2-Station 2 (0.5ft)	11/20/2005	2	0.5	21.043	20.604	41.9545
SDC-Basin 2-Station 2 (4.8ft)	11/20/2005		4.8	21.043	21.675	43.9933
SDC-Basin 1-Station 1 (0.5ft)	11/27/2004	1	0.5	17.818	17.925	39.9071
SDC-Basin 1-Station 1 (5.3ft)	11/27/2004		5.3	18.814	18.557	40.1283
SDC-Basin 1-Station 5 (0.5ft)	11/27/2004	5	0.5	17.646	17.604	35.9152
SDC-Basin 1-Station 5 (2.3ft)	11/27/2004		2.3	15.461	15.332	30.2651
SDC- Prebasin Station 1 (0.5ft)	12/15/2005	1	0.5	3.193	3.225	3.6764
SDC- Prebasin Station 1 (10.7ft)	12/15/2005		3.4	3.386	3.236	3.6216
SDC- Prebasin Station 3 (0.5ft)	12/15/2005	3	0.5	4.382	3.825	4.2748
SDC- Prebasin Station 3 (10.7ft)	12/15/2005		10.7	1.725	1.564	0.8886

Table 5.3 (continued): Total and Dissolved Selenium and Total Nitrate at Top and Bottom of the Water Column in Downstream Sedimentation Basins

Location	Date	Station	Depth (ft)	Diss. Se (µg/L)	Total Se (µg/L)	NO_3 (mg/L)
SDC-Basin 2-Station 1(0.5ft)	1/8/2006	1	0.5	18.118	17.668	39.0974
SDC-Basin 2-Station 1(3.5ft)	1/8/2006		3.5	18.986	20.079	43.6203
SDC-Basin 2-Station 2 (0.5ft)	1/8/2006	2	0.5	17.250	16.157	33.5484
SDC-Basin 2-Station 2 (6.4ft)	1/8/2006		6.4	18.804	18.171	40.7662
SDC-Basin 3-Station 1(0.5ft)	1/8/2006	1	0.5	20.432	20.282	42.5976
SDC-Basin 3-Station 1(4.2ft)	1/8/2006		4.2	22.832	22.854	50.4328
SDC-Basin 1-Station 1(0.5ft)	1/19/2006	1	0.5	18.204	19.050	33.0084
SDC-Basin 1-Station 1(4.8ft)	1/19/2006		4.8	7.307	7.361	6.0832
SDC-Basin 1-Station 5(0.5ft)	1/19/2006	5	0.5	12.621	13.221	20.2877
SDC-Basin 1-Station 5(1.5ft)	1/19/2006		1.5	12.386	10.886	12.9757
SDC-Prebasin Station 1 (0.5ft)	2/2/2006	1	0.5	12.718	12.589	22.9537
SDC-Prebasin Station 1 (5.7ft)	2/2/2006		5.7	4.575	4.468	5.6679
SDC-Prebasin Station 3 (0.5ft)	2/2/2006	3	0.5	11.550	11.539	20.8195
SDC-Prebasin Station 3 (10.6ft)	2/2/2006		10.6	1.854	1.757	0.8457
SDC-Basin 2-Station 1 (0.5ft)	2/16/2006	1	0.5	16.564	16.029	27.7878
SDC-Basin 2-Station 1 (3.7ft)	2/16/2006		3.7	16.221	15.943	26.7720
SDC-Basin 2-Station 2 (0.5ft)	2/16/2006	2	0.5	17.121	16.757	29.3479
SDC-Basin 2-Station 2 (4.0ft)	2/16/2006		4.0	17.368	17.379	27.3357
SDC-Basin 3-Station 1 (0.5ft)	2/16/2006	4	0.5	20.518	20.421	42.3254
SDC-Basin 3-Station 1 (3.9ft)	2/16/2006		3.9	20.325	20.164	38.6647
SDC-Basin 1-Station 1(0.5ft)	3/2/2006	1	0.5	8.025	8.046	28.2402
SDC-Basin 1-Station 1(3.8ft)	3/2/2006		3.8	8.036	8.207	28.1808
SDC-Basin 1-Station 5(0.5ft)	3/2/2006	5	0.5	6.300	6.268	25.3996
SDC-Basin 1-Station 5(2.2ft)	3/2/2006		2.2	6.343	6.225	25.5146
SDC-Prebasin Station 1(0.5ft)	3/16/2006	1	0.5	8.968	9.032	16.5981
SDC-Prebasin Station 1(3.9ft)	3/16/2006		3.9	3.396	3.375	6.4496
SDC-Prebasin Station 3(0.5ft)	3/16/2006	3	0.5	7.554	7.586	14.6365
SDC-Prebasin Station 3(11.4ft)	3/16/2006		11.4	1.950	1.961	2.6144
SDC-Basin 2 Station 1(0.5ft)	3/23/2006	1	0.5	7.457	7.404	25.3045
SDC-Basin 2 Station 1(4ft)	3/23/2006		4.0	7.864	7.961	16.3097
SDC-Basin 2 Station 2(0.5ft)	3/23/2006	2	0.5	6.525	6.782	16.3504
SDC-Basin 2 Station 2(4ft)	3/23/2006		4.0	7.993	7.971	17.5190
SDC-Basin 3 Station 1(0.5ft)	3/23/2006	1	0.5	13.907	13.693	40.0268
SDC-Basin 3 Station 1(4.2ft)	3/23/2006		4.2	15.150	15.011	42.2621
SDC-Basin 1-Station 1(0.5ft)	3/30/2006	1	0.5	4.757	4.671	21.0999
SDC-Basin 1-Station 1(5.3ft)	3/30/2006		5.3	4.714	4.586	21.1441
SDC-Basin 1-Station 5(0.5ft)	3/30/2006	5	0.5	3.096	3.118	13.8403
SDC-Basin 1-Station 5(3.8ft)	3/30/2006		3.8	3.429	3.557	15.4428
SDC-Prebasin Station 1 (0.5ft)	4/11/2006	1	0.5	9.461	9.354	12.9113
SDC-Prebasin Station 1 (4.4ft)	4/11/2006		4.4	4.489	4.243	6.7460
SDC-Prebasin Station 3 (0.5ft)	4/11/2006	3	0.5	7.784	7.864	10.8812
SDC-Prebasin Station 3 (10.1ft)	4/11/2006		10.1	2.250	2.175	3.0895

Table 5.3 (continued): Total and Dissolved Selenium and Total Nitrate at Top and Bottom of the Water Column in Downstream Sedimentation Basins

Location	Date	Station	Depth (ft)	Diss. Se (µg/L)	Total Se (µg/L)	NO_3 (mg/L)
Basin 2 Station 1(0.5ft)	4/18/2006	1	0.5	8.261	8.239	14.4318
Basin 2 Station 1(4.1ft)	4/18/2006		4.1	8.229	8.175	13.0555
Basin 2 Station 2(0.5ft)	4/18/2006	2	0.5	7.671	7.650	15.4915
Basin 2 Station 2(5.1ft)	4/18/2006		5.1	8.775	8.732	16.6376
Basin 3 Station 1(0.5ft)	4/18/2006	1	0.5	16.736	16.875	40.7157
Basin 3 Station 1(4.5ft)	4/18/2006		4.5	19.479	19.500	41.3128
Basin 1-Station 1(0.5ft)	5/2/2006	1	0.5	12.461	11.904	16.7341
Basin 1-Station 1(4.3ft)	5/2/2006		4.3	12.032	12.204	16.8473
Basin 1-Station 5(0.5ft)	5/2/2006	5	0.5	11.700	11.421	15.3195
Basin 1-Station 5(2.4ft)	5/2/2006		2.4	12.321	11.625	12.8878
Prebasin Station 1 (0.5ft)	5/9/2006	1	0.5	12.471	12.514	14.1114
Prebasin Station 1 (4.3ft)	5/9/2006		4.3	6.482	6.536	5.0025
Prebasin Station 3 (0.5ft)	5/9/2006	3	0.5	11.004	10.757	11.1647
Prebasin Station 3 (10.2ft)	5/9/2006		10.2	2.186	1.993	0.4873
Basin 2 Station 1 (0.5 ft)	5/18/2006	1	0.5	15.343	15.300	18.2219
Basin 2 Station 1 (3.6 ft)	5/18/2006		3.6	14.496	15.043	15.5524
Basin 2 Station 2 (0.5 ft)	5/18/2006	2	0.5	14.850	14.550	15.6751
Basin 2 Station 2 (3.5 ft)	5/18/2006		3.5	14.807	14.925	16.6782
Basin 3 Station 1 (0.5 ft)	5/18/2006	1	0.5	19.061	18.493	37.2636
Basin 3 Station 1 (4.1 ft)	5/18/2006		4.1	18.986	19.104	36.9787
Basin 1, Station 5 (0.5 ft)	5/31/2006	5	0.5	12.686	12.493	8.2322
Basin 1, Station 5 (2.2 ft)	5/31/2006		2.2	11.571	11.711	6.7305
Basin 1, Station 1 (0.5 ft)	5/31/2006	1	0.5	13.414	13.693	12.3708
Basin 1, Station 1 (bottom)	**sample**	**device**	**broken**	**cannot**	**sample**	**Bottom**
Pre-Basin Station 1 (0.5 ft)	6/8/2006	1	0.5	13.168	13.564	17.8810
Pre-Basin Station 1 (5.3 ft)	6/8/2006		5.3	5.400	5.561	3.2913
Pre-Basin Station 3 (0.5 ft)	6/8/2006	3	0.5	10.907	11.046	13.6952
Pre-Basin Station 3 (10.9 ft)	6/8/2006		10.9	1.682	2.239	0.4133
Basin 2 Station 1 (0.5 ft)	6/12/2006	1	0.5	14.496	14.411	29.2103
Basin 2 Station 1 (3.5 ft)	6/12/2006		3.5	13.864	13.864	26.9452
Basin 2 Station 2 (0.5 ft)	6/12/2006	2	0.5	13.639	13.725	24.8114
Basin 2 Station 2 (3.3 ft)	6/12/2006		3.3	13.543	13.329	24.7701
Basin 3 Station 1 (0.5 ft)	6/12/2006	1	0.5	15.332	15.343	34.0388
Basin 3 Station 1 (4.5 ft)	6/12/2006		4.5	15.471	15.579	33.2908
Basin 1 Station 1 (0.5 ft)	7/5/2006	1	0.5	11.271	11.111	9.1590
Basin 1 Station 1 (3.6 ft)	7/5/2006		3.6	10.661	10.629	9.1335
Basin 1 Station 5 (0.5 ft)	7/5/2006	5	0.5	8.732	8.400	2.8058
Basin 1 Station 5 (1.9ft)	7/5/2006		1.9	9.086	8.646	3.0036
Prebasin Station 1 (0.5 ft)	7/15/2006	1	0.5	10.436	10.318	7.1543
Prebasin Station 1 (4.2 ft)	7/15/2006		4.2	8.454	8.625	5.4576
Prebasin Station 3 (0.5 ft)	7/15/2006	3	0.5	9.214	9.204	5.9818
Prebasin Station 3 (13.3 ft)	7/15/2006		13.3	1.704	1.832	0.1607

Table 5.3 (continued): Total and Dissolved Selenium and Total Nitrate at Top and Bottom of the Water Column in Downstream Sedimentation Basins

Location	Date	Station	Depth (ft)	Diss. Se (µg/L)	Total Se (µg/L)	NO_3 (mg/L)
Basin 1 Station 1 (0.5 ft)	7/20/2006	1	0.5	16.125	15.375	20.4705
Basin 1 Station 1 (4 ft)	7/20/2006		4.0	15.793	14.796	20.5988
Basin 1 Station 5 (0.5 ft)	7/20/2006	5	0.5	15.011	14.025	17.4181
Basin 1 Station 5 (2.4 ft)	7/20/2006		2.4	12.707	11.904	11.2375
Basin 2 Station 1 (0.5 ft)	7/27/2006	1	0.5	10.564	10.393	14.5163
Basin 2 Station 1 (3.8 ft)	7/27/2006		3.8	8.882	8.646	10.3503
Basin 2 Station 2 (0.5 ft)	7/27/2006	2	0.5	9.000	8.989	10.2182
Basin 2 Station 2 (5.5 ft)	7/27/2006		5.5	9.032	8.861	10.2609
Basin 3 Station 1 (0.5 ft)	7/27/2006	1	0.5	13.757	13.521	24.4675
Basin 3 Station 1 (4.3 ft)	7/27/2006		4.3	13.661	14.014	28.5569
Basin 2 Station 1 (0.5 ft)	8/17/2006	1	0.5	9.750	8.936	6.8749
Basin 2 Station 1 (3.7 ft)	8/17/2006		3.7	10.350	9.536	8.2569
Basin 2 Station 2 (0.5 ft)	8/17/2006	2	0.5	10.821	10.114	8.9084
Basin 2 Station 2 (3.6 ft)	8/17/2006		3.6	9.632	9.696	9.0981
Prebasin Station 1 (0.5 ft)	8/17/2006	1	0.5	8.507	8.368	3.5488
Prebasin Station 1 (5.4 ft)	8/17/2006		5.4	4.254	4.382	0.4538
Prebasin Station 3 (0.5 ft)	8/17/2006	3	0.5	6.793	6.579	2.4538
Prebasin Station 3 (13.0 ft)	8/17/2006		13.0	2.079	1.821	ND
Basin 1 Station 1 (0.5 ft)	8/29/2006	1	0.5	9.814	8.925	6.8154
Basin 1 Station 1 (4.7 ft)	8/29/2006		4.7	9.246	9.075	6.8427
Basin 1 Station 5 (0.5 ft)	8/29/2006	5	0.5	8.721	8.250	2.6916
Basin 1 Station 5 (1.9 ft)	8/29/2006		1.9	8.561	8.636	2.6844
Basin 3 Station 1 (0.5 ft)	8/29/2006	1	0.5	17.979	18.032	29.8226
Basin 3 Station 1 (4.4 ft)	8/29/2006		4.4	16.982	16.918	27.8700
Basin 2 Station 1 (0.5 ft)	9/13/2006	1	0.5	15.407	15.043	23.3079
Basin 2 Station 1 (4.0 ft)	9/13/2006		4.0	15.343	15.482	23.9457
Basin 2 Station 2 (0.5 ft)	9/13/2006	2	0.5	13.554	13.596	18.7843
Basin 2 Station 2 (4.2 ft)	9/13/2006		4.2	13.157	12.986	18.1431
Prebasin Station 1 (0.5 ft)	9/13/2006	1	0.5	13.157	13.114	16.4551
Prebasin Station 1 (6.9 ft)	9/13/2006		6.9	5.196	5.196	3.9066
Prebasin Station 3 (0.5 ft)	9/13/2006	3	0.5	12.418	12.450	15.1187
Prebasin Station 3 (13.3 ft)	9/13/2006		13.3	1.929	1.736	0.6163
Basin 1 Station 1 (0.5 ft)	9/19/2006	1	0.5	14.068	14.121	17.7398
Basin 1 Station 1 (5.4 ft)	9/19/2006		5.4	13.971	14.368	17.6859
Basin 1 Station 5 (0.5 ft)	9/19/2006	5	0.5	13.757	14.046	18.5338
Basin 1 Station 5 (2.7 ft)	9/19/2006		2.7	13.393	13.200	15.8245
Basin 3 Station 1 (0.5 ft)	9/19/2006	1	0.5	17.796	18.086	32.1447
Basin 3 Station 1 (4.4 ft)	9/19/2006		4.4	17.861	17.711	31.9738

Table 5.3 (continued): Total and Dissolved Selenium and Total Nitrate at Top and Bottom of the Water Column in Downstream Sedimentation Basins

	Date	Station	Depth (ft)	Diss. Se (µg/L)	Total Se (µg/L)	NO_3 (mg/L)
Basin 1, Station 1 (0.5 ft)	10/11/2006	1	0.5	12.632	12.921	20.8781
Basin 1, Station 1 (5.0 ft)	10/11/2006		5.0	3.814	3.793	1.5497
Basin 1, Station 5 (0.5 ft)	10/11/2006	5	0.5	4.629	4.254	3.3614
Basin 1, Station 5 (2.5 ft)	10/11/2006		2.1	4.146	4.093	3.3303
Basin 3 Station 1 (0.5 ft)	10/11/2006	1	0.5	18.011	17.561	39.8709
Basin 3, Station 1 (4.4 ft)	10/11/2006		4.4	17.754	17.636	40.0597
Prebasin Station 1 (0.5 ft)	10/29/2006	1	0.5	11.529	11.336	13.1873
Prebasin Station 1 (7.6 ft)	10/29/2006		7.6	3.471	3.279	2.4789
Prebasin Station 3 (0.5 ft)	10/29/2006	3	0.5	9.750	9.364	11.6232
Prebasin Station 3 (13.5 ft)	10/29/2006		13.5	1.800	1.650	0.6709
Basin 2 Station 1 (0.5 ft)	11/15/2006	1	0.5	12.707	12.504	31.5138
Basin 2 Station 1 (3.6 ft)	11/15/2006		3.6	12.493	12.364	32.5486
Basin 2 Station 2 (0.5 ft)	11/15/2006	2	0.5	13.082	13.018	31.8916
Basin 2 Station 2 (4.9 ft)	11/15/2006		4.9	15.536	15.450	35.0763
Basin 1 Station 1 (0.5 ft)	12/6/2006	1	0.5	12.439	12.450	24.4989
Basin 1 Station 1 (5.0 ft)	12/6/2006		5.0	4.393	4.361	4.7945
Basin 1 Station 5 (0.5 ft)	12/6/2006	5	0.5	12.804	12.932	24.9329
Basin 1 Station 5 (4.0 ft)	12/6/2006		4.0	3.675	4.029	5.5670
Prebasin Station 1 (0.5 ft)	12/7/2006	1	0.5	9.536	9.354	17.2488
Prebasin Station 1 (6.1 ft)	12/7/2006		6.1	2.711	2.593	3.4396
Prebasin Station 3 (0.5 ft)	12/7/2006	3	0.5	7.832	7.961	14.0041
Prebasin Station 3 (11.3 ft)	12/7/2006		11.3	1.950	1.939	1.5505
Basin 2 Station 1 (0.5 ft)	12/12/2006	1	0.5	6.600	6.493	28.5905
Basin 2 Station 1 (4.0 ft)	12/12/2006		4.0	8.004	8.196	24.1159
Basin 2 Station 2 (0.5 ft)	12/12/2006	2	0.5	6.150	6.161	27.8291
Basin 2 Station 2 (5.0 ft)	12/12/2006		5.0	8.057	8.229	21.8739
Basin 3 Station 1 (0.5 ft)	12/12/2006	1	0.5	9.932	9.911	29.5590
Basin 3 Station 1 (4.2 ft)	12/12/2006		4.2	10.436	10.693	29.9041
Prebasin Station 1 (0.5 ft)	1/18/2007	1	0.5	14.379	14.679	44.3146
Prebasin Station 1 (6.0 ft)	1/18/2007		6.0	7.468	7.704	22.7112
Prebasin Station 3 (0.5 ft)	1/18/2007	3	0.5	11.636	11.957	37.0296
Prebasin Station 3 (11.0 ft)	1/18/2007		11.0	2.689	2.925	4.6664
Basin 3 Station 1 (1.25 ft)	1/18/2007	1	1.3	13.671	13.618	41.1663
Basin 1 Station 1 (0.5 ft)	2/1/2007	1	0.5	7.929	8.411	24.8502
Basin 1 Station 1 (4.8 ft)	2/1/2007		4.8	7.179	7.350	14.7459
Basin 1 Station 2 (0.5 ft)	2/1/2007	2	0.5	7.832	7.939	25.3592
Basin 1 Station 2 (2.0 ft)	2/1/2007		2.0	7.929	8.057	24.1437
Basin 1 Station 4 (0.5 ft)	2/1/2007	4	0.5	7.157	7.382	26.4803
Basin 1 Station 4 (2.2 ft)	2/1/2007		2.2	8.625	9.075	20.0471
Basin 1 Station 5 (0.5 ft)	2/1/2007	5	0.5	7.286	7.639	26.5267
Basin 1 Station 5 (2.9 ft)	2/1/2007		2.9	6.579	7.146	15.5763

3. Time Series Analysis of Nitrate, Selenium, and Chloride in Downstream Sedimentation Basins

Monthly time series data are plotted for the sediment basins and mixing prebasin (see Figures 5.15 to 5.21) for the time period lasting from November 2005 to February 2007. To provide context for the following discussion, it is restated here that some nitrate and selenium are removed from water flowing through San Joaquin Marsh (see chapter 4). A clear dilution effect is observed in downstream basins when IRWD releases water from the marsh (Figure 5.22). When flows are not cycled in and out of San Joaquin Marsh, concentrations of nitrate and selenium in the sediment basins are naturally higher. Other factors, such as elevated groundwater levels and groundwater baseflows at different times of the year, amount of nitrate-and-selenium consuming organic material in streambed interstices, and percentage of dry weather urban runoff all factor into the variable concentrations of selenium and nitrate in San Diego Creek.

Upstream of the marsh outlet, sediment basin 3 is not affected by discharge from the marsh. Therefore, nitrate and selenium concentrations in this sediment basin are derivative of other processes in the watershed. Overall, there was a general dilution of nitrate, selenium, and chloride in basin 3 during the fourteen-month monitoring period (Figure 5.15). Dilution is probably a result of decaying hydraulic head in the shallow aquifer in San Diego Creek Watershed. Lower hydraulic head in the shallow aquifer decreases the rate of groundwater flux. Groundwater flux, in turn, is responsible for much of the nitrate and selenium loading in surface streams in the watershed. Decay of hydraulic head in the shallow aquifer was manifested during one of the driest years on record, when little aquifer recharge was recorded (see Chapter 3).

There is little difference between the ion concentrations in the top and bottom of the water column at sediment basin 3 (Figure 5.15). This suggests that there is little removal of nitrate or selenium near the sediment/water interface. A noticeable drop in selenium and chloride concentrations occurs in sediment basin 3 during late March and early April, 2006 (Figure 5.15). Nitrate does not decrease during March and April 2006 (Figure 5.15), possibly because storm runoff and/or agricultural runoff carries a comparable amount of nitrate into surface streams compared to concentration delivered by groundwater baseflow.

A second important dilution effect is observed for all parameters in July, 2006 (Figure 5.15). Summer dilution in sediment basin 3 is probably due to urban runoff from urban sprinklers during the peak of the dry season. Dry weather runoff usually has very low concentrations of nitrate, except when it contains a lot of treated wastewater (Hibbs, 2000).

Downstream in sediment basin 2, the water released from San Joaquin Marsh clearly results in lower selenium and nitrate concentrations in this basin (compare Figures 5.16, 5.17, and 5.22). The flows discharged from the marsh contain about 20% lower selenium concentrations and about 90% lower nitrate concentrations than inlet flows. The contaminants in the creek become more dilute due to the discharge of these cleaner flows from the San Joaquin Marsh. This marsh-generated dilution effect is overprinted on other dilution and enrichment processes, including stormwater runoff, dry weather urban runoff, agricultural runoff, and groundwater baseflow. Determining the contribution of each of these individual processes is beyond the scope and budget of this study.

A noticeable decrease in selenium and nitrate concentration occurs during two time periods in sediment basin 2; March-April 2006 and July 2006 (Figures 5.16 and 5.17). Discharge from San Joaquin Marsh accounts for most of the nitrate decline in sediment basin 2 during March-April 2006 (compare figures 5.16, 5.17, and 5.22). Selenium concentrations are reasonably well correlated with chloride during most of the monitoring period at sediment basin 2 (compare Se and Cl curve shapes in Figures 5.16 and 5.17). This correlation is probably a function of the percentage of groundwater baseflow that makes up the total discharge of San Diego Creek.

There is usually little difference between ion concentrations in the top and bottom water samples at sediment basin 2. Slight differences are noted for chemistries in top and bottom water samples during March-April 2006 and especially during December 2006 (last sample event). Most likely a storm event diluted chloride and selenium concentration in the top sample during December 2006, while simultaneously enriching nitrate (Figure 5.16 and 5.17).

Trending downstream, sediment basin 1 exhibits radically different chemistry relationship in top and bottom water samples (Figures 5.18 and 5.19). At times when top and bottom samples have almost identical concentrations of nitrate and selenium (March 2006 to September 2006) the concentration of chloride is also nearly identical in top and bottom water samples. When this happens, the chloride concentration is primarily dilute, indicating that there is no intrusion of marine water. When concentrations of chloride at top and bottom water samples are different, the concentration of nitrate and selenium at top and bottom is also different (i.e., the chloride concentration is greatly enriched in the bottom samples, while nitrate and selenium concentrations are very dilute in the bottom

samples, Figures 5.18 and 5.19). The different chemical signatures at top and bottom stations is due to occasional intrusion of marine water into sediment basin 1 as a result of larger tidal fluctuations in Upper Newport Bay. Water from the terrestrial sources rides on top of the underlying layer of marine water that has advanced up into sediment basin 1 (Figure 5.6). The terrestrial layer contains most of the nitrate and selenium in the water column.

The process of stratification of marine and terrestrial water is indicated during most months in the mixing prebasin (Figures 5.20 and 5.21). The higher the chloride concentration, the lower the nitrate and selenium concentration. The waters are highly stratified with respect to these chemical parameters; chloride in particular is close to marine salinity in most bottom samples, particularly at prebasin station 3 (Figure 5.21). The delivery of nitrate and selenium to Upper Newport Bay via the terrestrial "sheetflow effect" is shown in these data during most months.

4. Selenium Speciation Data in Water Column in Downstream Sedimentation Basins

Selenium speciation data were collected in sediment basins on a one time basis (Table 5.4). Sediment basin 2 was being dredged when speciation data were collected, so no speciation data were collected there. The speciation data indicate that selenite (selenium IV) is a moderate to moderately low percentage of total selenium (9% to 20%). The relative percentage of selenite is greater than in most shallow groundwaters in San Diego Creek Watershed however. Shallow groundwater in the watershed often contains less than 4% selenite. Relative percentages of selenite and selenate (selenium VI) do not change substantially from top to bottom of the water column (Table 5.4). Stratification of

total selenium varies from top to bottom of the water column at some stations however, but this variance is more a function of mixing with marine water that contains little selenium.

Table 5.4: Selenium Speciation at Top and Bottom of the Water Column in Downstream Sedimentation Basins

Location	Date	Se (IV) (ug/L)	Se (VI) (ug/L)	Org-Se (ug/L)	Total-Se (ug/L)
Prebasin Station 1 TOP (0.5 ft)	1/18/2007	1.500	12.879	<0.5	14.379
Prebasin Station 1 Bottom (6.0 ft)	1/18/2007	0.783	6.685	<0.5	7.468
Prebasin Station 3 TOP (0.5 ft)	1/18/2007	1.337	10.299	<0.5	11.636
Prebasin Station 3 Bottom (11.0 ft)	1/18/2007	0.323	2.366	<0.5	2.689
Basin 3 Station 1 Mid-point (1.25 ft)	1/18/2007	1.003	12.668	<0.5	13.671
Basin 1 Station 5 TOP (0.5 ft)	2/1/2007	0.757	6.529	<0.5	7.286
Basin 1 Station 5 Bottom (2.9 ft)	2/1/2007	1.020	5.559	<0.5	6.579
Basin 1 Station 4 TOP (0.5 ft)	2/1/2007	1.007	6.150	<0.5	7.157
Basin 1 Station 4 Bottom (2.2 ft)	2/1/2007	1.197	7.428	<0.5	8.625
Basin 1 Station 2 TOP (0.5 ft)	2/1/2007	1.007	6.825	<0.5	7.832
Basin 1 Station 2 Bottom (2.0 ft)	2/1/2007	1.157	6.772	<0.5	7.929
Basin 1 Station 1 TOP (0.5 ft)	2/1/2007	1.150	6.779	<0.5	7.929
Basin 1 Station 1 Bottom (4.8 ft)	2/1/2007	1.100	6.079	<0.5	7.179

5. Water Column Dissolved Oxygen Profiles

One of the best indicators of a water bodies' health is its dissolved oxygen concentration (Table 5.5). Many organisms require oxygen for respiration, so it is crucial for their survival that there are adequate amounts of oxygen dissolved in the water. Extremely high levels of oxygen in the water also have negative consequences for aquatic organisms. For example, "water supersaturated with oxygen can cause gas bubble disease in fishes. Gas bubbles form beneath the epithelium of the fish externally and internally causing the fish great stress" (Horn 2001).

Table 5.5: Dissolved Oxygen Guidelines

Dissolved Oxygen Level	*Condition of Biota*
Above 5 mg/L	Fully supported aquatic life; most plants and animals can grow and reproduce unimpaired
Between 3 - 5 mg/L	Living organisms can become stressed
Between 0.5 - 3 mg/L (hypoxia)	Many species will relocate or perish if they are immobile
Below 0.5 mg/L (anoxia)	Death of any organism that requires oxygen for survival

Source: Ohrel and Register 2000

Oxygen enters surface waters mainly from the atmosphere and through aquatic plant photosynthesis. Dissolved oxygen (DO) concentrations indicate the amount of aeration in the water column, and can be expressed as percent saturation or the amount of oxygen in the water relative to the water's potential DO saturation. DO saturation refers to the highest DO concentration possible under limits of temperature, salinity, and atmospheric pressure. Oxygen solubility in water is not particularly high, usually around 12 mg/L, or 100% saturation. However, photosynthesis by aquatic plants can supersaturate dissolved oxygen in water to concentrations exceeding 25 mg/L.

Dissolved oxygen profile data collected in this study are cataloged in Appendix 5.0. Select dissolved oxygen profiles are presented for winter and summer periods at stations where selenium and nitrate data were also collected (Figures 5.23 to 5.29).

Sediment basin 3 has dissolved oxygen concentrations very close to 100% saturation during the winter (Figure 5.23). During the summer months, dissolved oxygen concentrations are supersaturated in basin 3. Water in sediment basin 3 has plenty of nitrogen to generate excessive algal growth (Figure 5.23). Proliferation of algae and phytoplankton during the summer probably causes supersaturation of DO due to high rates of photosynthesis in the water column.

Similar results are observed in sediment basin 2. Dissolved oxygen is near 100% saturation during the winter and is supersaturated during the summer, except near the bottom of the water column (Figures 5.24 and 5.25). Sometimes the very bottom sample contains no dissolved oxygen (Figure 5.24 and 5.25). This is because the dissolved oxygen probe was always allowed to rest on the bottom of the sediment basins at the sediment/water interface. Where bottom sediments are rich in oxygen-consuming organic detritus, the dissolved oxygen concentration plummets to zero. Where the bottom sediments are sand-rich and organic-poor, the dissolved oxygen values are sometimes close to 100% saturation (Figures 5.24 and 5.25). We never knew what kind of sediments were present at the sediment/water interface until the DO probe was placed on the bottom of the basin. Sediment types appeared to change regularly at individual stations due to erosion, deposition, and channel modifications.

Sediment basin 1 has stations that are both deep (~5 feet) and shallow (~2 feet) (Figures 5.26 and 5.27). Winter dissolved oxygen concentrations are sometimes higher than summer dissolved oxygen concentrations at this basin (Figures 5.26 and 5.27). Also, station 5 had extremely high concentrations of dissolved oxygen at the bottom of the water column during many winter sampling runs (Figure 5.27 and Appendix 5.0). These are anomalous results. We hypothesize that algae growing on the bottom sediments at station 5 may have received enough direct sunlight to supersaturate the water column with dissolved oxygen via photosynthesis. The water column at station 5, being very shallow (~2 ft), was relatively free of turbidity during several winter sample runs, allowing sunlight to penetrate to the bottom of the water column.

The mixing prebasin has the most unique dissolved oxygen profiles (Figures 5.28 and 5.29). The "terrestrial freshwater layer" at the upper part of the water column (discussed in previous sections) routinely contains supersaturated dissolved oxygen concentrations (Figures 5.28 and 5.29). The underlying predominantly marine water layer is always below 100% dissolved oxygen saturation. Sometimes the marine layer has no dissolved oxygen, even several feet above the sediment/water interface (Figure 5.29).

Two processes probably explain these dissolved oxygen profiles. First, dilute terrestrial freshwater layer in the basin contains a lot more nitrate, providing a fertile medium for growth of oxygen-emitting phytoplankton. Second, the decaying phytoplankton, dead algae, and detritus from riverine inputs are the organic sources that are decomposed by bacteria at the sediment/water interface. This oxygen-consuming decomposition outpaces the rate of oxygen diffusion from the surface, which explains the negligible dissolved oxygen concentrations during the summer months at station 3 (Figure 5.29) (Rabalais and others, 2002).

Dissolved oxygen concentrations in the prebasin affect nutrient biogeochemical processes. When anoxic conditions occur, nutrients bound to bottom sediments can be released into the water column, thereby permitting more plankton growth and eventually more oxygen depletion. Other pollutants such as heavy metals may also be released from sediments under low oxygen conditions, potentially causing problems for the water system (Ohrel and Register 2000).

6. Nutrient Biogeochemical Cycling Processes in Mixing Prebasin

Anoxia of bottom waters in the mixing prebasin was identified during summer months (Figures 5.28 and 5.29). The condition of anoxia in the water column can have a

considerable effect on nutrient biogeochemical cycling in prebasin sediments and waters. Longitudinal water quality sections in downstream basins indicates that nutrient redox transformations are occurring, due to a profound increase in orthophosphate and ammonium in the mixing prebasin during the summer months (Figure 5.30). Orthophosphate and ammonium concentrations increase from almost undetectable amounts above the mixing prebasin to over 0.7 mg/L orthophosphate and 1.5 mg/L ammonium within the prebasin. Increase in orthophosphate and ammonium concentrations at bottom stations is especially evident (Figure 5.30).

Time series data compares dissolved oxygen concentrations, orthophosphate concentrations, and ammonium concentrations in top and bottom stations in the mixing prebasin (Figures 5.31 and 5.32). Dissolved oxygen concentrations are saturated to supersaturated in the top stations throughout the year (Figures 5.31 and 5.32). Dissolved oxygen trends to zero values in bottom stations during the summer months. During winter, spring, and fall, dissolved oxygen concentrations trend back upward to nearly saturated levels at bottom stations (Figures 5.31 and 5.32). Higher temperatures during the summer decrease oxygen saturation slightly, and oxygen-consuming decomposition of summer organic matter outpaces the rate of oxygen diffusion from the surface. These processes lead to anoxia of bottom waters and sediments during the summer months.

In general, concentrations of orthophosphate and ammonium peak to very high levels during the summer months in bottom stations in the prebasin, especially at station 3 (Figures 5.31 and 5.32). Concentrations of orthophosphate and ammonium reach 1.5 mg/L and 1.6 mg/L respectively at bottom stations. Top stations usually have low concentrations of orthophosphate and ammonium, rarely exceeding 0.25 mg/L (Figures

5.31 and 5.32). Concentrations of these nutrients are inversely related to concentrations of dissolved oxygen, peaking when anoxia of bottom waters is observed. A few anomalies are identifiable; for instance a July 2006 event where prebasin station 1 had supersaturated dissolved oxygen in the bottom station ("dissolved oxygen anomaly" in Figure 5.33). Mixing between top and bottom waters occurred during this period, as indicated by the similar chloride and ammonium concentrations at top and bottom stations (Figure 5.33). Mixing and turbulence during this "anomaly" period distributed dissolved oxygen and other parameters more uniformly in the water column at station 1.

Apparent release of orthophosphate and ammonium from bottom sediments is directly related to redox conditions in the sediments and water column (Figures 5.34 and 5.35). Under oxygenated conditions, phosphate forms chemical complexes with metals such as iron, aluminum, and manganese in bottom sediments (Figure 5.34) (Ohrel and Register 2000). If the bottom waters becomes anoxic, phosphate bound to the sediments is released back into pore water due to reduction of the metal-phosphorous compounds, which frees phosphorous (Figure 5.34). This release is generally referred to as internal loading of phosphorous. The decomposition of organic matter being deposited into the bottom sediments can mineralize; thereby increasing concentrations of dissolved inorganic phosphorus in the sediment pore waters.

Pore water occupies liquid-filled interstitial spaces amid the solid particles of the sediments, which are usually mixed by wave action, tidal pumping, and benthic activity (Figure 5.36). The sediment-water interface acts as a barrier to the free interchange of phosphorous when waters are oxidizing (Figure 5.34). Phosphate ions can pass across the interface at a high rate if it is anoxic, especially due to processes such as tidal

pumping caused by fluid exchange between water column and interstitial waters in bottom sediments (Figure 5.36). Anoxic sediments can release phosphate up to 1000 times faster than releases from oxygenated sediments. This process is attributable to both classical chemical bonding and physiochemical desorptive mechanisms (Horne and Goldman 1994).

High ammonium concentrations in bottom waters during anoxia suggest that nitrate is either being reduced directly to ammonium through dissimilatory nitrate reduction (Equation 1) or organic materials are being remineralized through ammonification (Equation 2). Figure 5.35 shows a likely model for these processes. Dissimilatory nitrate reduction is a microbially mediated process that requires organic matter and oxygen-deficient conditions for reduction of nitrate to ammonium. Measuring dissolved oxygen was useful in showing that this chemical process is probably occurring because the amount of oxygen in the soil or water determines the aerobic or anaerobic nature of the waters and bottom sediments. Dentrification (producing nitrogen gas) is not the only speciation process that reduces nitrate; dissimilatory nitrate reduction is also an important process.

Ammonification is the biological transformation of organic nitrogen to ammonia, which proceeds in anaerobic as well as aerobic conditions (Equation 2). Although ammonification proceeds more slowly in reducing conditions because of the reduced efficiency of heterotrophic decomposition in anaerobic environments, ammonia is more likely to accumulate in these systems because of the decreased nitrification rates (Kadlec and Knight 1996). Ammonia released from these sources can then diffuse directly or be advected up to the water column through benthic flux and tidal pumping (Figure 5.36).

EQUATION 1: DISSIMILATORY NITRATE REDUCTION

$$NO_3^- + H_2O + 2CH_2O(\text{organic material}) = NH_4^+(\text{ammonium}) + 2HCO_3^-$$

EQUATION 2: AMMONIFICATION (MINERALIZATION)

$$CH_2O\ (NH_3) + O_2 = NH_4^+ + HCO_3^-$$

7. Basin No. 2 Site Specific Analysis of Hyporheic Zones.

In this section, studies of the sediment interstitial waters test hypotheses that dissimilatory nitrate reduction and reductive dissolution of metal-phosphorous compounds are possible internal sources of ammonium and orthophosphate. The section also examines redox conditions and possible selenium and nitrate removal in the interstitial streambed waters and sediments (hyporheic zone). These tests were done before intensive studies of the downstream sediment basins were underway, and were carried out in sediment basin 2 only.

Extrapolating results from sediment basin 2 to the prebasin is a risky step. Though we did not usually observe any significant internal input of orthophosphate and ammonium from the bottom sediments to surface water in sediment basin 2 (Figure 5.30), we did at times observe dissolved oxygen at zero saturation at the sediment/water interface (Figures 5.24 and 5.25). We also did not see tidal pulses that strongly accentuate exchange of sediment interstitial waters and free water above the sediment water interface. Nevertheless, site specific results for sediment basin 2 are meaningful, and are presented here for context on processes that occur in sediment interstitial waters in the sediment basins.

Two sets of field runs were done in sediment basin 2. The first was carried out June 2003 and the second was carried out October 2004. Results are presented for the two runs.

A. Sediment Interstitial/Water Column Studies in Sediment Basin 2, June, 2003

Sediment basin 2 was partially drained June 12, 2003. We used this opportunity to collect sediment and water quality samples from the sediment basin (Figure 5.37). The basin was not completely drained during the sampling period, and a few inches to a few feet of surface water head existed over a large part of the basin. Water samples were collected from the surface water column, sediment interstitial waters (hereafter called "hyporheic zone" or "hyporheic water"), and IRWD ground water outlet (Figures 5.37 and 5.38). Grab samples were collected from the stream and IRWD groundwater outlet. The hyporheic zone was sampled with a stainless steel mini-piezometer and peristaltic pump.

Water quality data collected from sediment basin 2 are presented in Table 5.6. Nutrient data collected from the three sample zones indicate that nitrate concentrations are relatively high in surface water (6.6 mg/L NO3-N), and are very low in hyporheic water and groundwater (<0.1 and 0.6 mg/L NO3-N) (Table 5.6). Ammonium concentrations are high in hyporheic water (3.9 mg/L NH4+-N), and are relatively low in surface water and groundwater (<0.1 and 0.3 mg/L NH4+-N) (Table 5.6).

High nitrate and low ammonium in surface water are probably due to relatively oxidizing conditions in the surface water column (see dissolved oxygen profiles, Figures 5.23 to 5.29). Likewise, negligible nitrate concentrations and high ammonium

concentrations in hyporheic water are probably due to reducing conditions in the hyporheic zone (Figure 5.39). Low nitrate and low ammonium concentration in local groundwater, as measured at the IRWD groundwater discharge, probably indicates that surface water was flowing into the hyporheic zone at this particular sampling location, and not groundwater. Groundwater in this location may not have a sufficient amount of nitrogen to produce the ammonium measured in the hyporheic zone.

Nitrate in infiltrating surface water is probably reduced to ammonium in the hyporheic zone by dissimilatory nitrate reduction (Equation 1, Section 6). Sufficient organic matter is available in the hyporheic zone (see Table 5.6) to accommodate dissimilatory nitrate reduction (Equation 1). The data also indicates that orthophosphate and total phosphorous are relatively high in the hyporheic zone (2.15 and 3.74 mg/L respectively) (Table 5.6); however, the same phosphorous species are well below 0.2 mg/L in surface water and groundwater.

Reducing conditions could produce high orthophosphate concentrations in the hyporheic zone, as iron-phosphorus compounds tend to go into solution when the iron is reduced (Figures 5.39 and 5.40). Along with reduction of sulfate in the hyporheic zone, the sulfide gas byproducts can bind with soluble iron to produce iron sulfide compounds (note the lower concentration of sulfate in the hyporheic zone, Table 5.6). Orthophosphate probably goes into solution in the hyporheic zone when iron-phosphorous compounds are reduced. Iron is simultaneously removed from the hyporheic waters as it binds with sulfides (Figure 5.39 and 5.40).

The water quality data appear to support this interpretation, as iron is low in surface water and hyporheic water (<0.02 mg/L dissolved Fe), orthophosphate is high in

hyporheic water only (2.15 mg/L), and sulfate is lowest in hyporheic water (Table 5.6). High manganese concentrations in hyporheic water (1.99 mg/L Mn) also suggest that the hyporheic zone is relatively reducing.

Table 5.6a. Nutrient water quality data collected June 19, 2003 at IRWD sediment basin 2, above the outlet of San Joaquin Marsh Wildlife Sanctuary and Treatment Wetland. Water samples were collected from the water column in the stream, hyporheic zone (interstitial water at the sediment-water column interface), and at the IRWD ground water discharge outlet just above sediment basin 2 (analysis by Associated Labs).

Station	Nitrate-N (mg/L)	Nitrite-N (mg/L)	Ammonia-N (mg/L)	TKN (mg/L)	Orthophosphate-P (mg/L)	Total P (mg/L)
Basin 2 Stream Water	6.6	0.22	<0.1	0.7	0.05	0.10
Basin 2 Hyporheic Water	<0.1	<0.1	3.9	4.6	2.15	3.74
IRWD Groundwater Outlet	0.6	<0.1	0.3	<0.5	<0.061	<0.02

Table 5.6b. Trace element, general inorganic constituents, and total organic carbon collected June 19, 2003 at IRWD Sediment Basin 2, above the outlet of San Joaquin Marsh Wildlife Sanctuary and Treatment Wetland. Water samples were collected from the water column in the stream, hyporheic zone (interstitial water at the sediment-water column interface), and at the IRWD ground water discharge outlet just above sediment basin 2 (analysis by Associated Labs).

Station	Selenium (ug/L)	Arsenic (ug/L)	Iron (mg/L)	Manganese (mg/L)	Sulfate (mg/L)	Total Org. Carbon (mg/L)
Basin 2 Stream Water	26	<5	<0.02	0.019	846	5.9
Basin 2 Hyporheic Water	<6	<5	<0.02	1.99	513	7.8
IRWD Groundwater Outlet	<6	<5	0.023	0.219	696	4.0

Arsenic is below 5 ug/L in all samples. Selenium is 26 ug/L in surface water and below 6 ug/L in hyporheic water and groundwater (Table 5.6). If surface water is percolating into the hyporheic zone, the selenium may be removed from the infiltrating water by reduction, and partitioning across the soil interface (for example, by forming iron-selenium compounds while simultaneously forming iron-sulfide compounds).

Otherwise the selenium may be removed from the hyporheic zone by biological uptake or by sorption.

It appears likely that redox conditions in the hyporheic zone favor reduction of selenium and nitrate. Even so, there is apparently not enough fluid exchange between surface water and hyporheic water to cause substantial removal of selenium and nitrate from the surface water column, at least not during our study of the sediment basins. Otherwise, we would have seen lower selenium concentrations and lower nitrate concentrations at bottom stations during top/bottom monitoring of the water column. This was clearly not the case during our intensive one year study from late 2005 to early 2007 (see Figures 5.12, 5.15, and 5.16).

Fairly low concentrations of selenium (usually <2 mg/kg dry weight Se) in sediments in sediment basin 2 (Earth Mechanics, Inc., 2003) may be due to scour of the upper part of the sediment column during the annual storm season. The scoured sediment is presumably replaced after peak storm discharge by fresh sediment containing small or negligible amounts of selenium. One year of hyporheic flows may not be a sufficient amount of time for selenium to accumulate in soils to concentrations above 2 mg/kg.

B. Sediment Interstitial/Water Column Studies in Sediment Basin 2, October, 2004

Prior to temporary shutdown of the inlet/outlet flows of San Joaquin Marsh Wildlife Sanctuary in late October, 2004, the research team collected water quality samples from sediment basin 2 (Figure 5.37). Water samples were collected on October 13, 2004 from the surface water column and hyporheic zone in the sediment basin. Grab samples were collected from the stream at the midpoint of sediment basin 2. At the same

location, the hyporheic zone (streambed interstitial waters and sediments) was sampled with a stainless steel mini-piezometer and peristaltic pump.

The research team returned to the same location in sediment basin 2 on October 25 to duplicate water quality sampling that was done on October 13. This was done after the inlet/outlet flows at San Joaquin Marsh were discontinued and after a significant rain event that post-dated October 13 sampling. By resampling the same site, a comparison can be made between water quality in the stream and hyporheic zone before and after the rain event, and after the inlet/outlet flows at San Joaquin Marsh were suspended.

Water quality data collected from sediment basin 2 are presented in Table 5.7. Nutrient data indicate that nitrate concentration is moderately-low in surface water on

October 13 (2.04 mg/L NO3-N), and is much higher when the sediment basins was resampled October 25 (11.49 mg/L NO3-N). The increase in nitrate concentration in San Diego Creek at this location is due to suspension of inlet/outlet flows at San Joaquin Marsh (the sample location is below the outlet of the marsh). Ammonium is very low in surface water during both sample periods (Table 5.7). Nitrate in hyporheic water was very low on October 13 and 25 (0.05 and 0.07 mg/L NO3-N), while ammonium is quite high in the hyporheic zone (7.99 and 0.55 mg/L NH4+-N), especially on October 13 when the ammonium concentration was 7.99 mg/L NH4+-N (Table 5.7). This implies that nitrate is being reduced in the hyporheic zone by dissimilatory nitrate reduction.

Table 5.7a: Select Hydrochemical Parameters at San Diego Creek Sediment Basin 2*

Sample ID	Dissolved Se (ug/L)	Total Se (ug/L)	As (ug/L)	Spec. Cond (uS)
October 13				
Hyporheic	1.14	1.14	2.92	3993
Surface Water	14.98	15.64	4.93	2916
October 25				
Hyporheic	2.24	2.49	12.25	2581
Surface Water	20.12	21.26	8.03	2812

Table 5.7b: Select Nutrient Parameters at San Diego Creek Sediment Basin 2*

Sample ID	Total N (mg/L)	NO3 as N (mg/L)	NH3-N (mg/L)
October 13			
Hyporheic	8.98	0.05	7.99
Surface Water	3.21	2.04	0.09
October 25			
Hyporheic	1.23	0.07	0.55
Surface Water	11.61	11.49	0.07

Table 5.7c: Select Nutrient Parameters and Silica at San Diego Creek Sediment Basin 2*

Sample ID	Total P (mg/L)	Ortho-P (mg/L)	Dissolved Silica (mg/L)
October 13			
Hyporheic	5.66	4.97	26.11
Surface Water	0.09	0.01	7.26
October 25			
Hyporheic	1.71	0.22	17.27
Surface Water	0.32	0.18	15.82

*All analysis by UC-Riverside

Relative to surface water, the higher specific conductance value and higher silica value in the hyporheic zone on October 13 may indicate that the hyporheic water was being fed at that particular time by upwelling groundwater, rather than by downwelling surface water (Table 5.7). When the sediment basin was resampled on October 25 (after rain), specific conductance in the hyporheic zone was lower than in surface water, whereas silica concentrations were about the same in both surface water and hyporheic

water. This suggests that surface water percolated down into the hyporheic zone during or shortly after the rains due to higher hydraulic head in the stream during surface runoff. In all cases, total phosphorous is very high in hyporheic water (5.66 and 1.71 mg/L total P) and moderately low to very low in surface water (0.09 to 0.32 mg/L total P). Orthophosphate is an especially high percentage of the total phosphorous in the hyporheic zone on October 13 (88%) and is a much lower percentage of total phosphorous in the hyporheic zone on October 25 (13%).

Reducing conditions can produce high orthophosphate concentrations in the hyporheic zone, as iron-phosphorus solids become soluble when iron is reduced (Figures 5.34 and 5.40). In previous sections, we speculated that orthophosphate becomes soluble in the hyporheic zone when iron-phosphorous compounds are reduced. The October 2004 support this hypothesis (Table 5.7). Shortly after rain events the streambed materials contain fresher, undecomposed organic material that probably had not yet created a highly anoxic redox condition in the hyporheic zone. This could explain the lower orthophosphate percentages on October 25 (Table 5.7).

Reducing conditions in the hyporheic zone have likely implications for selenium reduction and removal in streambed interstices. Selenium concentrations being relatively high in surface water (14.98 and 20.12 ug/L Se), the selenium is much lower in hyporheic water (1.14 and 2.49 ug/L Se) (Table 5.7). It is not known if the original source of the hyporheic water had high or low selenium concentrations. The original source of hyporheic water may have been from local groundwater (October 13) and from storm water (October 25). These sources may have had only small amounts of selenium. We

know that the nearby IRWD groundwater outlet contains low concentrations of selenium (Table 5.6).

Most of the selenium in surface water and hyporheic water is in dissolved form. Total selenium and dissolved selenium concentrations are nearly identical both in the surface water and in the hyporheic water (Table 5.7). It is apparent that the hyporheic zone has sufficiently low redox potential to reduce selenium and nitrate, but there doesn't appear to be enough fluid exchange between surface water and hyporheic water to cause substantial removal of selenium and nitrate from the surface water column in the sediment basins. At least this appears to be the case during our intensive study of the downstream sediment basins. At some locations in the sediment basins where streambed sediments are laden with organic material, it is likely that some selenium removal occurs from interstitial waters in the hyporheic zone by sorption and reduction. Not so much selenium removal appears to occur in the surface water column in these sediment basins however.

Fluid exchange between hyporheic zone and water column probably operates more efficiently in the mixing prebasin due to tidal pumping (Figure 5.36). The processes discovered during studies of the hyporheic zone in sediment basin 2 very likely operate in the streambed sediments in the mixing prebasin. This probably would explain why we see elevated orthophosphate and ammonium concentrations at the bottom of the prebasin during the summer months, when bottom waters are anoxic (Figures 5.30, 5.31 and 5.32). Similar studies of the hyporheic zone in the prebasin and elsewhere could clarify our understanding of internal loading of nutrients, and other speciation processes at and below the sediment/water interface.

CONCLUSIONS

In this project, water quality dynamics at the estuarine interface in the downstream sedimentation basins between San Diego Creek and Upper Newport Bay were studied. This study focused on selenium, nitrate, salinity, and dissolved oxygen in the water column of the downstream basins, along with some additional nutrient parameters. The study found that basin 2 and 3 are entirely terrestrially influenced basin, whereas basin 1 and the prebasin contain a mixture of marine water and terrestrial freshwater.

The top and the bottom samples of the water column within basins 3 and 2 show only small variability of selenium and nitrate, along with terrestrial salinity values, which suggests little or no removal of either selenium or nitrate in these basins, along with absence of marine water. On the other hand, there is a terrestrial freshwater/marine mixing interface observed at basin 1 and at the prebasin, which is located adjacent to the Upper Newport Bay. Tidal fluctuations allow marine waters to advance up from Upper Newport Bay into the prebasin. Prebasin in particular shows regular salinity stratification where a lens of terrestrial freshwater often flows on top of a dense layer of salt water of marine origin.

During the seasons the water quality analysis for selenium and nitrate in San Diego Creek indicates high concentrations of selenium (15 to 20 ug/L) and nitrate (4-8 mg/L NO3-N) versus low concentrations of selenium (<2 ug/L) and nitrate (<1.5 mg/L NO3-N) in Upper Newport Bay. The water quality data explains the fact that the lens of the terrestrial freshwater acts as a pipeline for delivering these solutes directly into Upper Newport Bay. Elevated selenium may impact a variety of marine species living in the

bay, while nitrate contributes to eutrophication problems that have plagued Upper Newport Bay for over 50 years.

Dissolved oxygen measurements at the water-sediment interface (bottom-most sample) in the basins often reaches zero, due to the presence of oxygen-consuming organic matter in the sediments, and in the organic detritus resting on the sediments. In basins 3 and 2, top and bottom samples showed little difference in nitrate and selenium concentrations because there is apparently very little or no removal of these constituents. Anoxia is present directly at the sediment-water interface, but there is not a sufficient water flux between bottom sediments and water column to allow sufficient reduction of selenium and nitrate. Otherwise, we would expect to see low selenium and nitrate concentrations at the bottom of the water column in basins 3 and 2. In basin 1 and especially in the prebasin, tidal pumping probably causes substantial hydraulic flux between the water column and the bottom sediments. Even so, the type of water at the sediment-water interface is primarily of marine origin, which contains very small concentrations of selenium and nitrate. Any removal in the anoxic bottom-sediments does not deplete the greater mass of selenium and nitrate flowing into Upper Newport Bay by the terrestrial freshwater “pipeline effect”.

Future studies should assess the role of phytoplankton and microorganisms on possible uptake of selenium and nitrate, and conversion of these inorganic constituents into organic forms. This study was one of many sub-studies conducted over a 12 to 16 month period (see other chapters in this report). It would be useful to cover all seasons in a subsequent study including phytoplankton, microorganisms, and more sediment work. Sediments and pore-water interstitial samples should also be studied to determine the

effects of surface water flux into the bottom sediment pore spaces where soils may reduce selenium and nitrate to low-solubility forms and gases.

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Figure 5.1. IRWD sediment control basins 3, 2, and 1 and the prebasin above Upper Newport Bay (from IRWD, 1999).

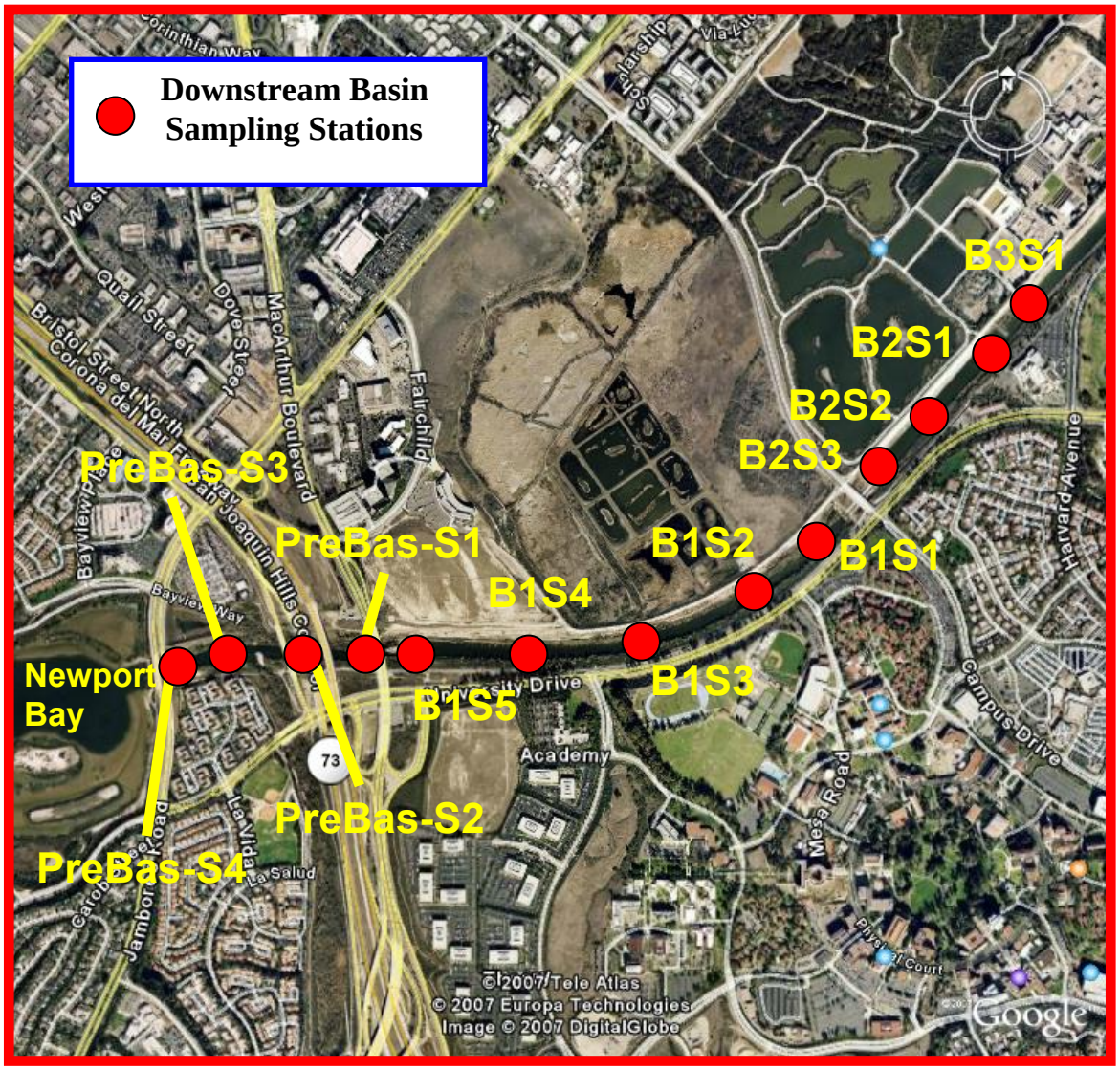
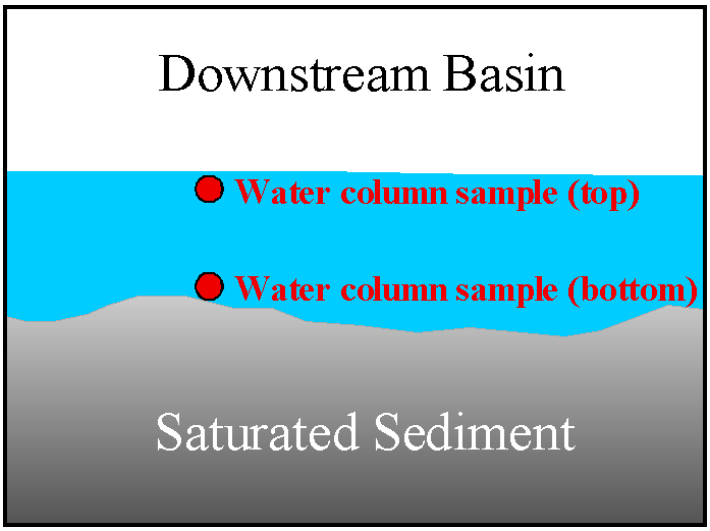


Figure 5.2. Sampling stations in downstream sediment basins 3, 2, and 1 and in the prebasin above Upper Newport Bay.



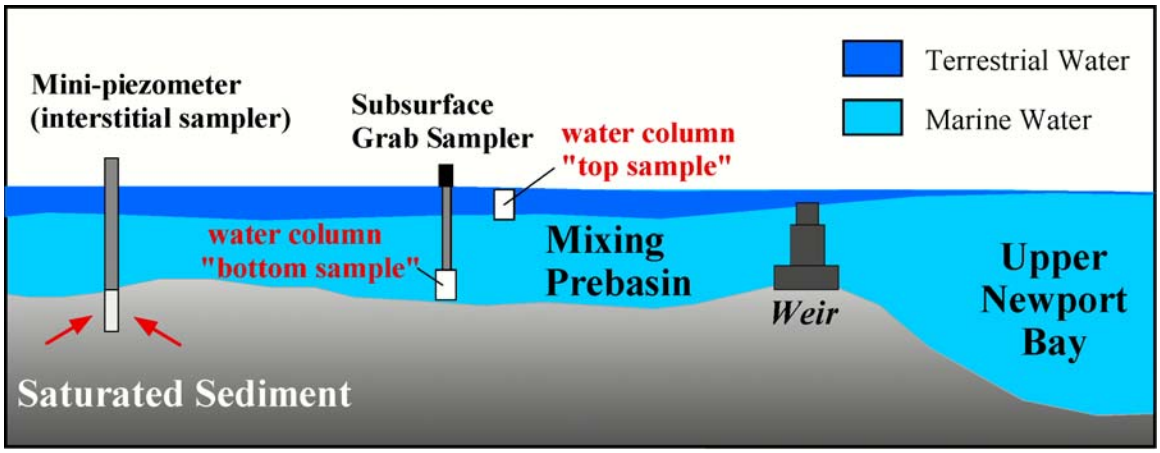


Figure 5.3. Two views of top and bottom sampling procedures for collecting water quality data in downstream sediment basins.

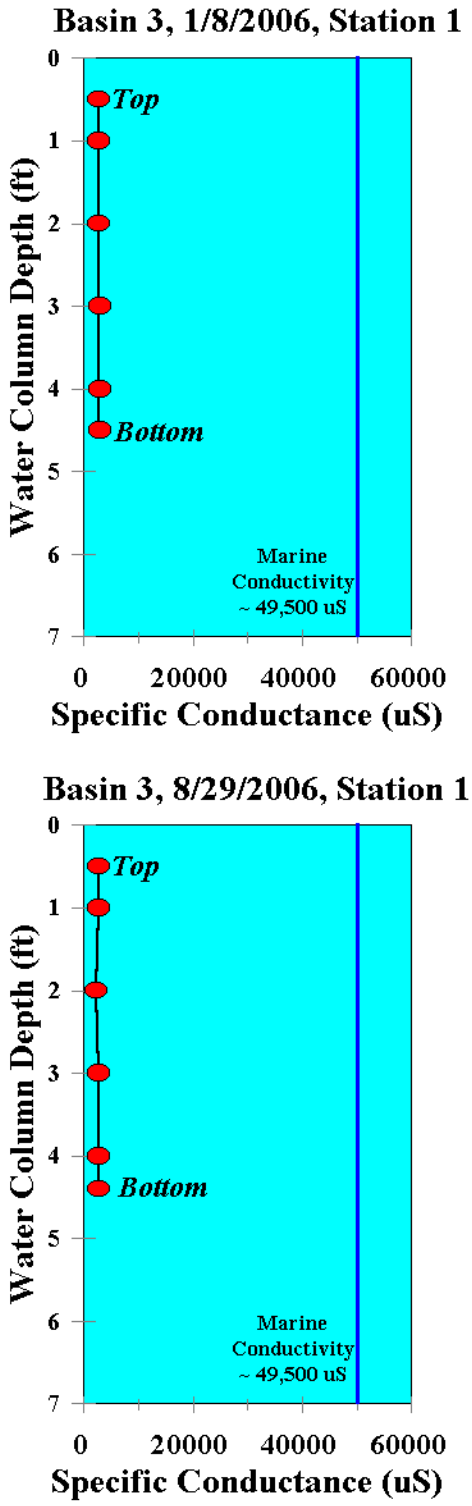


Figure 5.4. Vertical specific conductance profiles in the water column in sediment basin 3, station 1, winter and summer profiles.

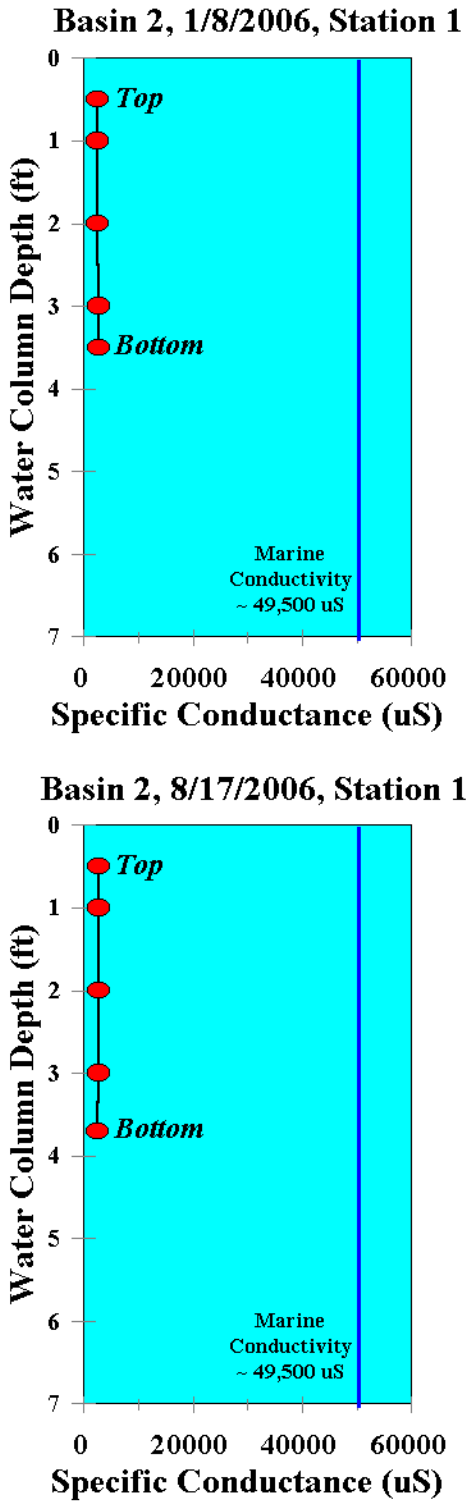
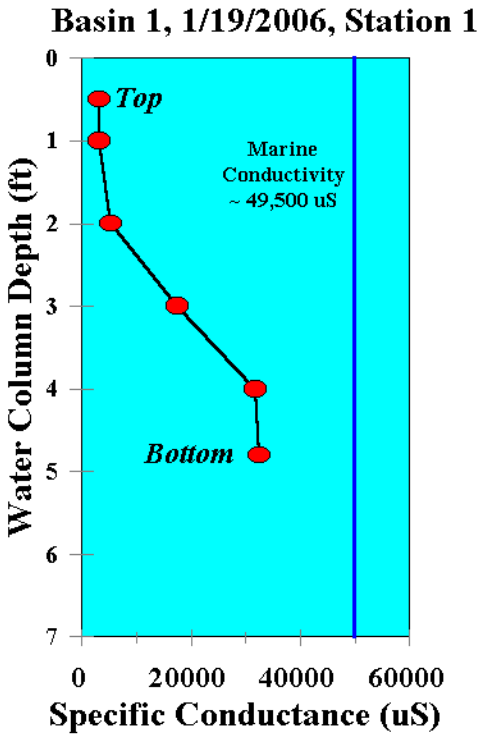


Figure 5.5. Vertical specific conductance profiles in the water column in sediment basin 2, station 1, winter and summer profiles.



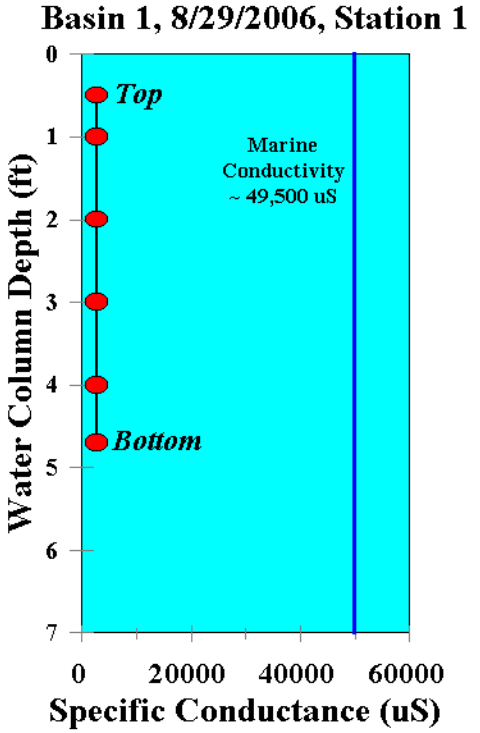


Figure 5.6. Vertical specific conductance profiles in the water column in sediment basin 1, station 1, winter and summer profiles.

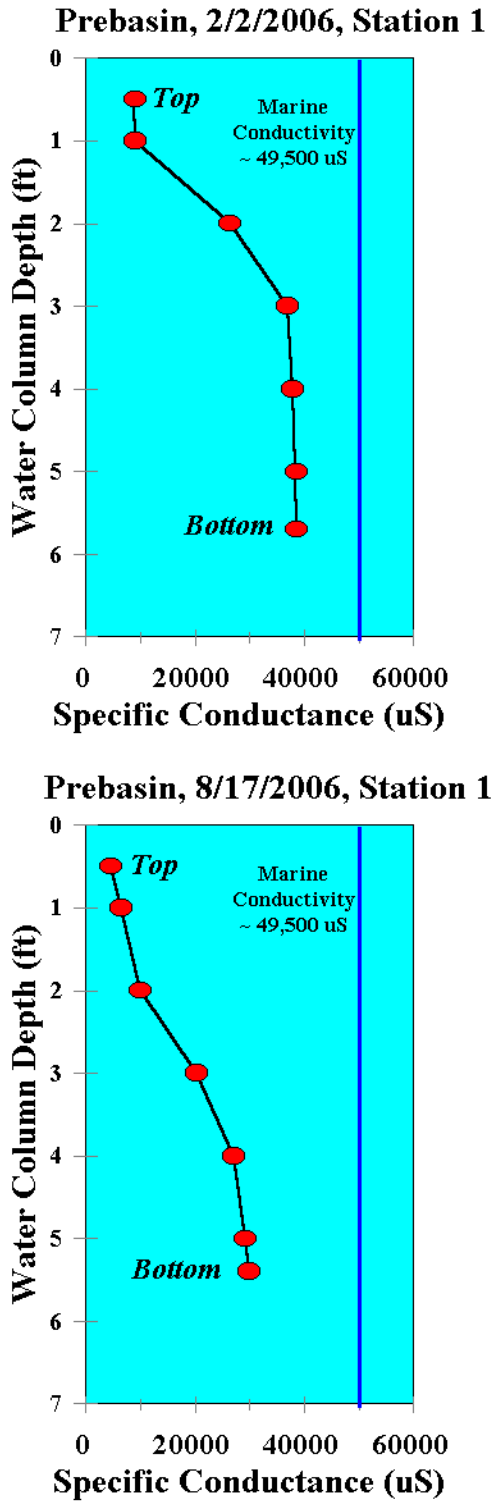


Figure 5.7. Vertical specific conductance profiles in the water column in mixing prebasin, station 1, winter and summer profiles.

Specific Conductance Data with Depth at Stations in Prebasin, October 29, 2006							
Depth (ft) Station 1	**Conductivity (uS)**	**Depth (ft) Station 2**	**Conductivity (uS)**	**Depth (ft) Station 3**	**Conductivity (uS)**	**Depth (ft) Station 4**	**Conductivity (uS)**
0.5	7680	0.5	10920	0.5	13140	0.5	19240
1.0	8700	1.0	11020	1.0	13670	1.0	19740
2.0	31930	2.0	33590	2.0	34470	2.0	35740
3.0	36630	3.0	36880	3.0	38270	3.0	38890
4.0	38210	4.0	38980	4.0	40580	4.0	40740
5.0	38560	5.0	40470	5.0	41560	5.0	41950
6.0	38980	6.0	40890	6.0	42490	6.0	43000
7.0	39160	6.2	41030	7.0	43620	7.0	43700
7.6	36160			8.0	44160	7.3	43960
				9.0	44760		
				10.0	44950		
				11.0	44980		
				12.0	45000		
				13.0	45010		
				13.5	44930		

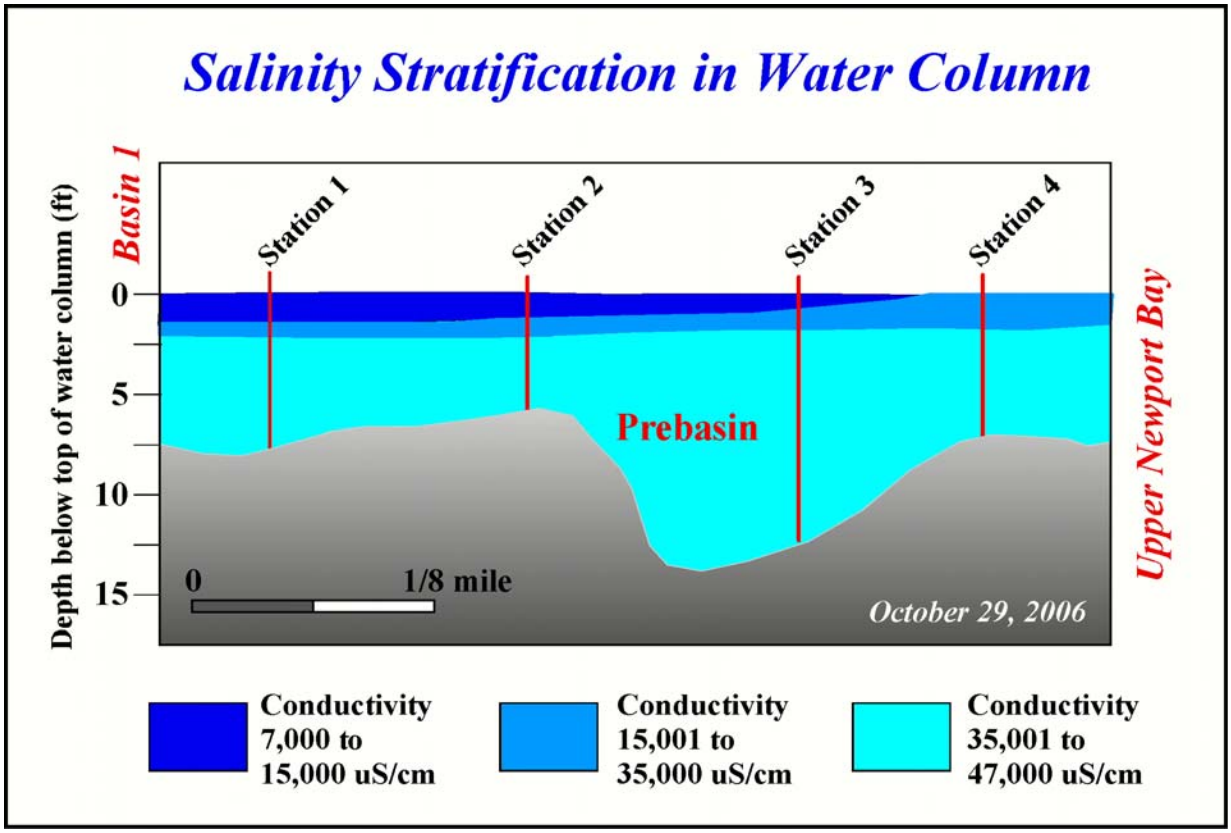


Figure 5.8. Vertical specific conductance profiles assembled for the mixing prebasin for October, 2006, showing a dilute sheetflow/salinity stratification scenario above Newport Bay.

Specific Conductance Data with Depth at Stations in Prebasin, July 15, 2006							
Depth (ft) Station 1	**Conductivity (uS)**	**Depth (ft) Station 2**	**Conductivity (uS)**	**Depth (ft) Station 3**	**Conductivity (uS)**	**Depth (ft) Station 4**	**Conductivity (uS)**
0.5	11570	0.5	11910	0.5	14660	0.5	15600
1.0	11640	1.0	12700	1.0	20280	1.0	22350
2.0	11810	2.0	16870	2.0	32730	2.0	32160
3.0	11950	3.0	26880	3.0	34330	3.0	34850
4.0	12110	4.0	31030	4.0	35360	4.0	35900
4.2	12420	4.9	38140	5.0	37090	5.0	38050
				6.0	38060	6.0	38770
				7.0	39960	7.0	40010
				8.0	44230	8.0	43630
				9.0	45140		
				10.0	45790		
				11.0	46160		
				12.0	46460		
				13.0	46540		
				13.3	46460		

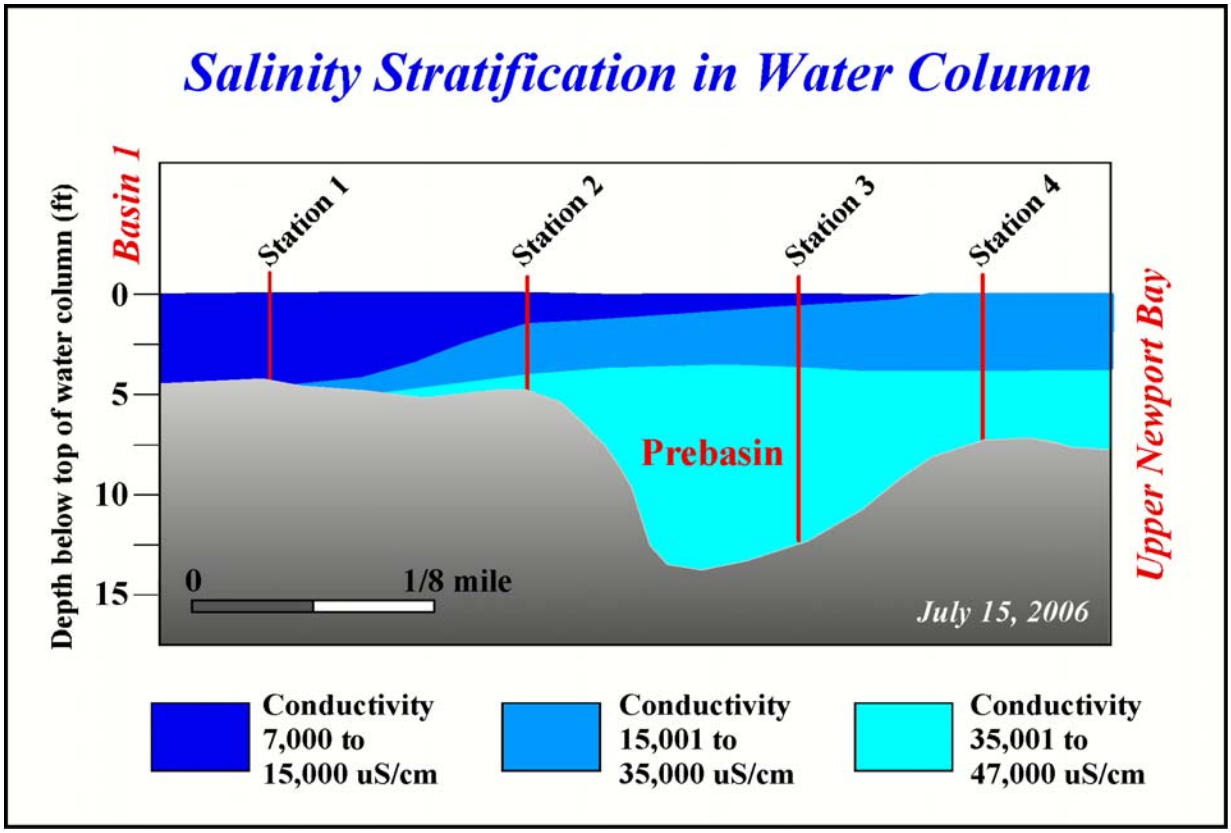


Figure 5.9. Vertical specific conductance profiles assembled for the mixing prebasin for July, 2006, showing a thicker sheetflow/salinity stratification scenario above Newport Bay.

Specific Conductance Data with Depth at Stations in Prebasin, December 15, 2005							
Depth (ft) Station 1	**Conductivity (uS)**	**Depth (ft) Station 2**	**Conductivity (uS)**	**Depth (ft) Station 3**	**Conductivity (uS)**	**Depth (ft) Station 4**	**Conductivity (uS)**
0.5	38560	0.5	36930	0.5	36420	0.5	36770
1.0	38520	1.0	36960	1.0	37340	1.0	37240
1.5	38530	1.5	37110	2.0	37890	2.0	38810
2.0	38510	2.0	38660	3.0	41570	3.0	42010
2.5	38530	2.6	39640	4.0	44260	4.0	44110
3.0	38530			5.0	45710	5.0	45230
3.4	38530			6.0	46100	5.6	45620
				7.0	46220		
				8.0	46230		
				9.0	46300		
				10.0	46350		
				10.7	46220		

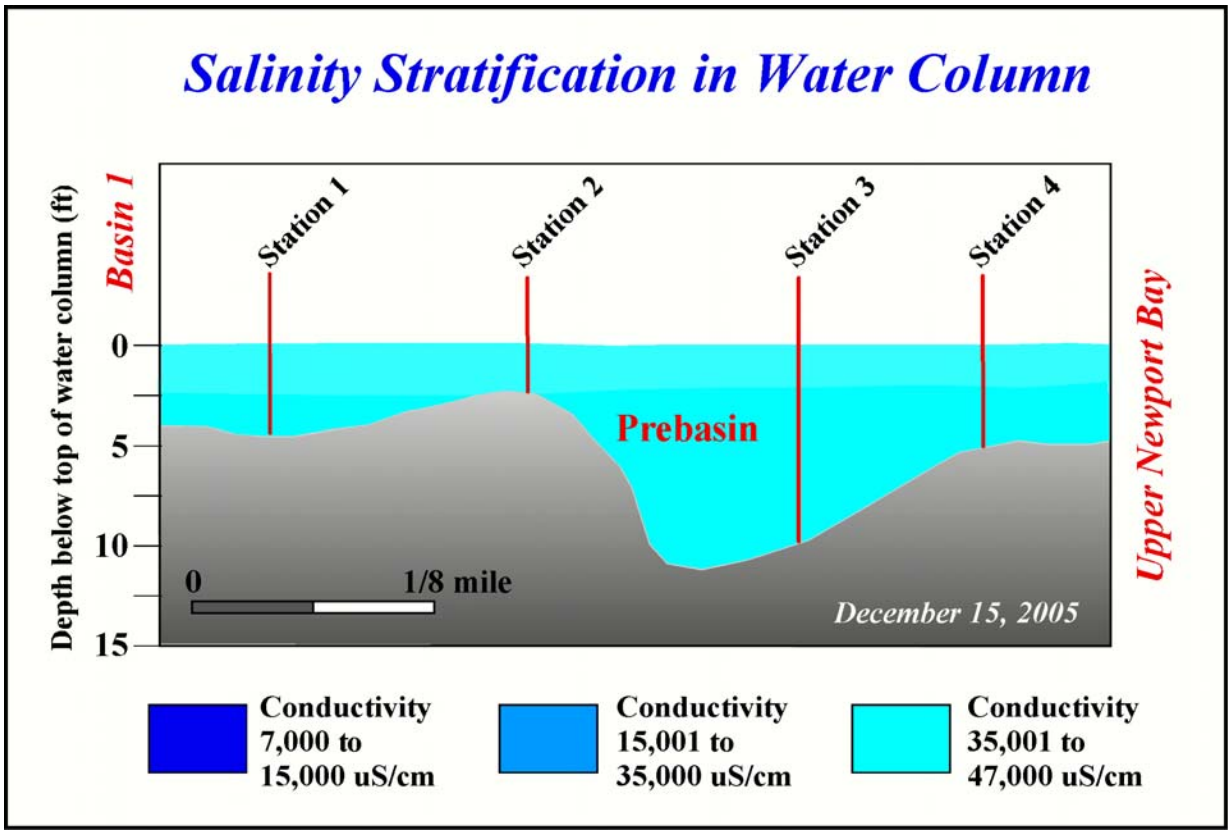


Figure 5.10. Vertical specific conductance profiles assembled for the mixing prebasin for December, 2005, shows mostly a marine water salinity above Newport Bay.

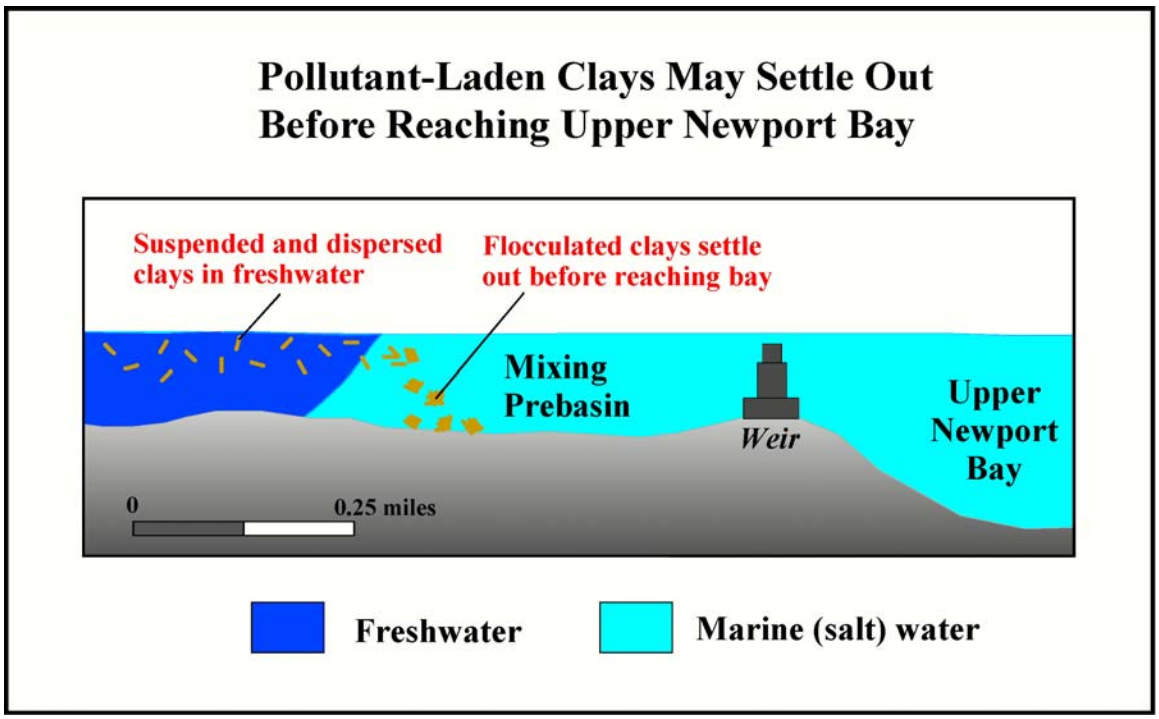
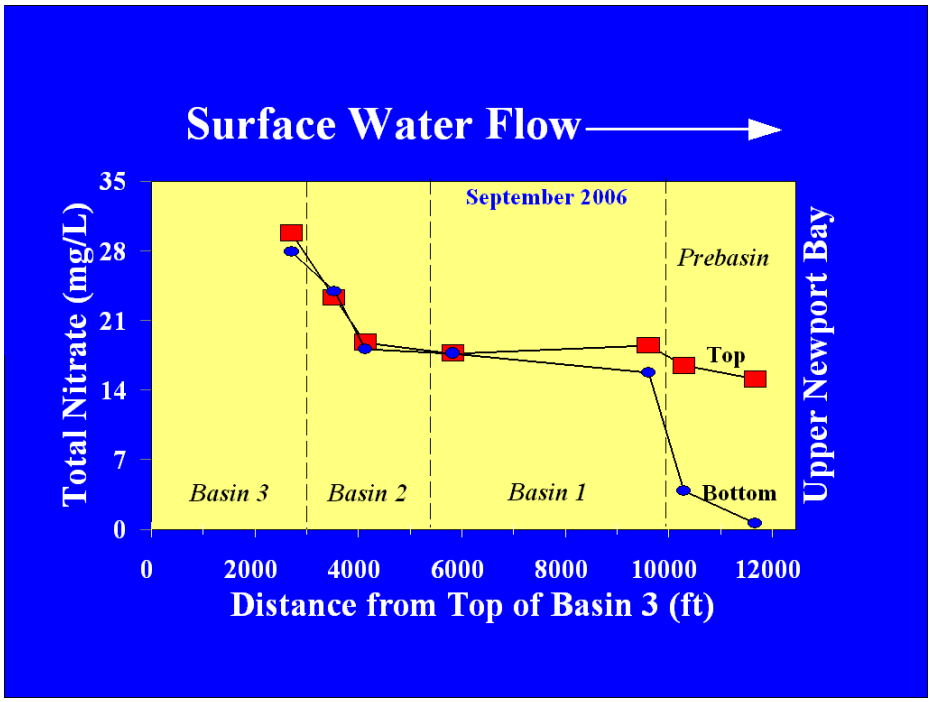
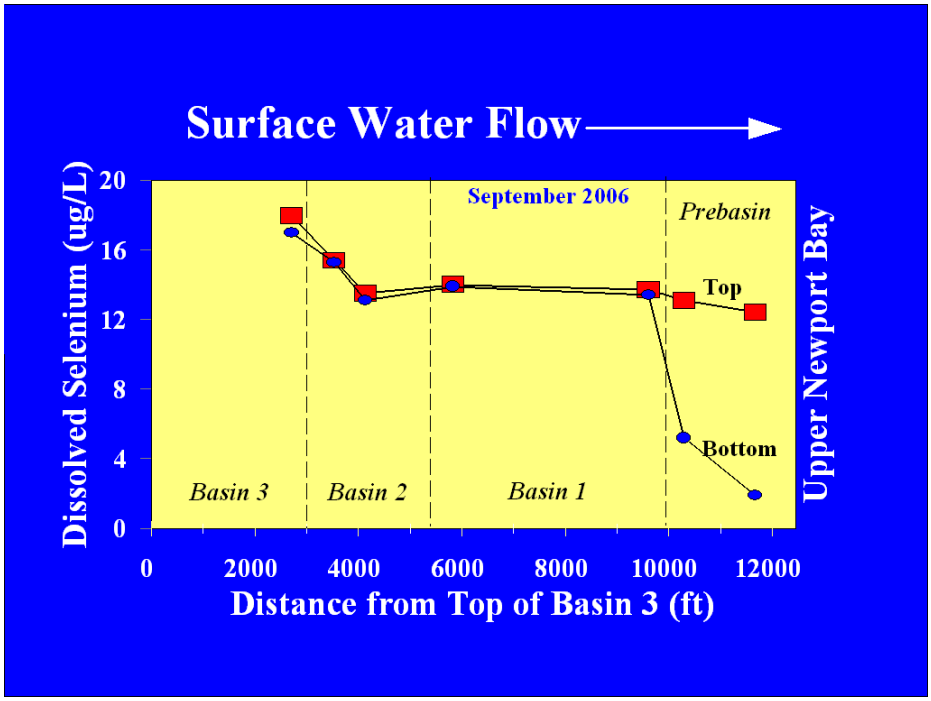


Figure 5.11. Suspended clay sediments will flocculate and sink to the bottom of a water body when mixed with saline waters of high ionic strength. Trace elements, pesticides, and phosphates that are sorbed to these sediments will be deposited during the sedimentation process.



A.



B.

Figure 5.12. Longitudinal profiles for nitrate (A) and selenium (B) in downstream sediment basins 3, 2, and 1 and the prebasin above Upper Newport Bay, September 2006. Dilution of parameters occurs downstream of sediment basin 3. No important differences are shown for top and bottom stations, except in the prebasin. See text for details.

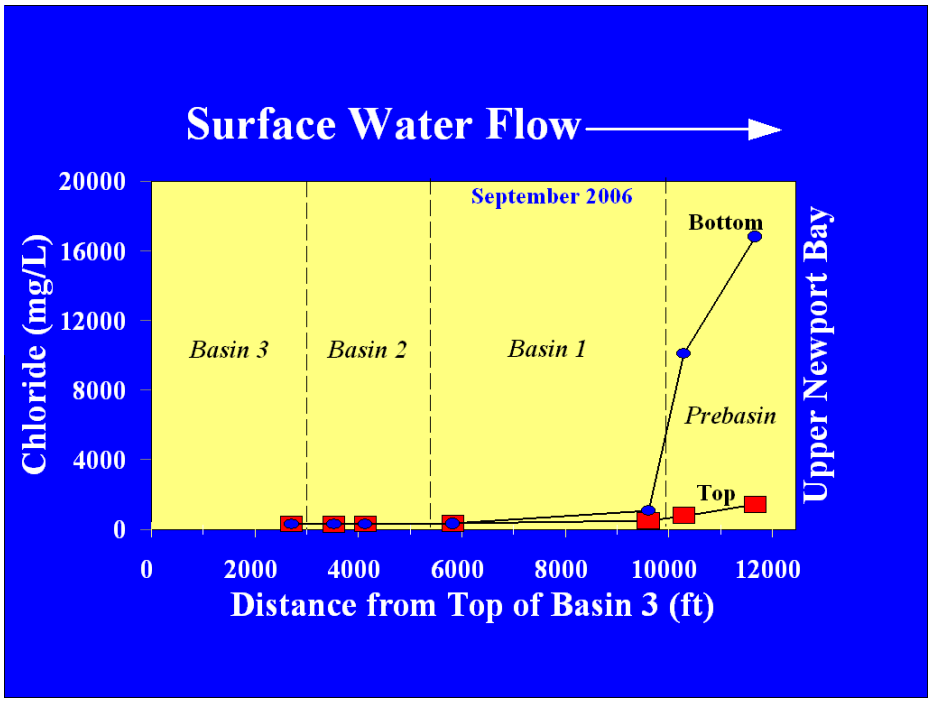


Figure 5.13. Longitudinal profiles for chloride in downstream sediment basins 3, 2, and 1 and the prebasin above Upper Newport Bay, September 2006. Dilution of parameters occurs downstream of sediment basin 3. No important differences are shown for top and bottom stations, except in the prebasin. Enrichment of chloride in the bottom station in the prebasin is due to marine intrusion due to tidally-forced fluctuation in Upper Newport Bay.

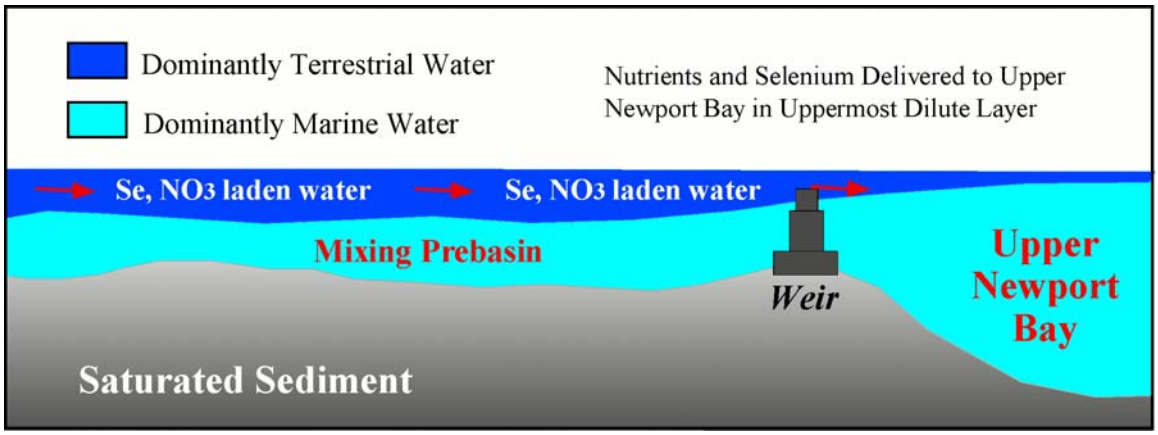
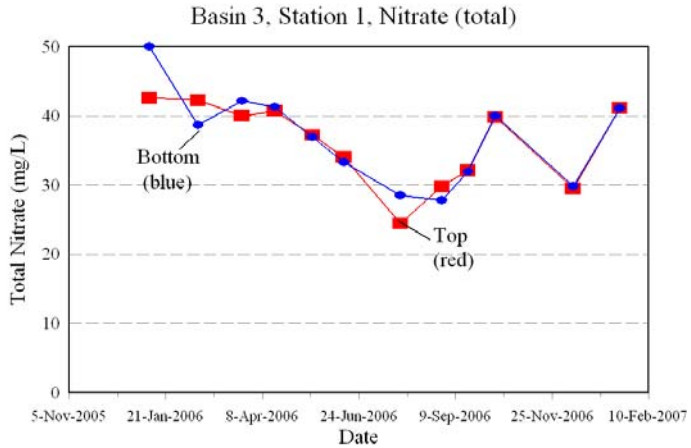
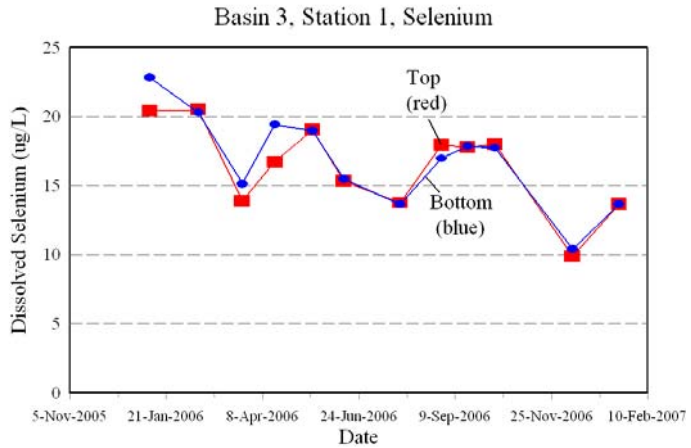


Figure 5.14. A lens of terrestrial water, sourced from San Diego Creek, “rides” on top of the marine layer and flows directly into Upper Newport Bay. This process delivers terrestrial nutrients, selenium, and other pollutants directly to the bay.





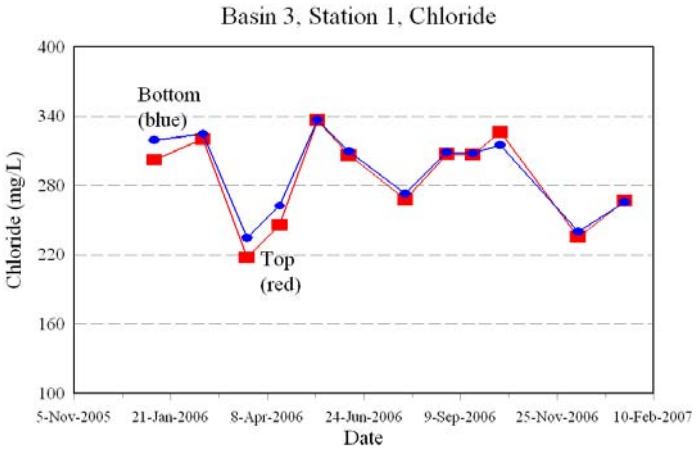
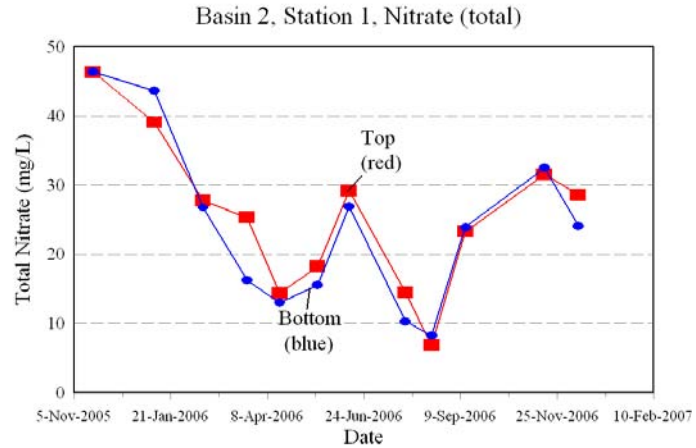
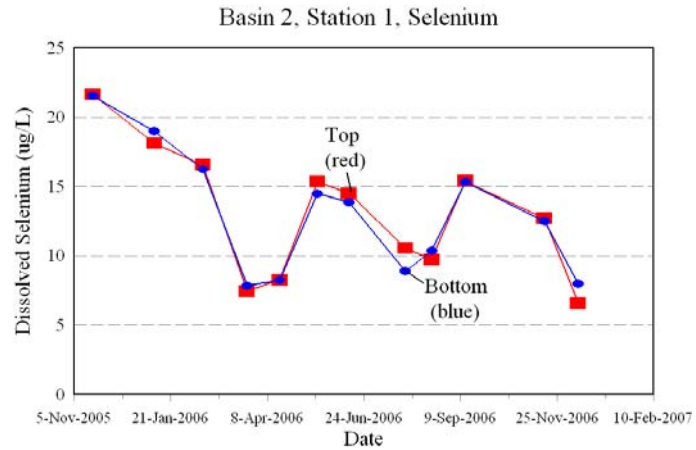


Figure 5.15. Time series analysis of nitrate, selenium, and chloride in sediment basin 3, station 1.





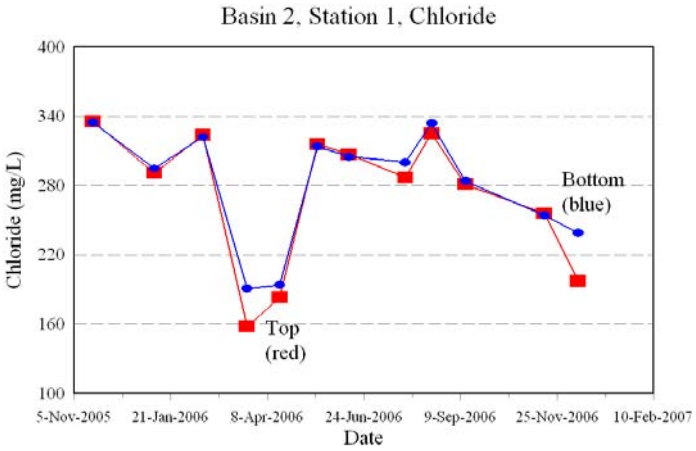
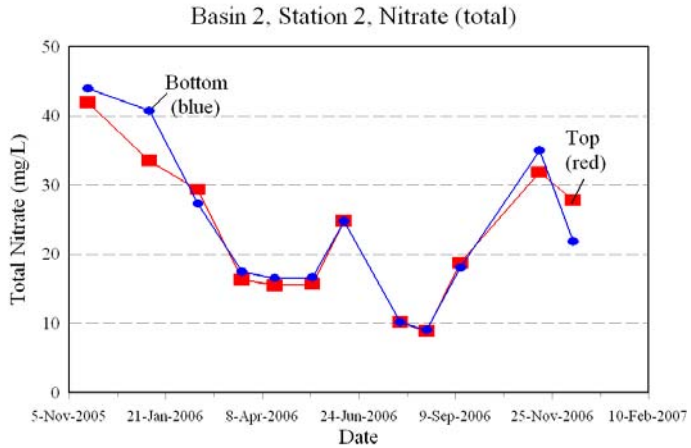
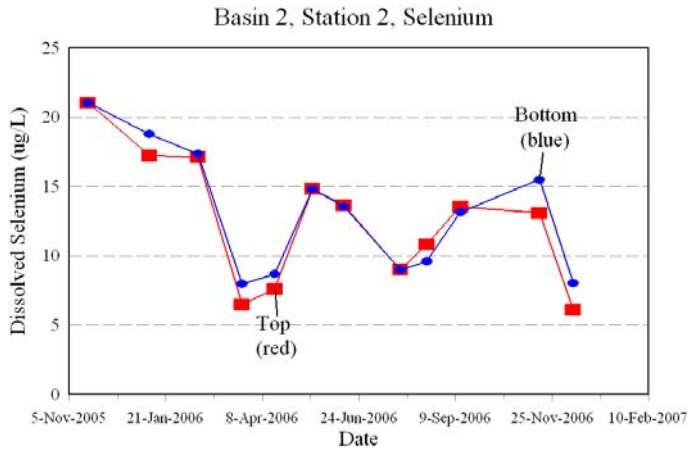


Figure 5.16. Time series analysis of nitrate, selenium, and chloride in sediment basin 2, station 1.





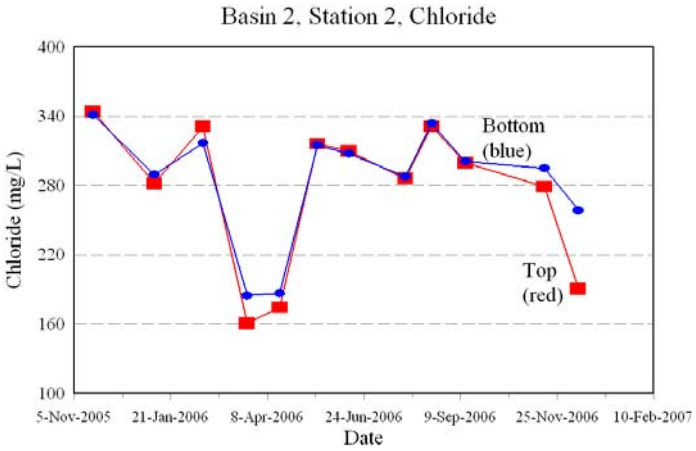


Figure 5.17. Time series analysis of nitrate, selenium, and chloride in sediment basin 2, station 2.

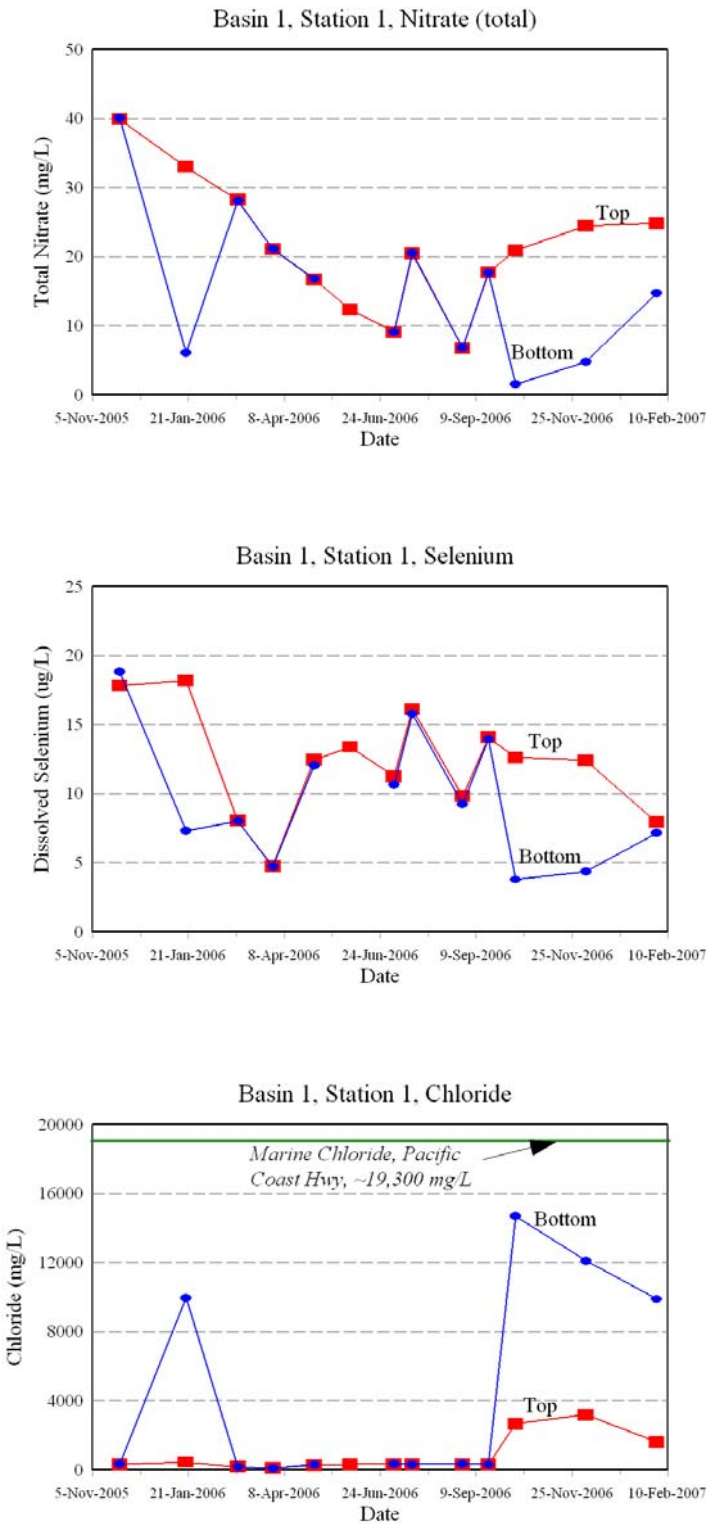
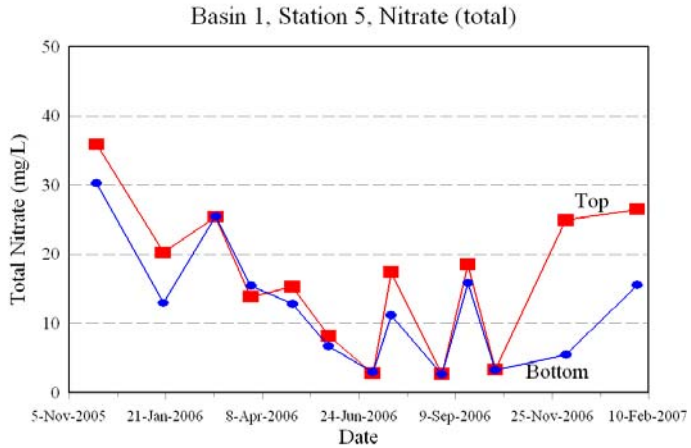
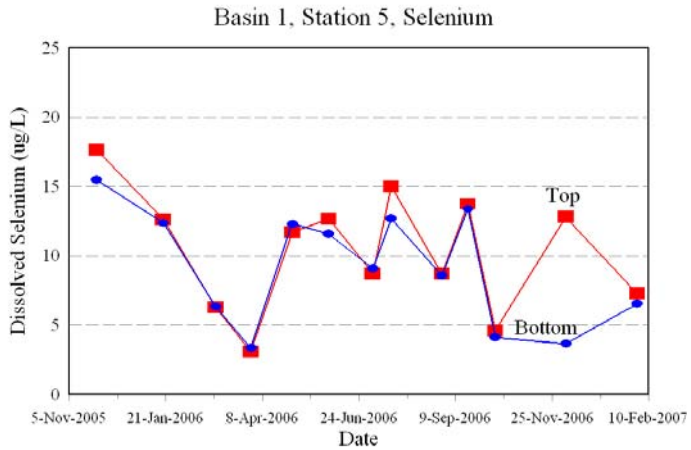


Figure 5.18. Time series analysis of nitrate, selenium, and chloride in sediment basin 1, station 1.





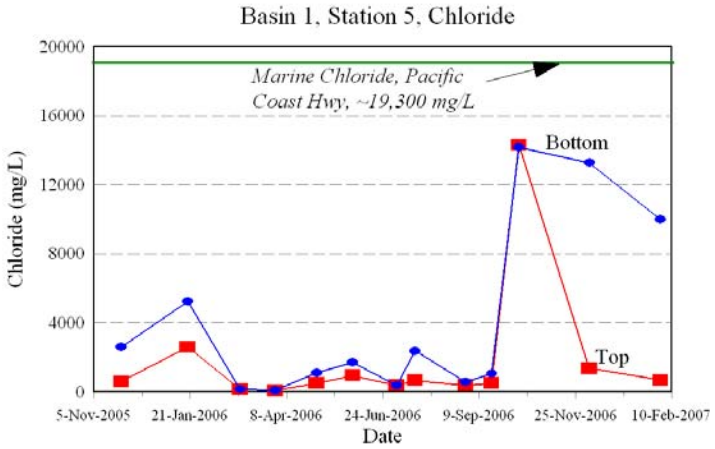
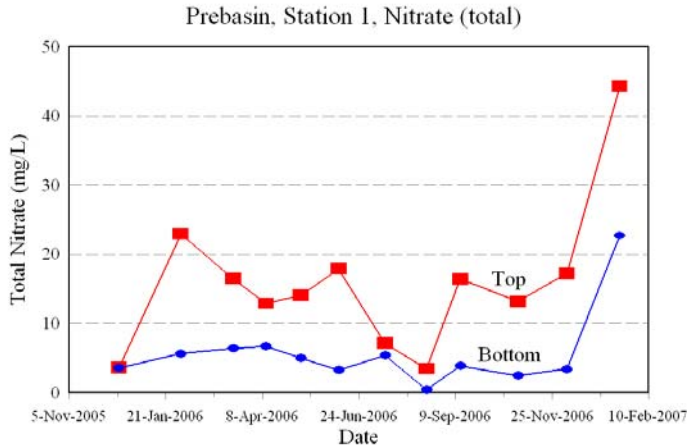
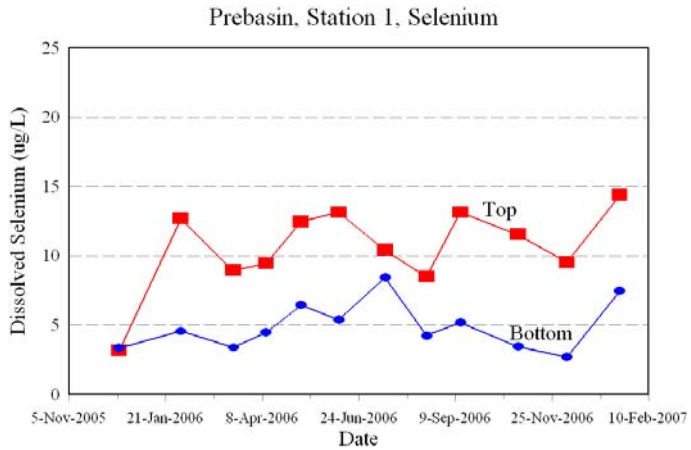


Figure 5.19. Time series analysis of nitrate, selenium, and chloride in sediment basin 1, station 5.





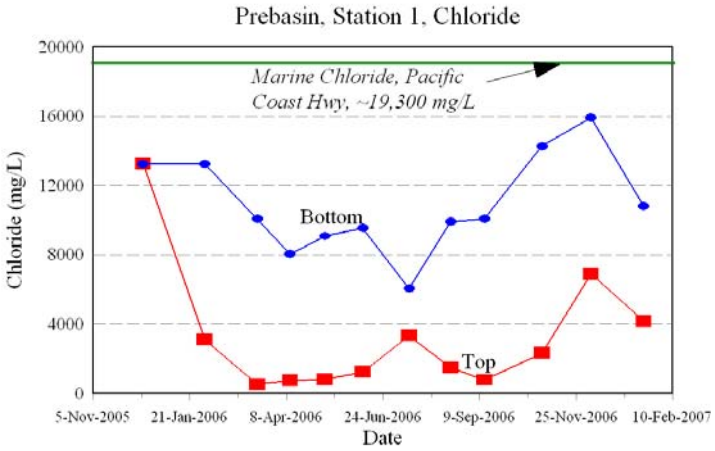
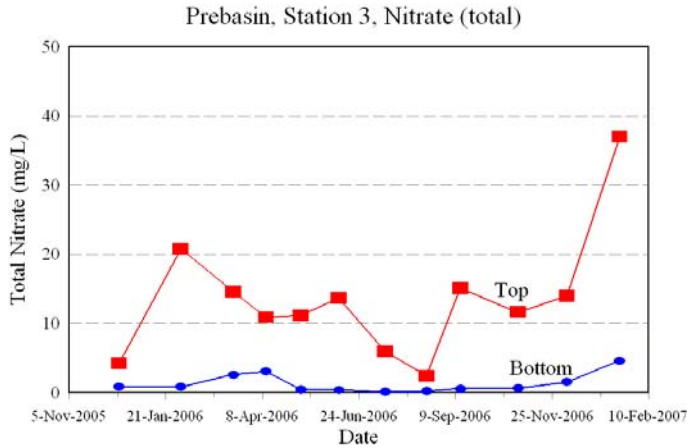
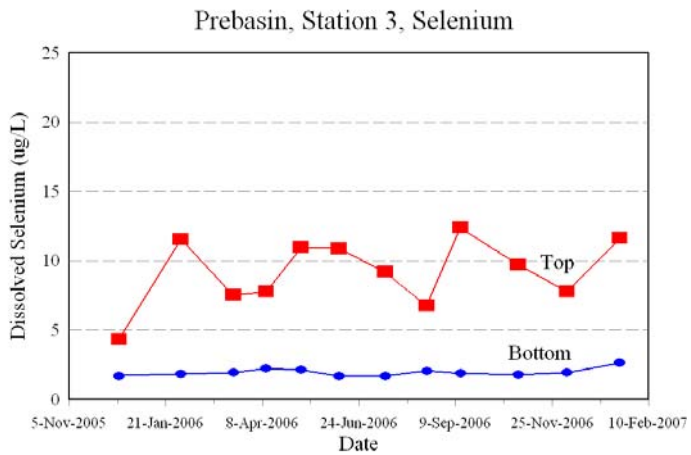


Figure 5.20. Time series analysis of nitrate, selenium, and chloride in prebasin, station 1.





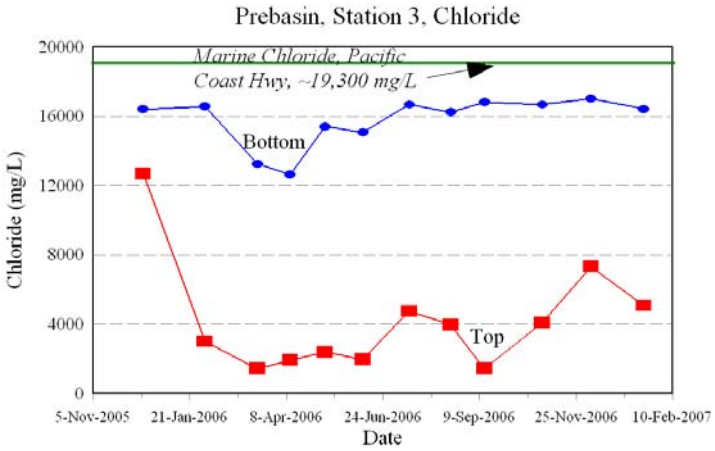
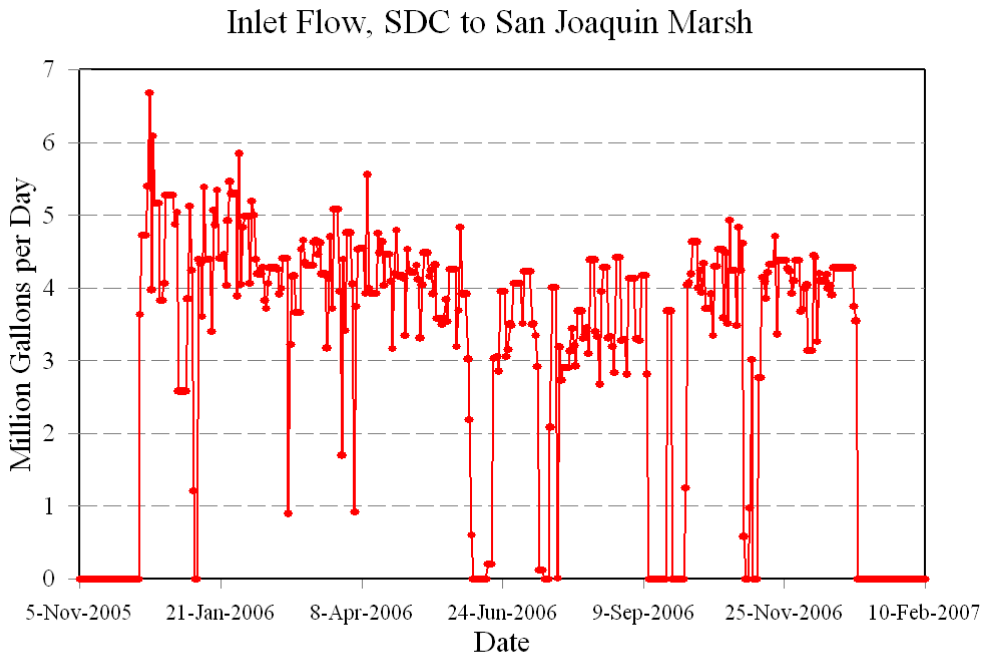


Figure 5.21. Time series analysis of nitrate, selenium, and chloride in prebasin, station 3.



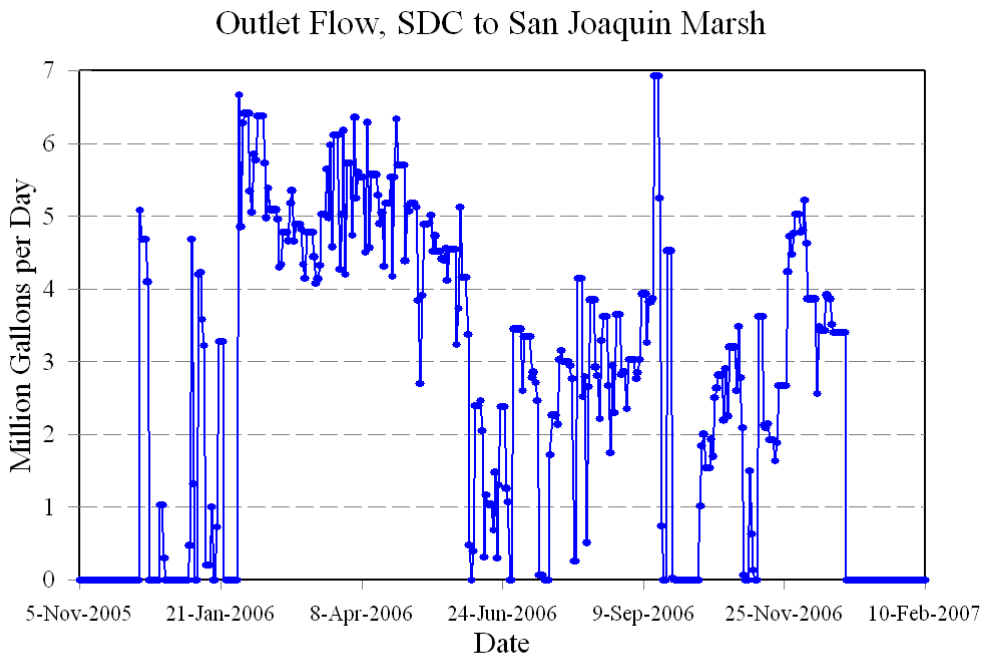


Figure 5.22. Inlet and outlet flows between San Diego Creek and San Joaquin Marsh, covering the time series monitoring interval shown in Figures 5.15 to 5.21 (data provided courtesy of IRWD).

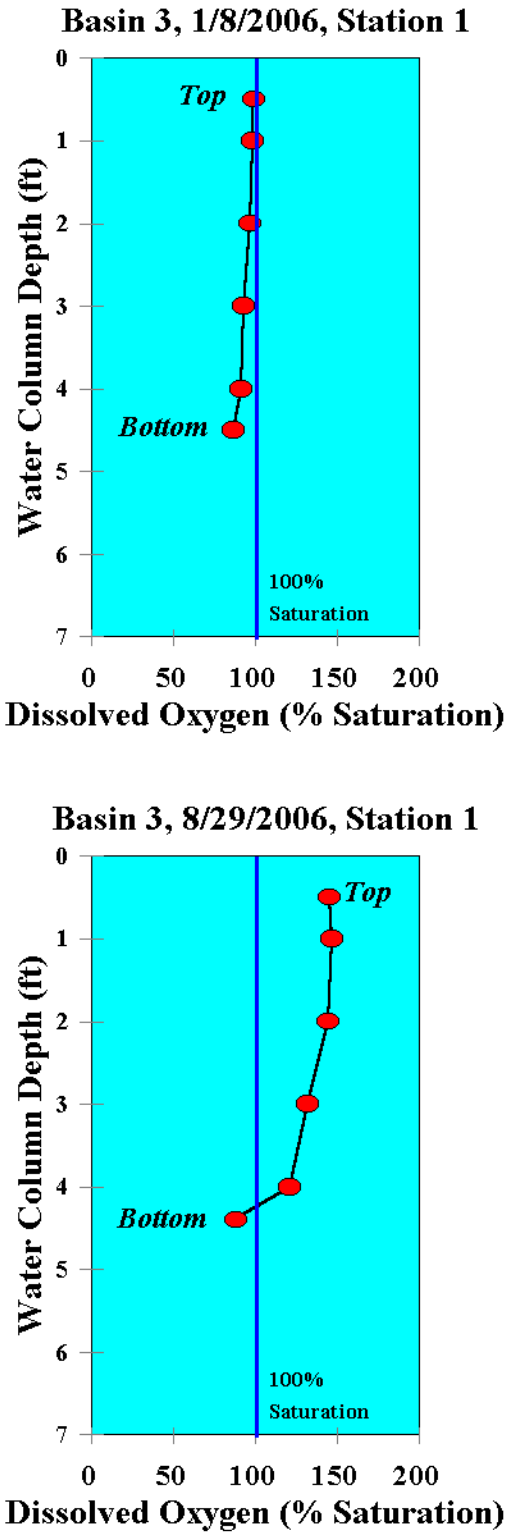
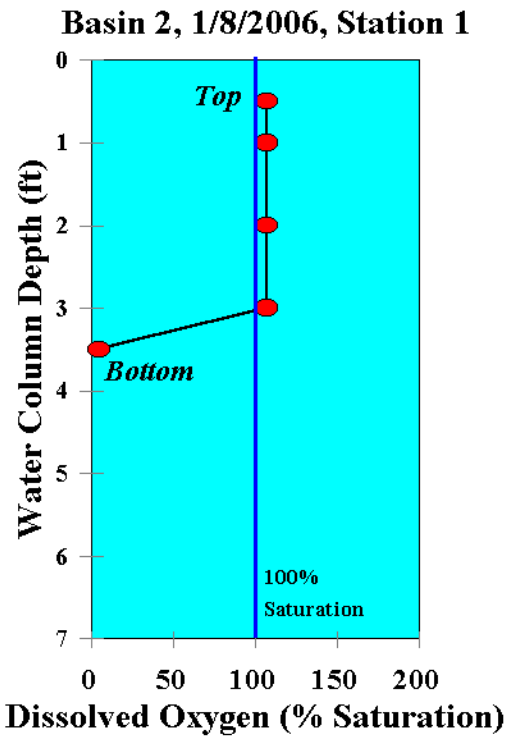


Figure 5.23. Vertical dissolved oxygen profiles in the water column in sediment basin 3, station 1, winter and summer profiles.



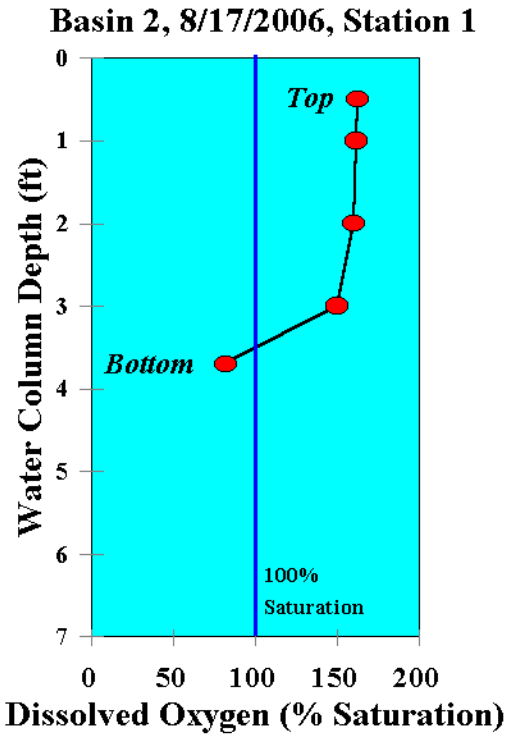


Figure 5.24. Vertical dissolved oxygen profiles in the water column in sediment basin 2, station 1, winter and summer profiles.

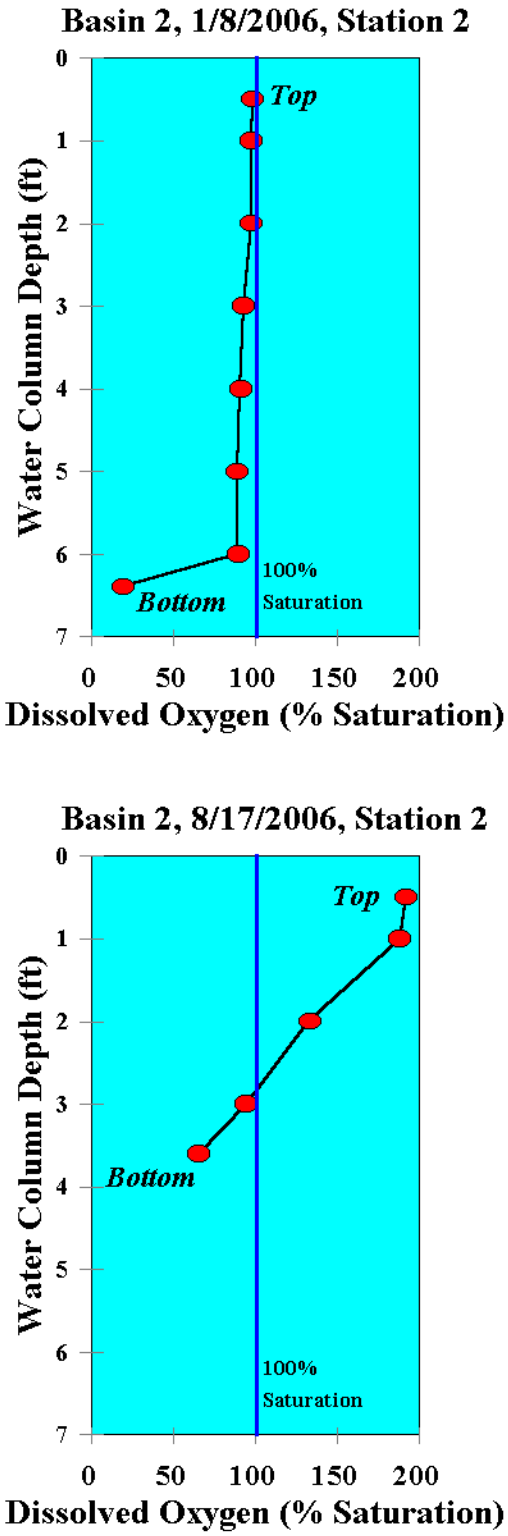
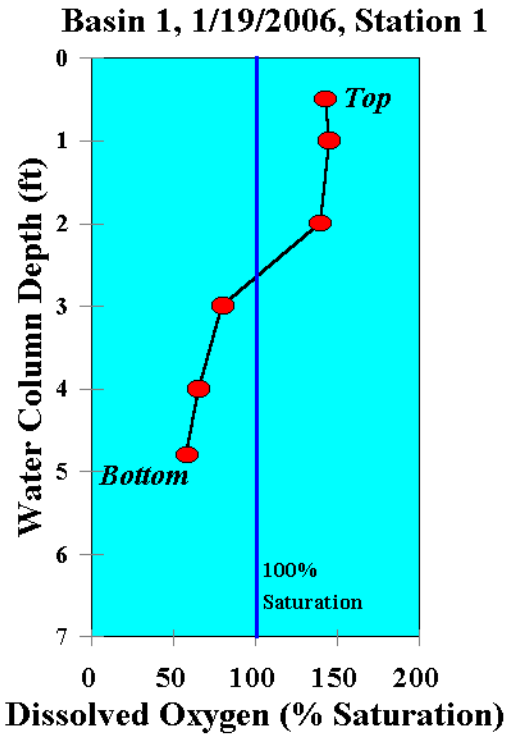


Figure 5.25. Vertical dissolved oxygen profiles in the water column in sediment basin 2, station 2, winter and summer profiles.



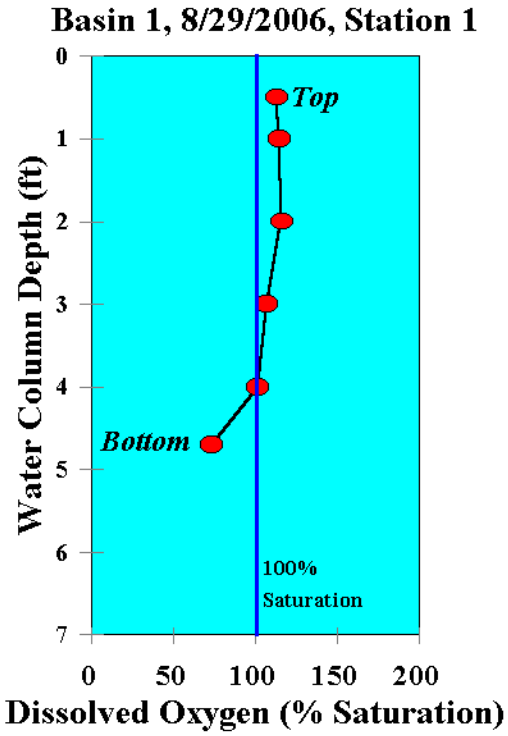
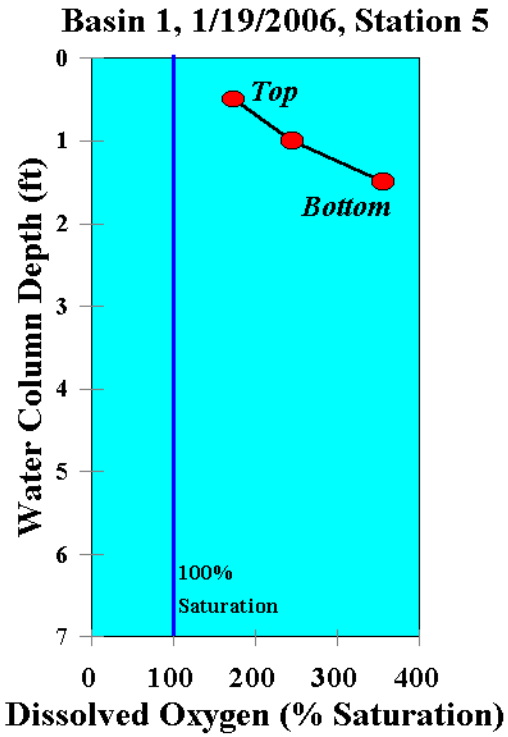


Figure 5.26. Vertical dissolved oxygen profiles in the water column in sediment basin 1, station 1, winter and summer profiles.



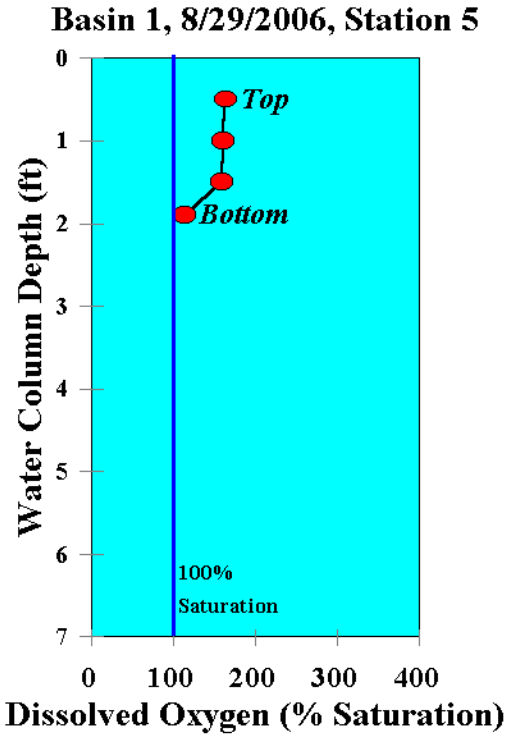
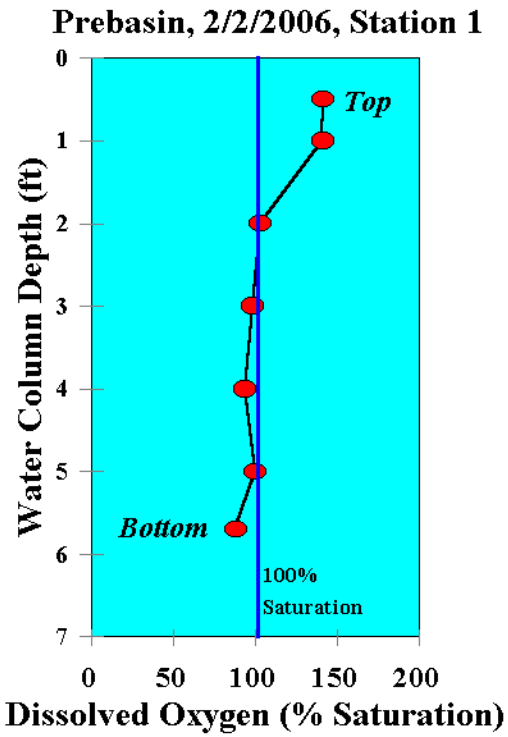


Figure 5.27. Vertical dissolved oxygen profiles in the water column in sediment basin 1, station 5, winter and summer profiles.



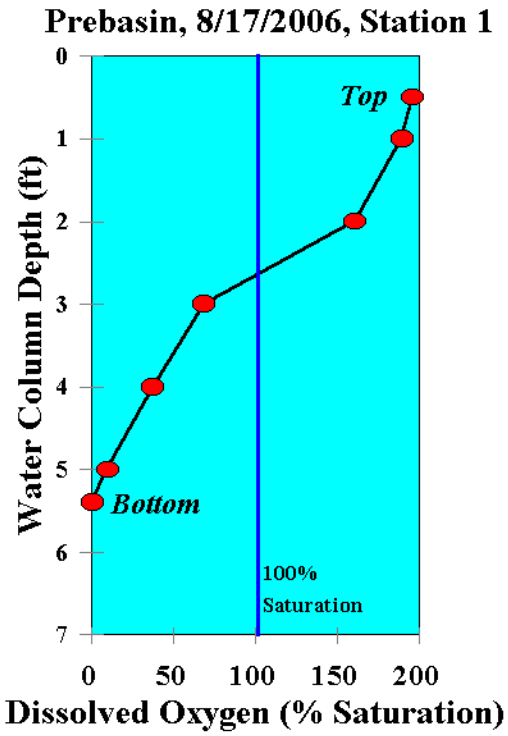


Figure 5.28. Vertical dissolved oxygen profiles in the water column in prebasin, station 1, winter and summer profiles.

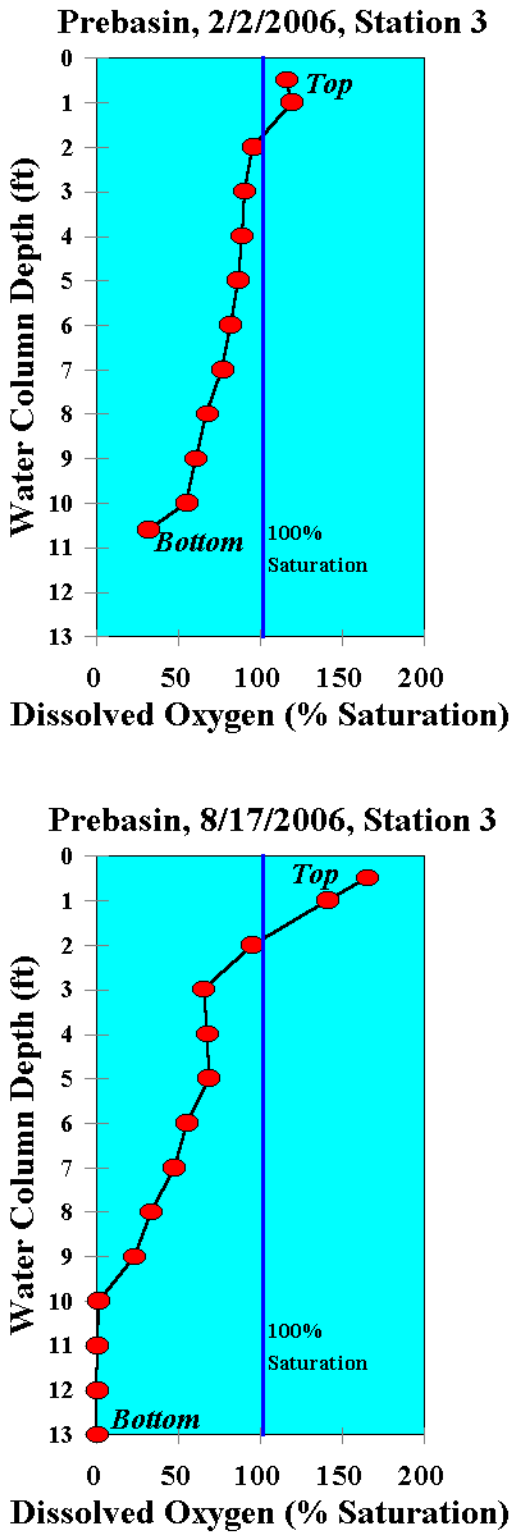
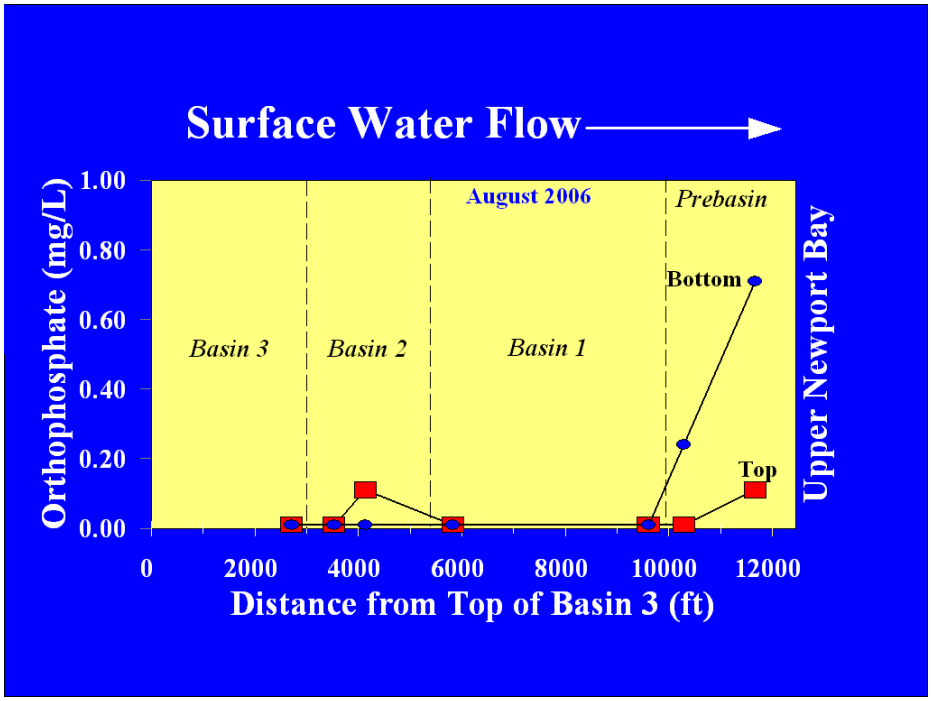
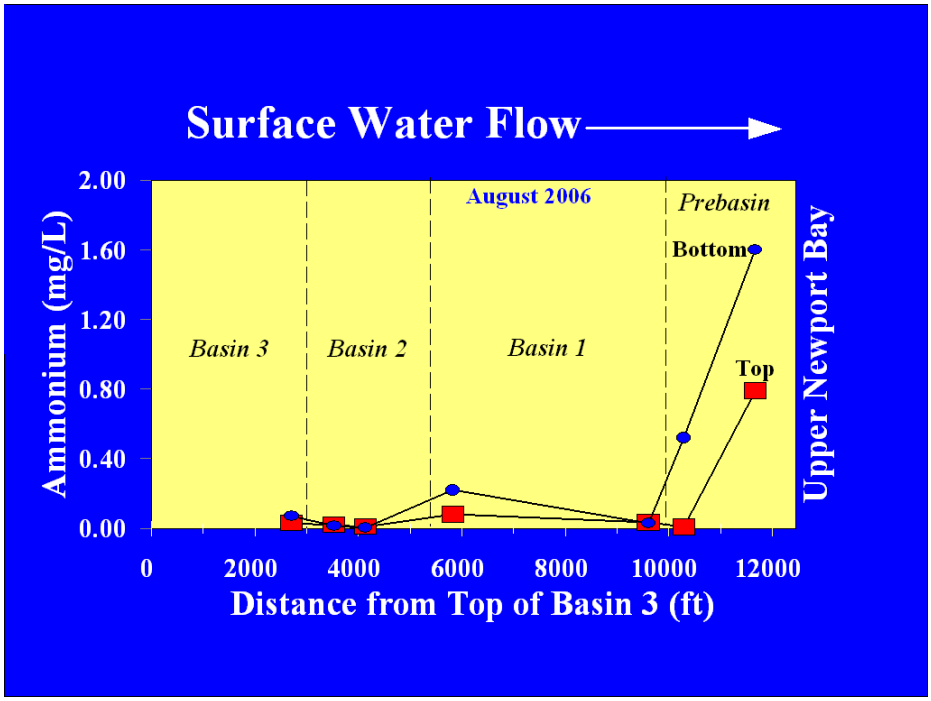


Figure 5.29. Vertical dissolved oxygen profiles in the water column in prebasin, station 3, winter and summer profiles.



A.



B.

Figure 5.30. Longitudinal profiles for orthophosphate (A) and ammonium (B) in downstream sediment basins 3, 2, and 1 and the prebasin above Upper Newport Bay, August 2006. There is a marked increase in orthophosphate and ammonium concentrations in the mixing prebasin, particularly at the bottom station.

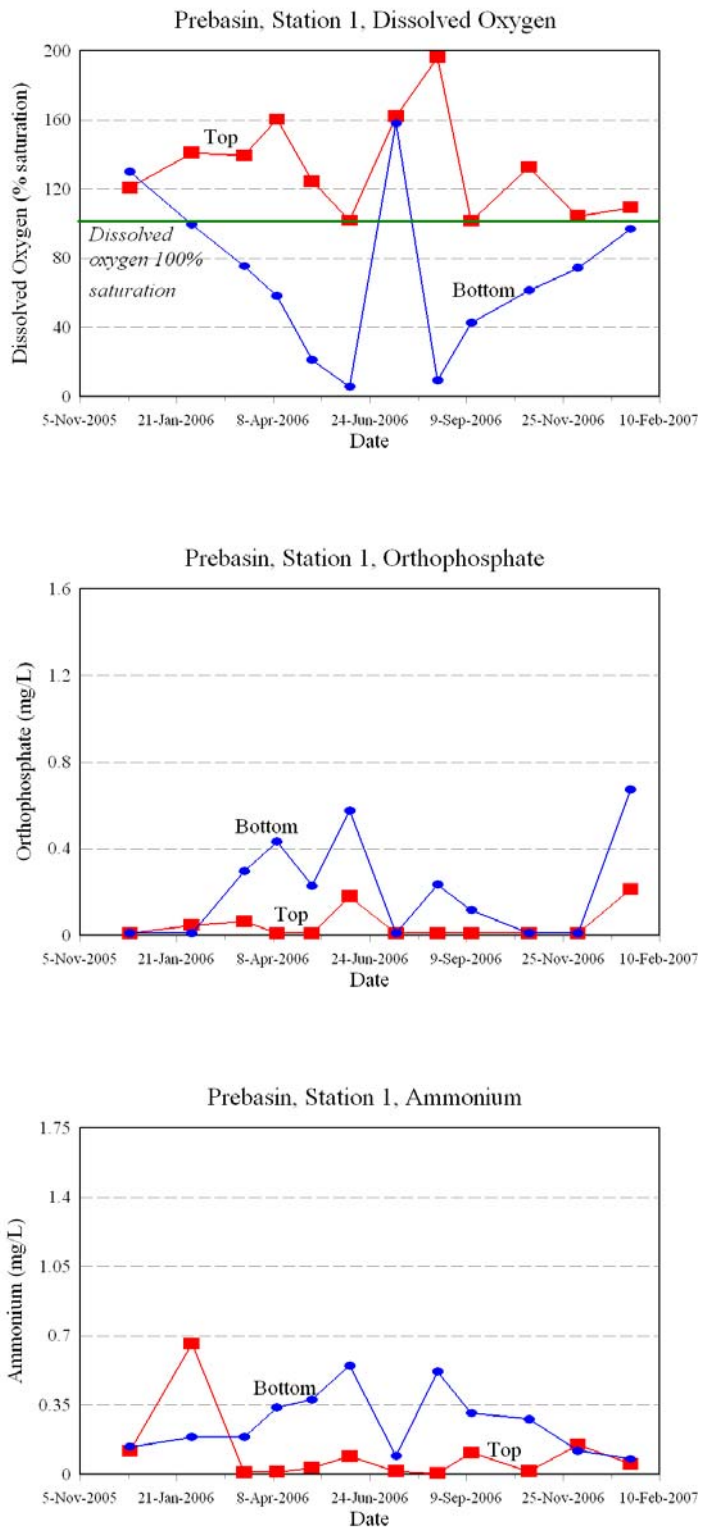


Figure 5.31. Time series comparisons of dissolved oxygen, orthophosphate, and ammonium concentrations in the mixing prebasin, station 1.

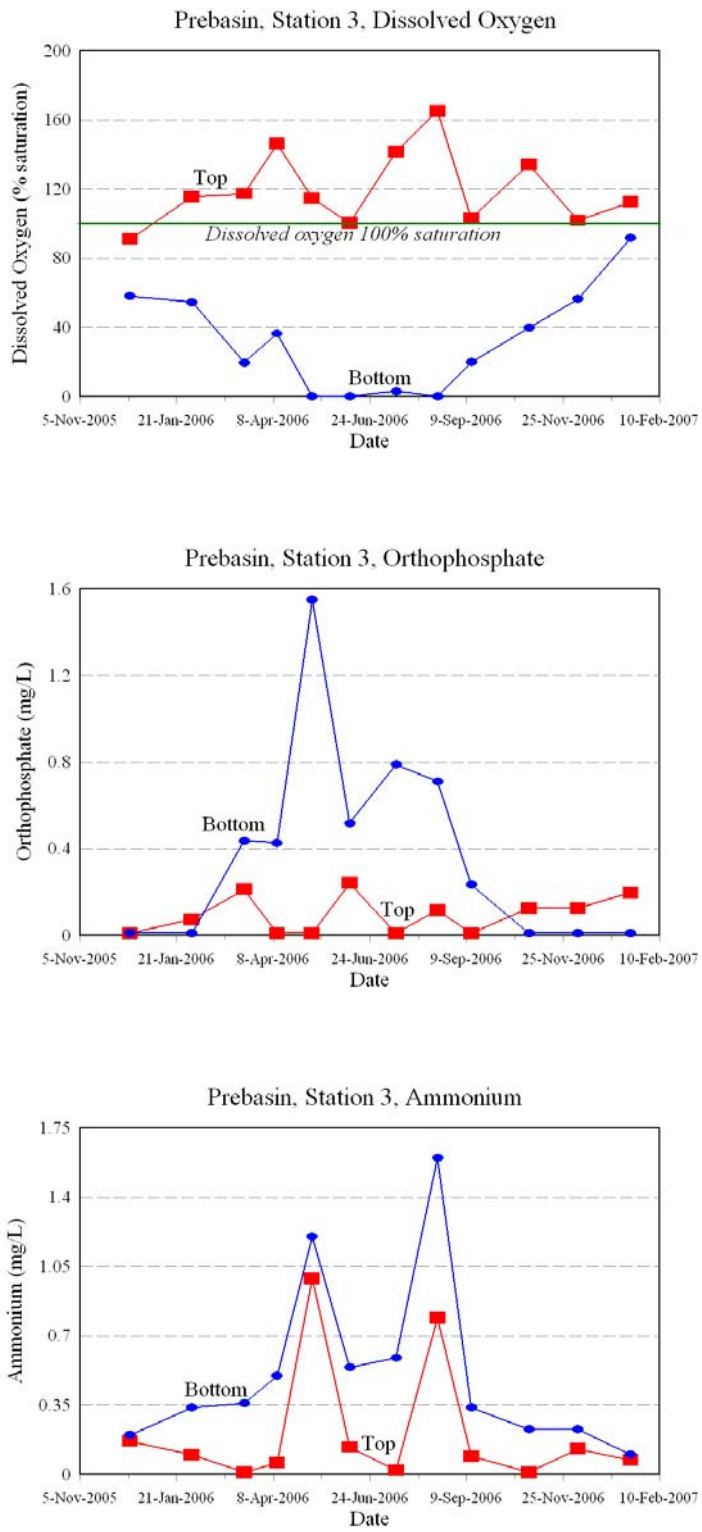


Figure 5.32. Time series comparisons of dissolved oxygen, orthophosphate, and ammonium concentrations in the mixing prebasin, station 3.

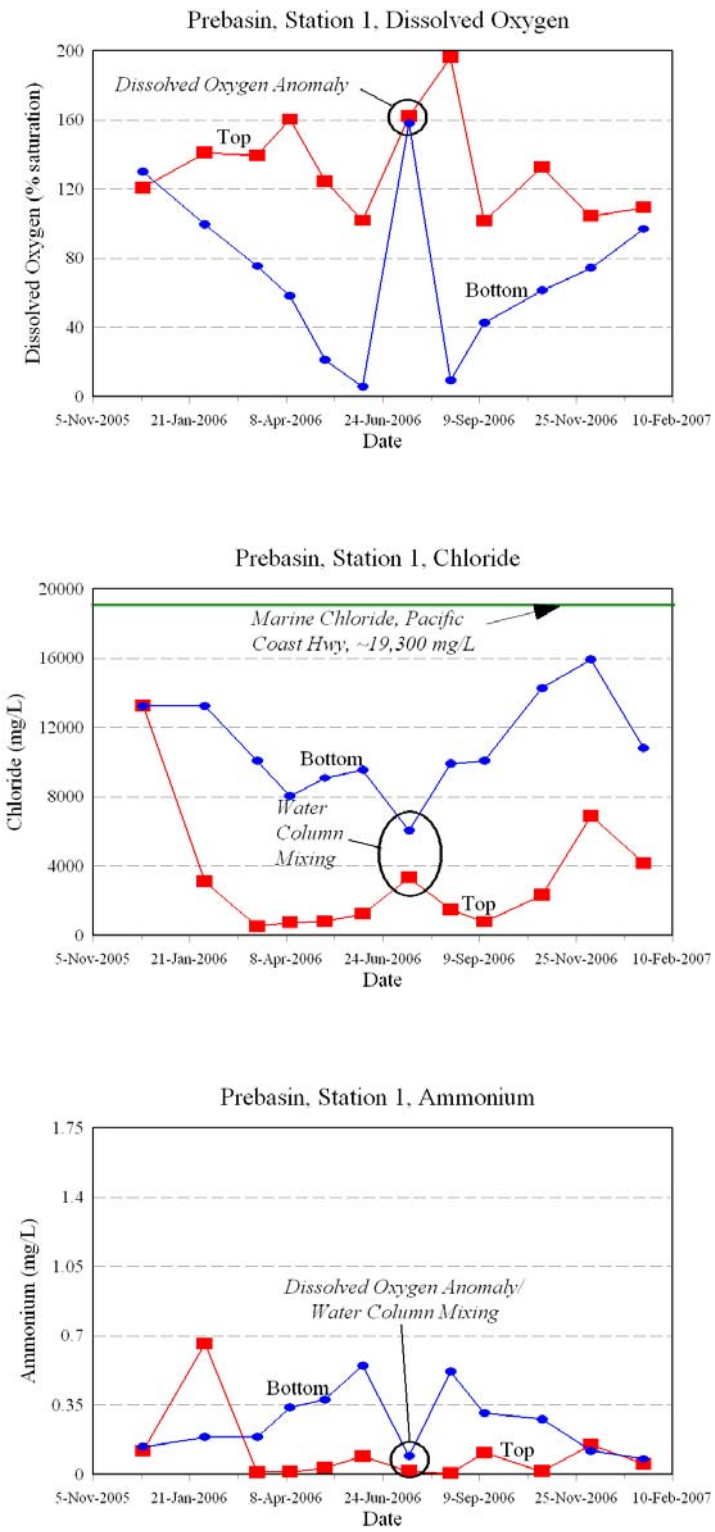
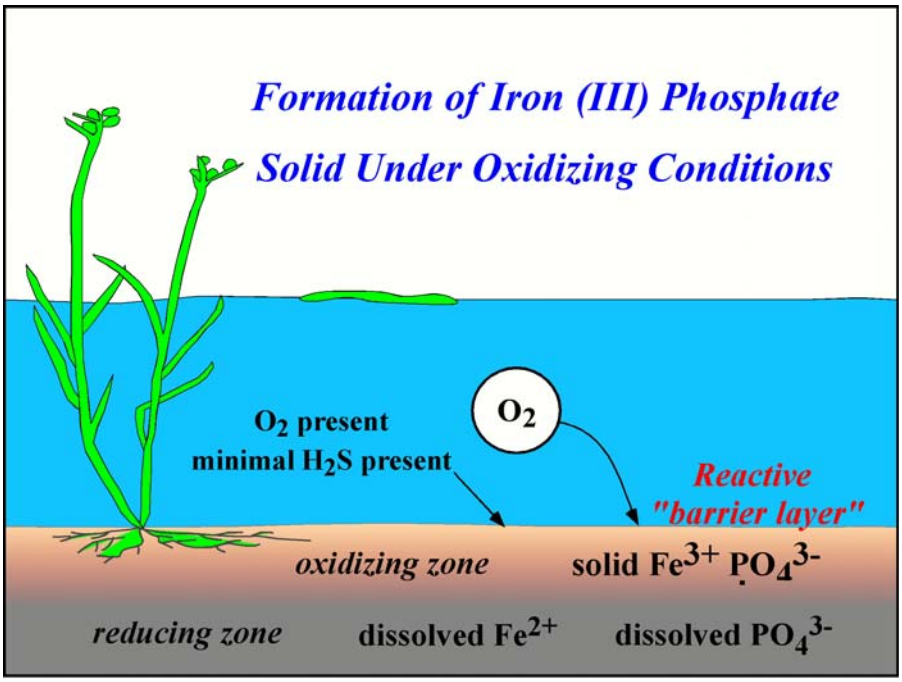
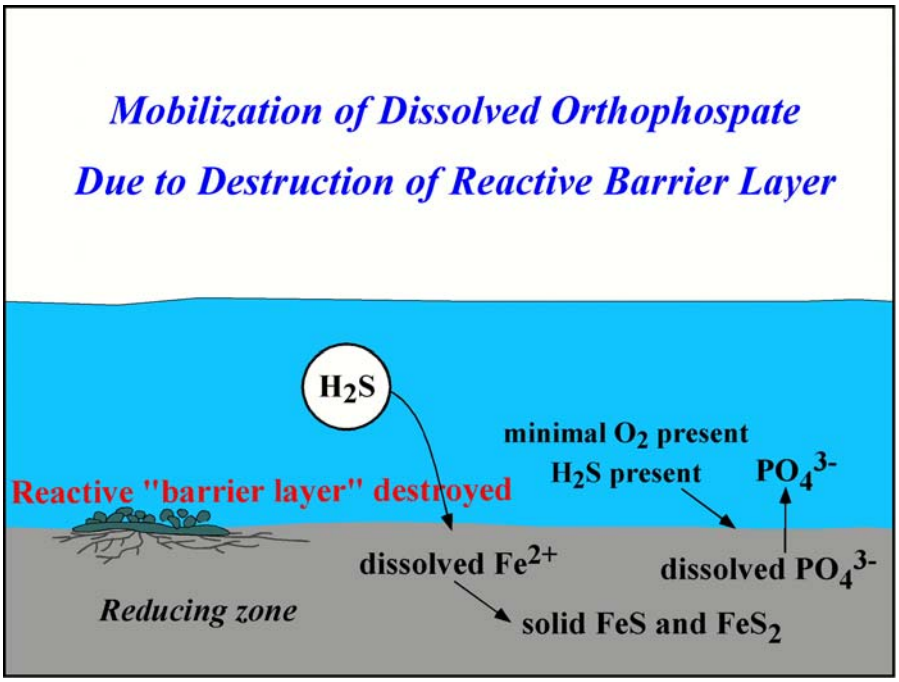


Figure 5.33. Time series comparisons of dissolved oxygen, chloride, and ammonium concentrations in the mixing prebasin, station 1. Dissolved oxygen anomaly is due to water column mixing, as shown in the chloride and ammonium data.



A.



B.

Figure 5.34. Phosphorous is stable in oxidizing waters and sediments due to the formation of iron-phosphorous complexes (A). Release of phosphorous occurs when iron-phosphorous compounds are reduced in anoxic sediments, solubilizing phosphorous (B). Reduced iron binds with sulfide to create iron-sulfide compounds in sediments, while phosphorous is released (modified from Uhlmann, 1975).

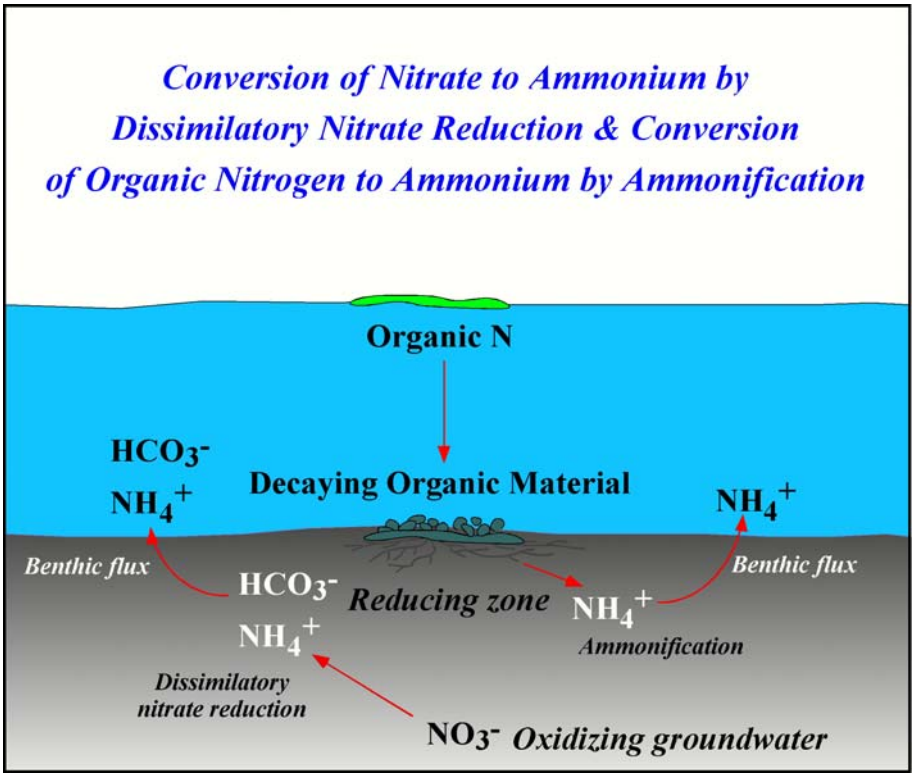


Figure 5.35. Conceptual model of nitrogen cycling in the mixing prebasin, focusing on dissimilatory nitrate reduction and ammonification as sources of ammonium.

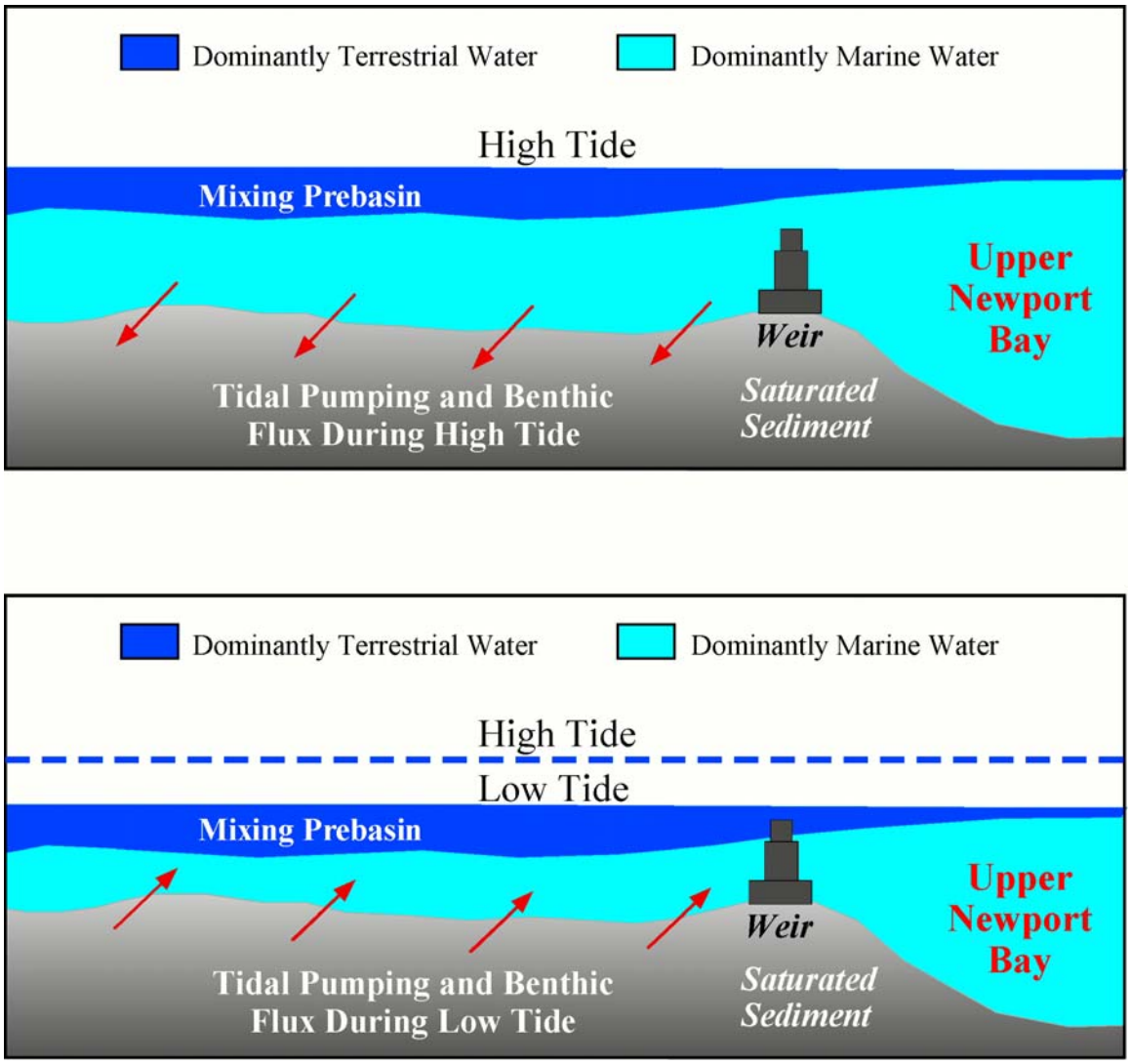


Figure 5.36. Benthic flux due to tidal pumping effects between water column and anoxic bottom sediments can accentuate release of orthophosphate and ammonium from the sediments due to processes shown in Figures 5.34 and 5.35.

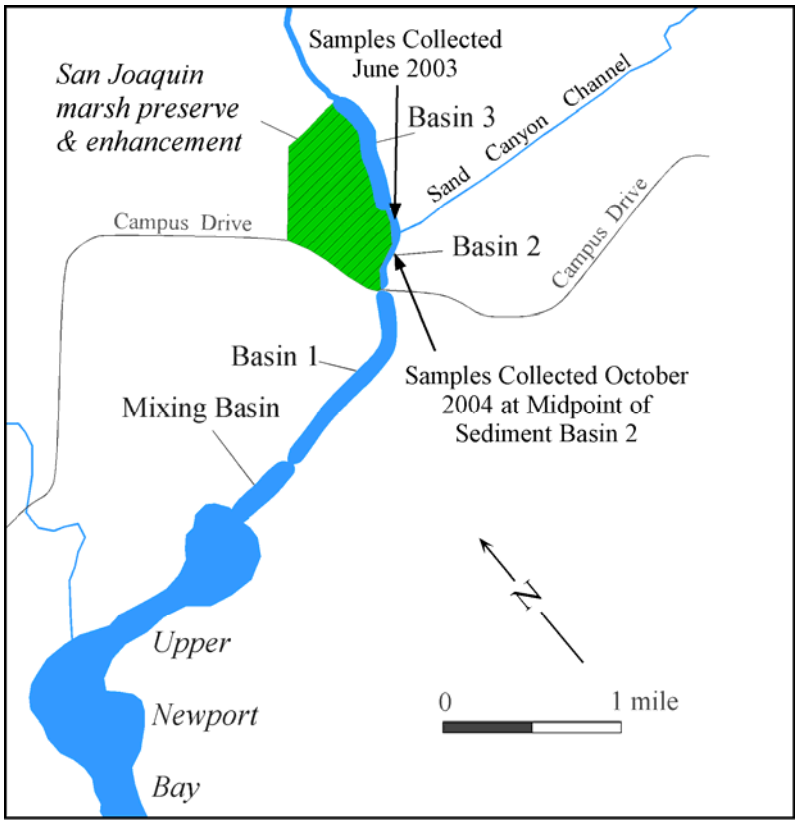


Figure 5.37. Locations of downstream sedimentation basins and sites of sediment Interstitial/water column investigations, June 2003 and October 2004.

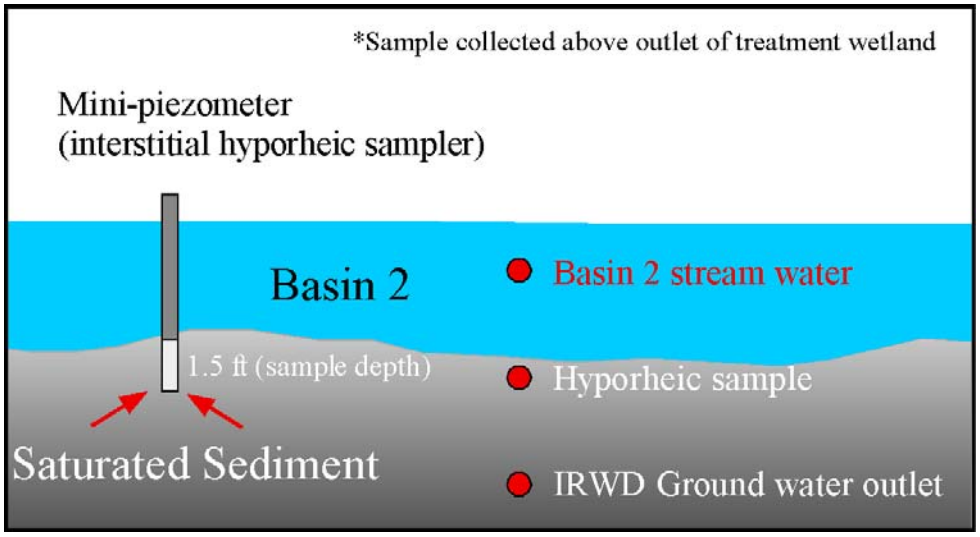


Figure 5.38. Schematic diagram illustrating water sampling zones at IRWD sediment basin 2, above the outlet of San Joaquin Marsh Wildlife Sanctuary and Treatment Wetland. Water samples were collected from the water column in the stream, hyporheic zone (interstitial water at the sediment-water column interface), and at the IRWD ground water discharge outlet just above sediment basin 2.

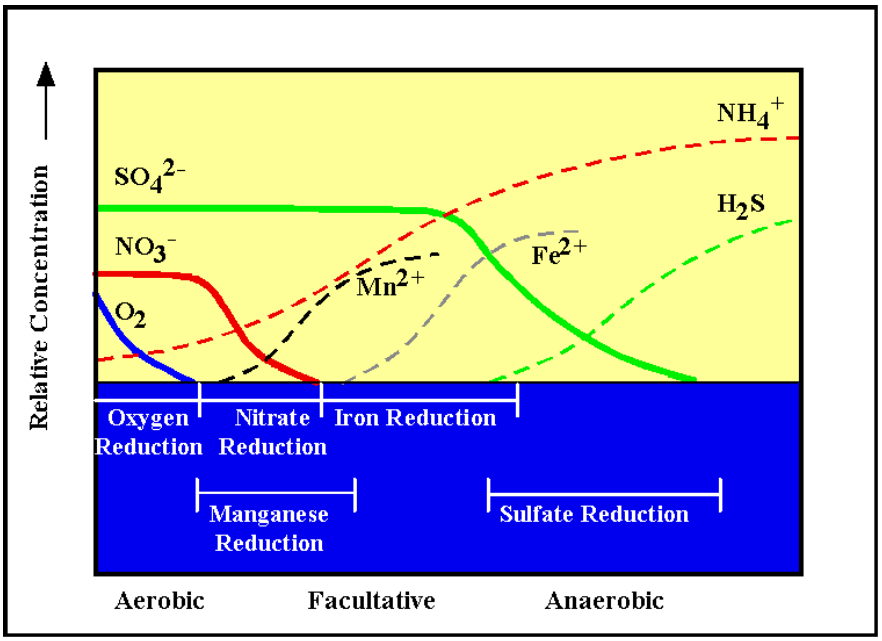


Figure 5.39. Reduction processes deplete oxygen, sulfate, and nitrate in natural waters, releasing ammonium, iron and manganese into solution. If dissolved sulfide (H2S) is produced in the presence of iron, iron sulfides may precipitate out of solution. Iron selenides can form as a result of similar reduction processes (modified from Kadlec and Knight, 1996).

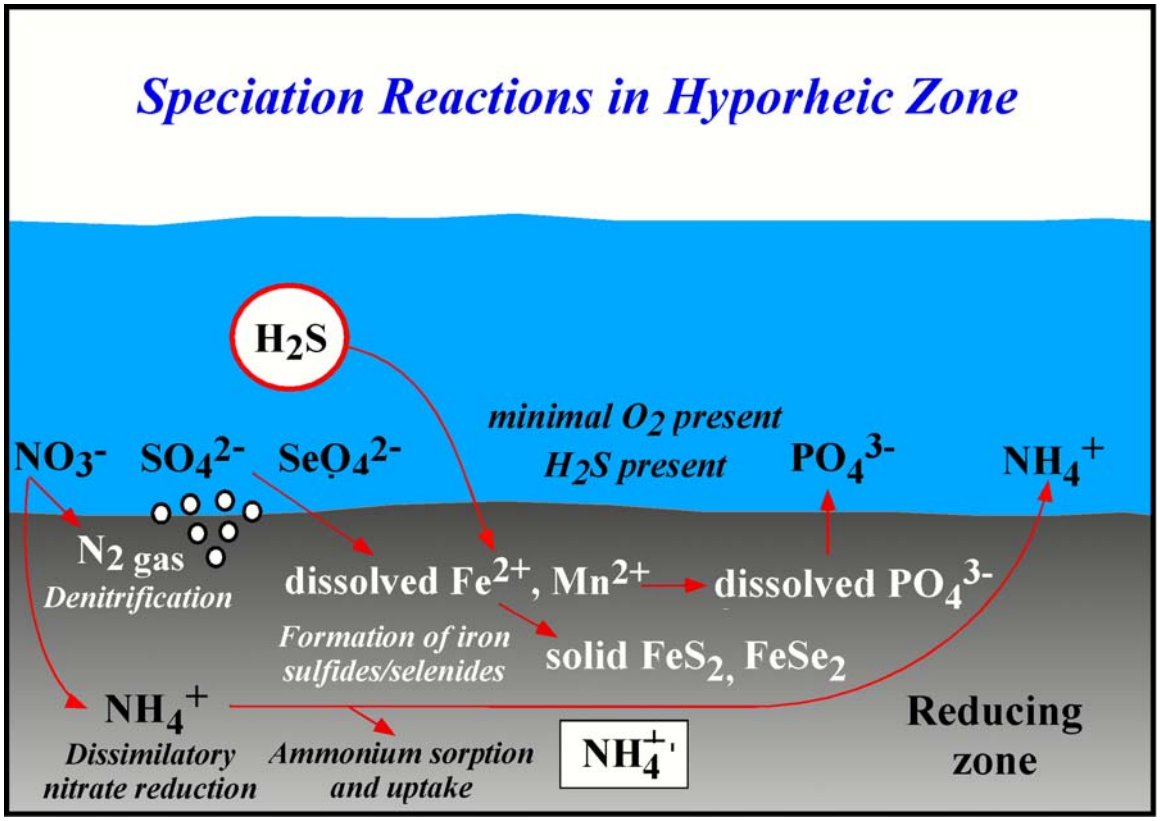


Figure 5.40. Schematic diagram illustrating interpreted hydrochemical processes in sediment basin 2, June 2003. Processes include downwelling of surface water into the hyporheic zone; consumption of dissolved oxygen through decay of organic material; reduction of nitrate by dissimilatory nitrate reduction to produce ammonium; probable sorption and possible uptake of ammonium; solution of phosphate, iron, and manganese through reduction; reduction of sulfate and selenate to produce iron-sulfides and iron-selenides; possible release of small amounts of phosphorous and ammonium from the hyporheic zone back into the surface water column.

Appendix 5.0

Vertical Specific Conductance, Dissolved Oxygen, and Temperature Profile Data

(These data also contained in Excel Data Base for downstream sediment basins)

Index Parameters with Depth in Basin 2 (November 20, 2005)

Station	Time	Depth (ft)	SC-TC (uS)	D.O. (mg/L)	D.O. (%)	Temp (^oC)
1	10:50AM	0.5	2922	13.91	139.4	16.0
		1.0	2931	14.04	143.2	16.0
		1.5	2932	13.92	142.0	15.9
		2.0	2935	14.06	143.3	15.6
		2.5	2932	14.89	150.0	15.6
		2.8	2929	0.56	5.9	15.6
2	11:50AM	0.5	2902	14.30	151.5	16.9
		1.0	2898	14.35	151.9	17.5
		2.0	2921	14.66	152.1	16.6
		3.0	2915	14.70	150.6	16.2
		4.0	2920	14.62	147.8	15.7
		4.8	2925	0.26	3.1	15.4
3	12:50PM	0.5	2908	12.88	132.1	15.7
		1.0	2906	13.44	135.0	15.6
		2.0	2904	13.50	135.6	15.3
		3.0	2902	13.44	134.8	15.3
		4.0	2899	13.48	135.3	15.2
		4.4	2898	0.12	1.3	15.2

Index Parameters with Depth in Basin 1 (November 27, 2005)

Station	Time	Depth (ft)	SC-TC (uS)	D.O. (mg/L)	D.O. (%)	Temp.
1	12:55PM	0.5	2825	12.99	135.7	16.8
		1.0	2809	13.45	138.1	16.4
		2.0	2796	13.60	139.4	16.3
		3.0	2802	13.78	140.4	16.1
		4.0	2812	13.52	137.7	16.0
		5.0	2820	13.30	134.8	15.8
		5.3	2821	0.13	1.2	15.8
2	1:50PM	0.5	2752	11.80	121.0	16.6
		1.0	2755	11.90	123.5	16.4
		1.5	2756	11.86	122.1	16.3
3	2:15PM	0.5	2959	10.75	112.1	16.4
		1.0	2957	10.95	114.5	16.5
		1.5	2996	11.10	115.3	16.4
		2.0	5350	13.20	137.4	16.3
		2.5	8550	13.58	141.5	16.1
		2.9	9580	0.20	2.2	16.1
4	2:50PM	0.5	3721	11.99	122.0	16.2
		1.0	3732	12.47	128.0	16.2
		1.5	5630	16.49	169.8	16.3
5	3:10PM	0.5	3642	10.94	112.4	15.7
		1.0	3659	12.97	133.1	15.7
		1.5	7170	15.32	158.1	16.1
		2.0	10150	16.96	177.3	16.6
		2.3	10680	15.05	158.8	16.7

Index Parameters with Depth in Prebasin (December 15, 2005)

Station	Time	Depth (ft)	SC-TC (uS)	D.O. (mg/L)	D.O. (%)	Temp (^oC)
1	2:50PM	0.5	38560	10.36	120.9	15.9
		1.0	38520	10.81	125.9	15.9
		1.5	38530	10.93	127.7	15.9
		2.0	38510	11.00	128.3	15.9
		2.5	38530	11.10	129.8	15.9
		3.0	38530	11.14	130.1	15.9
		3.4	38530	0.69	8.1	15.9
2	2:20PM	0.5	36930	9.52	110.2	15.8
		1.0	36960	9.85	114.8	15.8
		1.5	37110	9.74	113.6	15.8
		2.0	38660	9.66	112.9	15.8
		2.6	39640	0.28	3.9	15.8
3	1:15PM	0.5	36420	7.72	91.2	15.5
		1.0	37340	7.69	90.5	15.5
		2.0	37890	7.29	85.8	15.4
		3.0	41570	6.72	79.1	15.4
		4.0	44260	6.18	72.5	15.3
		5.0	45710	5.59	65.9	15.1
		6.0	46100	5.35	62.7	15.1
		7.0	46220	5.19	61.0	15.1
		8.0	46230	5.25	61.4	15.1
		9.0	46300	5.09	59.7	15.1
		10.0	46350	4.97	58.4	15.2
		10.7	46220	0.51	5.3	15.2
4	12:40PM	0.5	36770	8.22	96.2	15.8
		1.0	37240	7.95	93.3	15.6
		2.0	38810	7.54	88.2	15.5
		3.0	42010	6.62	77.2	15.3
		4.0	44110	5.99	69.1	15.3
		5.0	45230	4.95	58.2	15.3
		5.6	45620	0.13	1.7	15.4

Index Parameters with Depth in Basin 2 (January 8, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	12:00PM	0.5	2550	10.46	106.6	15.8
		1.0	2558	10.40	106.6	15.7
		2.0	2594	10.56	106.7	15.6
		3.0	2635	10.58	106.9	15.5
`		3.5	2640	0.44	4.6	15.3
2	12:55PM	0.5	2428	9.62	98.2	15.9
		1.0	2428	9.54	97.2	15.9
		2.0	2451	9.60	97.7	15.7
		3.0	2536	9.31	92.8	15.3
		4.0	2623	9.16	90.8	14.9
		5.0	2626	8.97	89.0	14.7
		6.0	2621	8.98	89.3	14.7
		6.4	2623	1.96	19.4	14.7
3	1:30PM	0.5	2530	9.07	92.2	15.3
		1.0	2538	8.82	87.8	15.1
		2.0	2541	8.47	84.4	15.0
		3.0	2569	8.41	83.7	14.8
		4.0	2580	8.43	83.5	14.8
		5.0	2585	8.34	82.6	14.7
		6.0	2586	8.36	82.7	14.7
		7.1	2584	0.85	8.60	14.7

Index Parameters with Depth in Basin 3 (January 8, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	3:40PM	0.5	2752	9.66	98.7	15.6
		1.0	2748	9.66	98.3	15.6
		2.0	2752	9.50	96.6	15.5
		3.0	2821	9.29	93.0	15.3
		4.0	2869	9.14	91.5	15.1
		4.2	2875	8.73	86.7	15.0

Index Parameters with Depth in Basin 1 (January 19, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	12:35PM	0.5	3172	14.55	142.7	14.8
		1.0	3234	14.59	145.1	14.6
		2.0	5390	14.01	139.4	14.2
		3.0	17530	7.71	79.8	15.6
		4.0	31750	6.23	65.4	16.7
		4.8	32470	5.51	58.1	16.8
2	1:25PM	0.5	4473	13.27	137.4	15.8
		1.0	4570	14.31	147.5	15.8
		1.2	5390	15.37	158.5	15.9
3	2:00PM	0.5	7270	15.46	157.9	15.5
		1.0	8840	17.34	180.4	15.8
		1.5	11160	20.60	224.0	17.8
		2.0	23050	16.00	176.1	18.3
4	2:27PM	0.5	11050	19.81	207.3	16.0
		0.8	16510	24.79	263.2	18.6
5	2:50PM	0.5	10500	19.14	172.6	16.1
		1.0	13610	23.22	245.3	17.6
		1.5	30670	30.79	356.1	21.2

Index Parameters with Depth in Pre-Basin (February 2, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	1:25PM	0.5	8980	12.40	141.1	15.7
		1.0	9180	12.44	140.8	15.7
		2.0	26530	8.95	102.9	15.6
		3.0	36880	7.93	89.4	15.6
		4.0	37880	8.23	93.2	15.7
		5.0	38500	8.75	99.6	15.7
		5.7	38640	7.60	87.5	15.8
2	2:30PM	0.5	9290	10.59	121.0	16.2
		1.0	9430	10.92	125.4	16.2
		2.0	31880	8.36	95.7	15.6
		3.0	38270	7.79	89.1	15.7
		3.8	40140	2.80	32.0	15.9
3	3:05PM	0.5	9330	9.81	115.7	16.2
		1.0	9890	9.93	119.2	16.0
		2.0	33290	8.09	95.5	15.9
		3.0	39960	7.69	90.3	15.7
		4.0	42250	7.51	89.0	15.8
		5.0	43640	7.29	86.6	16.0
		6.0	45010	6.92	81.6	16.0
		7.0	45670	6.52	76.8	16.0
		8.0	46190	5.67	67.4	15.9
		9.0	46670	5.13	60.9	15.8
		10.0	46870	4.63	54.7	15.8
		10.6	46910	2.68	31.9	15.8
4	4:20PM	0.5	11390	10.11	121.1	16.2
		1.0	11920	10.47	124.9	16.3
		2.0	34360	8.64	103.9	15.9
		3.0	39180	8.06	96.5	15.8
		4.0	43050	7.55	90.4	16.0
		4.9	44430	0.99	12.2	16.2

Index Parameters with Depth in Basin 2 (February 16, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	2:05PM	0.5	2840	14.84	154.3	16.3
		1.0	2838	14.84	150.3	16.3
		1.5	2840	14.84	154.3	16.3
		2.0	2840	14.83	153.5	16.3
		2.5	2844	14.83	153.4	16.2
		3.0	2845	14.82	152.2	16.2
		3.5	2843	14.76	151.2	16.1
		3.7	2848	14.34	147.1	16.0
2	1:15PM	0.5	2817	15.41	159.8	16.5
		1.0	2815	15.41	155.8	16.5
		2.0	2813	15.04	155.5	16.4
		3.0	2812	15.07	155.2	16.4
		4.0	2814	15.08	155.3	16.2
3	12:55PM	0.5	2818	13.85	141.8	15.8
		1.0	2825	13.75	141.2	15.6
		2.0	2823	13.13	132.8	15.5
		3.0	2824	12.81	130.7	15.5
		4.0	2822	12.60	127.2	15.5
		4.6	2822	11.60	117.9	15.4

Index Parameters with Depth in Basin 3 (February 16, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
4	11:40AM	0.5	2811	12.90	131.8	16.6
		1.0	2807	13.22	136.8	16.5
		1.5	2802	13.49	139.4	16.5
		2.0	2812	13.72	141.9	16.5
		2.5	2808	13.72	140.5	16.4
		3.0	2806	13.69	139.7	16.0
		3.5	2808	13.71	140.0	15.9
		3.9	2809	13.28	136.3	15.9

Index Parameters with Depth in Basin 1 (March 2, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	1:50PM	0.5	1710	8.70	92.8	17.4
		1.0	1717	8.70	91.8	17.3
		2.0	1724	8.86	92.6	17.2
		3.0	1731	8.78	91.2	17.0
		3.8	1735	8.54	87.7	17.0
2	1:20PM	0.5	1548	8.30	88.3	17.7
		1.0	1547	8.34	88.5	17.7
		1.5	1579	8.64	89.7	17.3
		2.0	1585	7.40	83.2	17.2
3	12:50PM	0.5	1443	8.73	93.2	17.9
		1.0	1441	8.68	92.6	18.0
		1.5	1504	8.79	93.0	17.8
		2.0	1514	8.87	92.6	17.5
		2.5	1523	8.60	83.1	16.8
4	12:25PM	0.5	1477	8.70	92.3	17.9
		1.0	1476	8.73	92.0	17.9
		1.5	1480	8.82	91.8	17.8
		1.8	1500	8.75	90.9	17.2
5	11:50AM	0.5	1446	8.97	94.3	17.8
		1.0	1445	8.95	94.2	17.8
		1.5	1454	9.20	95.3	17.4
		2.0	1475	9.27	96.1	16.6
		2.2	1474	9.40	97.1	16.5

Index Parameters with Depth in Pre-Basin (March 16, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	1:50PM	0.5	2558	12.90	139.7	18.2
		1.0	2946	12.38	141.6	18.2
		1.5	6040	7.79	87.0	18.1
		2.0	29900	6.35	69.6	16.5
		2.5	30220	6.36	70.2	16.4
		3.0	30370	6.36	70.1	16.5
		3.5	30650	6.84	75.5	16.5
		3.9	30590	5.98	6.6	16.7
2	1:30PM	0.5	4636	11.06	124.0	18.0
		1.0	5170	11.08	123.8	17.8
		1.5	5960	7.59	80.8	17.6
		2.0	28530	7.26	78.9	16.5
		2.5	31300	6.70	72.5	16.3
		2.8	31840	5.99	65.0	16.2
3	12:35PM	0.5	5320	10.04	117.3	17.5
		1.0	5390	9.99	115.5	17.5
		2.0	26240	6.74	73.2	16.6
		3.0	30970	5.93	67.0	16.2
		4.0	34980	5.43	61.0	16.1
		5.0	36470	4.54	51.4	15.9
		6.0	37150	4.47	50.1	15.8
		7.0	37490	3.89	43.5	15.9
		8.0	37760	3.05	34.0	15.7
		9.0	37830	2.55	28.4	15.6
		10.0	37860	2.10	23.2	15.5
		11.0	37930	1.79	19.9	15.4
		11.4	37850	1.58	17.6	15.5
4	12:10PM	0.5	6550	9.45	110.5	17.9
		1.0	6670	6.54	74.0	17.9
		2.0	28360	6.32	71.7	16.4
		3.0	31100	6.15	69.2	16.2
		4.0	34230	5.59	63.0	16.0
		5.0	36130	5.15	58.0	15.9
		5.3	36480	5.09	57.3	15.9

Index Parameters with Depth in Basin 2 (March 23, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	1:15PM	0.5	1605	10.07	110.7	19.6
		1.0	1607	10.05	109.9	19.6
		2.0	1609	10.10	110.9	19.6
		3.0	1619	10.32	112.0	19.3
		4.0	1737	8.78	93.8	18.5
2	12:01PM	0.5	1457	9.86	107.5	19.6
		1.0	1472	10.86	113.0	18.5
		2.0	1485	11.08	115.7	17.1
		3.0	1587	10.37	107.9	17.0
		4.0	1665	6.10	63.1	16.3
3	11:30AM	0.5	1443	9.22	101.7	20.1
		1.0	1420	9.46	102.3	19.7
		2.0	1522	8.51	88.0	16.6
		3.0	1542	8.12	83.2	16.2
		4.0	1564	7.64	78.1	16.1
		5.0	1572	7.44	76.1	16.1
		5.8	1566	4.44	42.5	16.1

Index Parameters with Depth in Basin 3 (March 23, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	2:15PM	0.5	1976	8.38	88.9	17.7
		1.0	1965	8.30	87.8	17.7
		2.0	1984	7.77	80.6	17.7
		3.0	2133	7.72	80.2	16.9
		4.0	2140	7.36	76.3	16.7
		4.2	2140	6.70	69.3	16.7

Index Parameters with Depth in Basin 1 (March 30, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	1:55PM	0.5	1047	8.22	86.1	17.1
		1.0	1042	8.24	86.1	17.1
		2.0	1038	8.24	85.7	17.1
		3.0	1038	8.19	85.2	17.0
		4.0	1043	8.17	85.0	17.0
		5.0	1045	8.25	86.2	17.0
		5.3	1045	7.78	81.2	17.0
2	1:12PM	0.5	1025	8.44	90.1	17.8
		1.0	1023	8.25	87.5	17.9
		1.5	1024	8.29	87.2	17.8
		2.0	1029	8.23	86.9	17.4
		2.5	1029	8.19	86.0	17.4
3	12:30PM	0.5	961	8.24	89.9	18.9
		1.0	962	8.13	88.4	19.0
		2.0	970	8.07	86.7	18.7
		3.0	983	8.19	86.8	17.9
		4.0	983	7.28	77.0	17.8
4	12:07PM	0.5	919	8.10	89.4	19.7
		1.0	921	8.03	87.9	19.6
		2.0	941	7.99	85.6	18.4
		3.0	945	7.90	84.4	18.3
		3.7	944	7.07	76.0	18.3
5	11:45AM	0.5	858	7.64	85.2	20.4
		1.0	866	7.78	84.9	19.6
		2.0	876	8.62	86.3	19.0
		3.0	899	7.92	85.0	18.5
		3.8	898	7.46	80.6	18.5

Index Parameters with Depth in Pre-Basin (April 11, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	12:20PM	0.5	3330	14.24	160.4	18.7
		1.0	3650	13.90	158.6	18.7
		2.0	11980	7.43	84.4	18.6
		3.0	23570	5.51	62.6	18.7
		4.0	24230	5.09	58.1	18.7
		4.4	24450	4.44	50.5	18.7
2	1:10PM	0.5	4898	13.99	161.6	18.9
		1.0	5210	12.38	142.5	19.0
		1.5	7820	7.53	86.5	19.0
		2.0	19910	5.53	64.0	18.8
		2.5	26890	1.15	13.1	18.7
3	2:00PM	0.5	6940	11.5	146.3	19.2
		1.0	7060	11.61	146.6	19.2
		2.0	11170	7.08	89.1	19.0
		3.0	27830	3.30	40.2	18.7
		4.0	33180	3.67	45.4	18.4
		5.0	33700	3.45	42.6	18.4
		6.0	34270	3.19	39.0	18.3
		7.0	35130	3.30	40.7	18.2
		8.0	35690	3.15	38.6	18.2
		9.0	36220	2.99	36.5	18.1
		10.1	36490	2.20	27.8	18.1
4	2:55PM	0.5	7160	13.71	163.4	20.3
		1.0	7230	13.47	160.3	20.2
		1.5	7310	13.27	158.1	20.2
		2.0	12560	6.71	79.6	19.6
		2.5	22830	5.63	64.9	19.2
		3.0	27740	4.63	53.8	18.9
		3.5	31530	4.04	46.7	18.7
		4.1	33510	1.40	16.2	18.8

Index Parameters with Depth in Pre-basin (April 11, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	12:20PM	0.5	3330	14.24	160.4	18.7
		1.0	3650	13.90	158.6	18.7
		2.0	11980	7.43	84.4	18.6
		3.0	23570	5.51	62.6	18.7
		4.0	24230	5.09	58.1	18.7
		4.4	24450	4.44	50.5	18.7
2	1:10PM	0.5	4898	13.99	161.6	18.9
		1.0	5210	12.38	142.5	19.0
		1.5	7820	7.53	86.5	19.0
		2.0	19910	5.53	64.0	18.8
		2.5	26890	1.15	13.1	18.7
3	2:00PM	0.5	6940	11.50	146.3	19.2
		1.0	7060	11.61	146.6	19.2
		2.0	11170	7.08	89.1	19.0
		3.0	27830	3.30	40.2	18.7
		4.0	33180	3.67	45.4	18.4
		5.0	33700	3.45	42.6	18.4
		6.0	34270	3.19	39.0	18.3
		7.0	35130	3.30	40.7	18.2
		8.0	35690	3.15	38.6	18.2
		9.0	36220	2.99	36.5	18.1
		10.1	36490	2.20	27.8	18.1
4	2:55PM	0.5	7160	13.71	163.4	20.3
		1.0	7230	13.47	160.3	20.2
		1.5	7310	13.27	158.1	20.2
		2.0	12560	6.71	79.6	19.6
		2.5	22830	5.63	64.9	19.2
		3.0	27740	4.64	53.8	18.9
		3.5	31530	4.04	46.7	18.7
		4.1	33510	1.40	16.2	18.8

Index Parameters with Depth in Basin 2 (April 18, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	11:15AM	0.5	1721	13.83	157.3	21.0
		1.0	1722	13.53	153.8	21.0
		1.5	1721	12.46	140.9	21.0
		2.0	1724	12.51	140.8	20.9
		2.5	1732	11.90	133.7	20.5
		3.0	1746	10.68	118.8	20.1
		3.5	1753	9.93	109.9	20.0
		4.1	1762	8.88	97.8	19.8
2	12:00PM	0.5	1640	11.83	133.4	20.8
		1.0	1642	11.94	134.6	20.8
		2.0	1644	11.99	134.6	20.7
		3.0	1658	11.94	133.6	20.5
		4.0	1679	11.55	129.2	20.4
		5.1	1723	0.94	10.6	20.0
3	12:40PM	0.5	1752	7.90	87.8	20.3
		1.0	1752	8.01	90.9	20.3
		2.0	1765	7.95	87.5	19.6
		3.0	1782	7.77	85.4	19.2
		4.0	1790	7.52	81.3	19.1
		4.8	1790	0.05	0.6	19.1

Index Parameters with Depth in Basin 3 (April 18, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	1:10PM	0.5	2375	9.07	101.2	20.1
		1.0	2359	8.86	98.8	20.1
		2.0	2353	8.82	99.2	20.2
		3.0	2495	8.49	93.3	19.7
		4.0	2520	8.04	88.1	19.3
		4.5	2517	7.21	79.0	19.3

Index Parameters with Depth in Basin 1 (May 2, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	3:30PM	0.5	2435	9.60	111.4	22.0
		1.0	2433	9.54	110.8	22.0
		2.0	2430	9.65	112.4	22.0
		3.0	2472	9.82	112.3	21.9
		4.0	2491	10.07	116.4	21.8
		4.3	2497	0.03	0.3	21.8
2	1:16PM	0.5	2435	5.44	62.6	21.7
		1.0	2432	10.70	125.0	21.7
		1.5	2431	5.50	63.1	21.7
		2.0	2432	4.41	50.6	21.7
3	1:35PM	0.5	2552	5.81	66.9	21.7
		1.0	2552	10.62	124.0	21.7
		1.5	2644	5.82	67.0	21.7
		2.0	2655	5.76	66.2	21.7
		2.6	2768	0.06	0.6	21.7
4	1:52PM	0.5	3515	10.88	127.8	22.3
		1.0	3533	10.92	128.8	22.3
		1.5	3617	11.00	129.2	22.3
5	2:13PM	0.5	2992	10.10	119.8	22.5
		1.0	3007	10.21	121.2	22.6
		1.5	3544	10.69	127.0	22.5
		2.0	5050	11.00	130.9	22.6
		2.4	7130	11.22	133.9	22.9

Index Parameters with Depth in Pre-basin (May 9, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	11:40 AM	0.5	3533	10.37	124.5	20.1
		1.0	3887	8.69	107.0	20.1
		2.0	18900	2.34	28.8	20.3
		3.0	26970	2.18	26.1	20.4
		4.0	27330	1.75	21.4	20.4
		4.3	27390	1.80	21.8	20.4
2	12:30 PM	0.5	4787	10.33	125.6	20.5
		1.0	5120	8.40	100.6	20.5
		1.5	11500	3.77	46.3	20.5
		2.0	21740	3.38	40.5	20.5
		2.5	29630	3.40	41.0	20.4
		2.9	30130	2.37	27.9	20.4
3	1:15 PM	0.5	7750	8.91	114.9	21.1
		1.0	8090	8.71	112.5	21.1
		2.0	21200	5.71	74.1	20.6
		3.0	31550	4.84	61.5	20.5
		4.0	36210	3.09	39.8	20.6
		5.0	39020	1.64	20.3	20.7
		6.0	40070	0.08	1.1	20.9
		7.0	42830	0.06	0.8	20.7
		8.0	43100	0.06	0.6	20.4
		9.0	43180	0.05	0.4	20.2
		10.0	43280	0.02	0.2	20.1
		10.2	43270	0.01	0.2	20.0
4	2:42 PM	0.5	9480	10.06	125.5	21.8
		1.0	9480	10.14	127.2	21.8
		2.0	19540	5.88	73.5	21.0
		3.0	31200	5.06	63.3	20.7
		4.0	36870	5.89	73.8	21.1

Index Parameters with Depth in Basin 2 (May 18, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	12:00 PM	0.5	2739	11.29	133.2	22.7
		1.0	2742	11.24	135.6	22.8
		2.0	2735	11.33	133.6	22.8
		3.0	2720	9.95	115.0	22.9
		3.6	2717	2.15	26.0	22.7
2	12:59 PM	0.5	2708	15.38	184.0	23.2
		1.0	2705	15.46	183.2	23.3
		2.0	2705	15.17	183.8	23.4
		3.0	2711	14.58	176.5	23.4
		3.5	2716	7.99	93.5	23.3
3	1:24 PM	0.5	2710	12.50	147.2	23.4
		1.0	2710	12.42	152.4	23.4
		2.0	2715	12.60	148.8	23.3
		3.0	2725	9.00	105.3	22.9
		4.0	2723	0.05	0.5	22.9

Index Parameters with Depth in Basin 3 (May 18, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	2:27 PM	0.5	2812	14.70	173.1	23.5
		1.0	2798	14.60	179.8	23.6
		2.0	2801	14.16	174.9	23.6
		3.0	2818	10.30	124.8	23.4
		4.1	2817	9.73	118.2	23.4

Index Parameters with Depth in Basin 1 (May 31, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	2:21 PM	0.5	2821	13.65	168.8	25.6
		1.0	2820	13.66	169.3	25.7
		2.0	2815	12.55	155.1	25.7
		3.0	2836	10.45	126.7	24.6
		4.0	2917	8.59	103.3	24.3
		4.2	2909	8.19	98.7	24.2
2	2:03 PM	0.5	2872	15.52	192.9	25.9
		1.0	2871	15.22	189.5	25.9
		1.3	2876	0.52	6.5	25.8
3	1:10 PM	0.5	3142	17.67	226.2	26.5
		1.0	3132	18.30	233.4	26.6
		1.5	3223	18.14	229.2	26.6
		2.0	3323	13.09	167.9	26.3
		2.5	5550	0.09	1.2	24.3
4	12:47 PM	0.5	4721	22.01	283.3	27.3
		1.0	4864	23.03	294.5	27.3
		1.5	4607	23.52	298.4	27.1
		1.8	4563	0.30	3.7	27.0
5	11:44 AM	0.5	4720	20.65	260.3	26.8
		1.0	4660	20.82	254.3	26.5
		1.5	7100	17.53	213.8	25.0
		2.0	8170	12.51	151.5	24.7
		2.2	14870	0.08	1.2	24.8

Index Parameters with Depth in Pre-basin (June 8, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	11:45 AM	0.5	5590	8.25	102.0	22.4
		1.0	5670	7.96	98.9	22.4
		2.0	12820	4.80	60.1	22.4
		3.0	25070	1.33	16.0	22.6
		4.0	28200	1.07	13.2	22.7
		5.0	29640	0.50	5.8	22.8
		5.3	30020	0.00	0.1	22.8
2	12:32 PM	0.5	6910	8.44	105.2	22.4
		1.0	6620	8.00	100.1	22.4
		1.5	6780	6.72	84.7	22.5
		2.0	8860	2.08	26.9	22.5
		2.5	23010	1.06	14.0	22.6
		3.1	35690	0.02	0.3	23.4
3	12:55 PM	0.5	7460	7.81	100.4	21.7
		1.0	7470	7.72	98.7	22.2
		2.0	10040	3.36	43.5	22.3
		3.0	28940	2.47	32.1	22.6
		4.0	34850	0.83	13.0	22.9
		5.0	41450	0.20	2.9	23.5
		6.0	42180	0.09	1.5	23.4
		7.0	42630	0.03	0.5	23.2
		8.0	42940	0.03	0.4	23.1
		9.0	43200	0.03	0.4	23.2
		10.0	43460	0.02	0.2	23.1
		10.9	43380	0.00	0.0	22.9
4	2:08 PM	0.5	7780	9.06	114.6	22.8
		1.0	7790	8.93	112.3	22.8
		2.0	11370	6.59	83.7	22.7
		3.0	23610	4.47	57.6	22.6
		4.0	33760	1.91	24.3	22.9
		4.8	40710	0.29	3.1	23.5

Index Parameters with Depth in Basin 2 (June 12, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	12:53 PM	0.5	2634	13.00	157.2	24.5
		1.0	2633	13.88	166.8	24.5
		2.0	2631	12.55	152.5	24.5
		3.0	2615	12.21	147.6	24.5
		3.5	2624	0.14	1.8	23.8
2	11:52 AM	0.5	2647	13.24	157.9	24.0
		1.0	2631	13.78	166.1	24.1
		2.0	2639	13.50	162.2	24.0
		3.0	2628	12.60	150.6	23.9
		3.3	2634	11.55	132.3	23.8
3	11:06 AM	0.5	2645	9.79	117.0	23.6
		1.0	2637	9.97	119.7	23.5
		2.0	2632	9.02	106.4	23.2
		3.0	2639	8.04	95.0	23.1
		4.0	2640	7.50	88.4	23.1
		5.0	2641	7.32	86.4	23.1
		5.9	2633	0.06	0.8	23.1

Index Parameters with Depth in Basin 3 (June 12, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	1:55 PM	0.5	2626	10.47	128.0	25.0
		1.0	2619	10.77	131.0	24.9
		2.0	2628	10.56	127.1	24.5
		3.0	2639	9.37	110.7	23.9
		4.0	2634	8.96	105.1	23.7
		4.5	2641	6.85	81.2	23.7

Index Parameters with Depth in Basin 1 (July 5, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	11:40 AM	0.5	2772	9.56	123.8	28.6
		1.0	2776	9.79	128.1	28.6
		2.0	2769	9.49	122.8	28.2
		3.0	2771	8.90	114.2	28.0
		3.6	2770	6.73	86.7	27.9
2	12:46 PM	0.5	2809	10.28	135.9	29.4
		1.0	2767	10.48	138.0	29.4
		1.1	2808	8.92	118.5	29.4
3	1:16 PM	0.5	2792	12.18	161.5	29.4
		1.0	2796	12.79	172.2	29.3
		1.5	2788	13.06	171.5	29.2
		2.0	2777	0.13	1.9	29.0
4	1:41 PM	0.5	2801	15.23	202.0	30.2
		1.0	2757	15.71	210.8	30.2
		1.1	2758	12.94	173.6	30.2
5	1:59 PM	0.5	2810	17.61	235.2	30.4
		1.0	2756	17.64	233.5	30.5
		1.5	2731	18.14	244.1	30.5
		1.9	2664	5.51	74.0	30.2

Index Parameters with Depth in Pre-basin (July 15, 2006)

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	11:10 AM	0.5	11570	12.26	162.1	27.9
		1.0	11640	12.35	165.1	28.0
		2.0	11810	12.57	168.9	27.7
		3.0	11950	12.60	166.0	27.9
		4.0	12110	11.71	158.1	27.8
		4.2	12420	0.17	2.4	27.6
2	12:00 PM	0.5	11910	10.30	143.8	28.1
		1.0	12700	10.75	147.0	28.1
		2.0	16870	9.22	128.9	27.4
		3.0	26880	8.68	118.5	26.9
		4.0	31030	8.03	110.1	26.7
		4.9	38140	1.02	12.3	26.8
3	12:57 PM	0.5	14660	9.54	141.6	28.6
		1.0	20280	10.41	153.0	28.4
		2.0	32730	10.28	148.6	27.0
		3.0	34330	9.61	137.3	26.7
		4.0	35360	9.51	134.2	26.7
		5.0	37090	9.16	131.3	26.6
		6.0	38060	9.34	133.9	26.5
		7.0	39960	8.87	126.9	26.4
		8.0	44230	6.53	92.0	26.1
		9.0	45140	4.45	64.1	25.7
		10.0	45790	2.04	29.4	25.5
		11.0	46160	0.61	8.8	25.4
		12.0	46460	0.31	4.9	25.2
		13.0	46540	0.22	3.2	25.0
		13.3	46460	0.06	0.8	24.9
4	2:04 PM	0.5	15600	9.71	143.6	29.3
		1.0	22350	10.15	148.2	28.9
		2.0	32160	10.95	155.8	27.4
		3.0	34850	10.43	148.1	27.2
		4.0	35900	10.21	146.1	27.2
		5.0	38050	10.58	150.1	27.2
		6.0	38770	9.63	138.0	27.1
		7.0	40010	9.12	130.0	27.0
		8.0	43630	0.89	11.6	26.2

Index Parameters with Depth in Basin 1 (July 20, 2006)

Basin 1 7/20/2006

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	3:02 PM	0.5	2712	10.75	140.9	29.4
	3:02 PM	1.0	2711	11.12	147.6	29.4
	3:02 PM	2.0	2710	10.95	144.0	29.3
	3:02 PM	3.0	2716	10.49	136.9	29.0
	3:02 PM	4.0	2729	0.05	0.7	28.6
2	2:38 PM	0.5	2740	11.86	177.7	30.2
	2:38 PM	1.0	2732	12.33	165.3	30.2
	2:38 PM	1.3	2724	6.60	88.3	30.1
3	1:51 PM	0.5	3196	13.07	176.2	30.6
	1:51 PM	1.0	3227	13.68	186.0	30.7
	1:51 PM	1.5	3791	13.83	188.2	30.6
	1:51 PM	2.0	3863	13.85	187.6	30.6
	1:51 PM	2.5	4820	0.10	1.5	30.4
	1:51 PM	2.8	5360	0.05	0.8	30.4
4	1:19 PM	0.5	4119	14.11	191.9	31.0
	1:19 PM	1.0	4045	15.61	215.2	30.9
	1:19 PM	1.2	5550	13.48	184.2	31.1
5	12:30 PM	0.5	3632	11.63	154.2	29.5
	12:30 PM	1.0	3519	12.15	161.8	29.6
	12:30 PM	1.5	7710	19.71	266.5	30.5
	12:30 PM	2.0	10430	18.19	248.2	31.0
	12:30 PM	2.4	10350	0.59	7.9	31.0

Index Parameters with Depth in Basin 2 (July 27, 2006)

Basin 2 7/27/2006

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	12:38 PM	0.5	2501	11.08	144.3	29.4
	12:38 PM	1.0	2498	11.67	153.0	29.4
	12:38 PM	2.0	2567	10.74	141.2	29.3
	12:38 PM	3.0	2580	10.78	142.1	29.3
	12:38 PM	3.8	2579	0.23	3.0	29.2
2	11:36 AM	0.5	2412	7.54	98.8	29.1
	11:36 AM	1.0	2420	7.53	97.8	29.0
	11:36 AM	2.0	2434	7.63	99.4	29.0
	11:36 AM	3.0	2446	7.52	98.4	29.0
	11:36 AM	4.0	2450	7.60	99.6	28.9
	11:36 AM	5.0	2466	7.23	94.2	28.9
	11:36 AM	5.5	2490	2.84	37.6	28.7
3	10:56 AM	0.5	2437	4.34	57.4	28.9
	10:56 AM	1.0	2437	4.57	60.3	29.0
	10:56 AM	2.0	2508	5.18	67.3	28.4
	10:56 AM	3.0	2525	4.77	31.6	28.2
	10:56 AM	4.0	2543	4.44	57.7	28.1
	10:56 AM	5.0	2564	4.32	55.4	28.1
	10:56 AM	6.0	2564	0.17	1.6	28.1
	10:56 AM	6.3	2554	0.50	6.4	28.1

Index Parameters with Depth in Basin 3 (July 27, 2006)

Basin 3 7/27/2006

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	1:41 PM	0.5	2352	11.90	158.0	29.6
	1:41 PM	1.0	2361	11.66	154.0	29.4
	1:41 PM	2.0	2369	10.39	136.6	29.0
	1:41 PM	3.0	2390	8.14	105.7	28.4
	1:41 PM	4.0	2392	7.52	97.2	28.3
	1:41 PM	4.3	2392	4.15	53.5	28.2

Index Parameters with Depth in Basin 2 (August 17, 2006)

Basin 2 8/17/2006

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	12:14 PM	0.5	2684	12.84	162.3	26.8
	12:14 PM	1.0	2682	12.86	161.8	26.8
	12:14 PM	2.0	2679	12.78	160.2	26.8
	12:14 PM	3.0	2673	12.02	149.9	26.7
	12:14 PM	3.7	2685	6.53	81.3	26.6
2	11:12 AM	0.5	2677	15.21	191.6	27.0
	11:12 AM	1.0	2669	14.91	188.0	26.8
	11:12 AM	2.0	2669	10.66	133.1	25.9
	11:12 AM	3.0	2633	7.61	94.5	25.2
	11:12 AM	3.6	2576	5.39	65.6	24.9
3	10:50 AM	0.5	2695	13.21	169.5	27.3
	10:50 AM	1.0	2707	14.05	177.7	27.0
	10:50 AM	2.0	2685	13.30	164.6	26.2
	10:50 AM	3.0	2682	9.77	122.1	25.7
	10:50 AM	3.9	2690	7.77	95.8	25.5

Index Parameters with Depth in Pre-basin (August 17, 2006)

Pre-basin 8/17/2006

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	1:45 PM	0.5	4647	14.53	196.2	28.0
	1:45 PM	1.0	6440	13.65	189.1	28.0
	1:45 PM	2.0	10000	11.75	160.5	27.5
	1:45 PM	3.0	20360	5.25	68.4	26.4
	1:45 PM	4.0	27010	2.49	37.2	26.2
	1:45 PM	5.0	29320	0.64	9.5	26.1
	1:45 PM	5.4	29870	0.00	0.0	26.1
2	2:35 PM	0.5	11170	10.89	150.9	27.0
	2:35 PM	1.0	11330	10.57	145.1	27.0
	2:35 PM	2.0	11940	10.34	143.9	27.2
	2:35 PM	3.0	19620	6.75	91.5	26.8
	2:35 PM	4.0	28600	4.62	63.3	26.5
	2:35 PM	5.0	32960	0.08	1.0	26.4
	2:35 PM	5.3	37700	0.01	0.1	26.5
3	3:14 PM	0.5	13340	11.67	165.0	28.3
	3:14 PM	1.0	13490	10.20	141.1	28.4
	3:14 PM	2.0	26970	6.84	95.0	27.2
	3:14 PM	3.0	30410	4.78	65.1	27.2
	3:14 PM	4.0	34190	4.94	67.8	27.4
	3:14 PM	5.0	36190	4.90	68.5	27.1
	3:14 PM	6.0	37000	4.04	55.5	26.6
	3:14 PM	7.0	39370	3.50	47.6	26.4
	3:14 PM	8.0	42500	2.42	33.7	26.4
	3:14 PM	9.0	42930	1.71	23.2	26.3
	3:14 PM	10.0	43490	0.09	1.4	26.2
	3:14 PM	11.0	45200	0.05	0.6	25.5
	3:14 PM	12.0	45540	0.02	0.2	25.0
	3:14 PM	13.0	45600	0.00	0.0	24.9
4	4:01 PM	0.5	19810	9.95	141.8	27.9
	4:01 PM	1.0	20010	8.14	113.2	27.8
	4:01 PM	2.0	28830	6.95	98.8	27.5
	4:01 PM	3.0	32850	6.76	96.2	27.7
	4:01 PM	4.0	34550	6.78	96.8	27.8
	4:01 PM	5.0	37160	6.75	96.8	27.9
	4:01 PM	6.0	38840	6.18	90.6	27.6
	4:01 PM	7.0	39270	5.62	78.9	27.5
	4:01 PM	7.5	39730	0.03	0.5	27.2

Index Parameters with Depth in Basin 1 (August 29, 2006)

Basin 1 8/29/2006

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	1:57 PM	0.5	2729	8.85	112.8	27.8
	1:57 PM	1.0	2777	8.97	114.6	27.8
	1:57 PM	2.0	2778	9.04	115.8	27.7
	1:57 PM	3.0	2780	8.45	107.1	27.3
	1:57 PM	4.0	2780	7.98	101.2	26.9
	1:57 PM	4.7	2780	5.75	72.9	26.9
2	12:40 PM	0.5	2814	9.60	120.6	27.8
	12:40 PM	1.0	2815	8.70	124.5	27.6
	12:40 PM	1.5	2808	8.15	104.5	27.4
3	12:19 PM	0.5	2829	9.06	113.6	26.4
	12:19 PM	1.0	2830	8.86	111.6	26.4
	12:19 PM	1.5	2826	9.07	113.6	26.4
	12:19 PM	2.0	2834	9.20	114.8	26.4
	12:19 PM	2.5	2833	7.75	97.3	26.4
4	12:02 PM	0.5	2876	12.75	160.6	26.9
	12:02 PM	1.0	2843	12.89	162.3	26.9
	12:02 PM	1.4	2869	11.23	142.0	26.7
5	11:21 AM	0.5	2918	12.91	162.5	26.4
	11:21 AM	1.0	2899	12.72	161.0	26.3
	11:21 AM	1.5	2896	12.75	159.0	26.3
	11:21 AM	1.9	2908	9.11	113.6	26.2

Index Parameters with Depth in Basin 3 (August 29, 2006)

Basin 3 8/29/2006

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	3:06 PM	0.5	2750	11.68	145.0	26.3
	3:06 PM	1.0	2743	11.59	146.5	26.3
	3:06 PM	2.0	2343	11.60	144.6	26.1
	3:06 PM	3.0	2741	10.58	131.9	25.9
	3:06 PM	4.0	2742	9.75	121.0	25.8
	3:06 PM	4.4	2742	7.04	87.6	25.8

Index Parameters with Depth in Basin 2 (September 13, 2006)

Basin 2 9/13/2006

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	12:27 PM	0.5	2467	13.38	166.0	25.8
	12:27 PM	1.0	2456	13.50	166.6	25.9
	12:27 PM	2.0	2473	14.15	175.5	25.8
	12:27 PM	3.0	2489	13.34	164.4	25.6
	12:27 PM	4.0	2513	8.31	101.7	25.3
2	11:25 AM	0.5	2587	14.00	170.2	25.1
	11:25 AM	1.0	2585	14.08	173.5	25.2
	11:25 AM	2.0	2577	11.85	144.4	24.8
	11:25 AM	3.0	2591	9.31	113.5	24.6
	11:25 AM	4.0	2647	8.18	99.2	24.5
	11:25 AM	4.2	2665	3.71	45.0	24.5
3	10:40 AM	0.5	2712	7.94	96.4	24.8
	10:40 AM	1.0	2742	8.49	102.0	24.5
	10:40 AM	2.0	2734	8.41	102.2	24.4
	10:40 AM	3.0	2743	8.06	98.3	24.3
	10:40 AM	4.0	2749	7.21	87.2	24.3
	10:40 AM	5.0	2742	7.31	88.1	24.3
	10:40 AM	6.0	2745	7.01	84.0	24.3
	10:40 AM	7.0	2731	0.00	0.0	24.4

Index Parameters with Depth in Pre-basin (September 13, 2006)

Pre-basin 9/13/2006

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	2:00 PM	0.5	4103	7.77	101.7	25.5
	2:00 PM	1.0	4537	7.60	100.3	25.4
	2:00 PM	2.0	6270	7.41	96.9	25.2
	2:00 PM	3.0	17450	3.79	50.1	24.8
	2:00 PM	4.0	25370	3.56	46.4	24.7
	2:00 PM	5.0	26750	3.47	44.1	24.6
	2:00 PM	6.0	28510	3.19	42.9	24.7
	2:00 PM	6.9	29970	0.00	0.0	24.7
2	2:47 PM	0.5	5560	6.90	92.3	24.6
	2:47 PM	1.0	5560	6.95	92.8	24.6
	2:47 PM	2.0	6600	6.77	91.6	24.8
	2:47 PM	3.0	19120	4.99	67.5	24.6
	2:47 PM	4.0	29770	4.64	61.4	24.6
	2:47 PM	5.0	33810	4.39	59.1	24.7
	2:47 PM	6.0	35750	4.05	54.3	24.7
	2:47 PM	6.7	39800	0.11	1.2	24.9
3	3:33 PM	0.5	5990	7.27	103.0	25.0
	3:33 PM	1.0	6080	7.25	102.5	25.0
	3:33 PM	2.0	10600	7.09	99.8	24.8
	3:33 PM	3.0	25360	6.37	89.5	24.7
	3:33 PM	4.0	35470	6.11	86.5	24.9
	3:33 PM	5.0	38940	5.92	86.4	24.8
	3:33 PM	6.0	41640	5.48	77.0	24.7
	3:33 PM	7.0	42260	5.47	78.0	24.8
	3:33 PM	8.0	44020	5.20	73.1	24.7
	3:33 PM	9.0	45370	4.16	58.2	24.5
	3:33 PM	10.0	46140	3.24	46.2	24.3
	3:33 PM	11.0	46280	2.50	35.1	24.2
	3:33 PM	12.0	46510	1.95	27.5	24.1
	3:33 PM	13.0	46490	1.40	20.0	24.0
	3:33 PM	13.3	46430	0.32	6.8	24.0
4	4:15 PM	0.5	6740	7.69	106.0	25.1
	4:15 PM	1.0	6750	7.78	107.2	25.2
	4:15 PM	2.0	8390	7.34	100.8	25.8
	4:15 PM	3.0	24800	6.23	87.7	24.8
	4:15 PM	4.0	36510	6.91	94.0	25.0
	4:15 PM	5.0	40280	6.08	83.3	24.9
	4:15 PM	6.0	42140	6.06	83.3	24.9
	4:15 PM	6.9	43590	0.47	6.7	25.0

Index Parameters with Depth in Basin 1 (September 19, 2006)

Basin 1 9/19/2006

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	1:20 PM	0.5	2766	9.25	110.1	23.8
	1:20 PM	1.0	2765	9.26	110.5	23.8
	1:20 PM	2.0	2761	9.23	109.6	23.7
	1:20 PM	3.0	2762	9.17	109.0	23.5
	1:20 PM	4.0	2766	9.02	106.3	23.4
	1:20 PM	5.0	2760	9.04	106.4	23.4
	1:20 PM	5.4	4008	6.19	2.2	23.3
2	12:36 PM	0.5	2775	9.17	109.3	24.0
	12:36 PM	1.0	2775	9.27	110.8	24.0
	12:36 PM	1.5	2773	9.44	113.4	23.9
	12:36 PM	2.0	2774	3.20	38.5	23.8
3	12:00 PM	0.5	2858	9.39	112.7	24.0
	12:00 PM	1.0	2855	9.53	113.8	23.8
	12:00 PM	1.5	2868	9.47	112.6	23.7
	12:00 PM	2.0	2907	9.03	106.5	23.3
	12:00 PM	2.5	2928	0.27	3.2	23.2
4	11:33 AM	0.5	3269	10.17	122.5	24.1
	11:33 AM	1.0	3258	10.27	121.8	24.0
	11:33 AM	1.5	3960	10.38	123.7	23.7
	11:33 AM	1.9	4420	0.64	7.8	23.7
5	10:44 AM	0.5	3259	8.87	104.3	22.9
	10:44 AM	1.0	3256	8.97	104.8	23.0
	10:44 AM	1.5	4895	8.34	110.2	23.1
	10:44 AM	2.0	5470	9.46	111.8	23.2
	10:44 AM	2.5	5540	9.57	113.6	23.2
	10:44 AM	2.7	5600	6.59	78.2	23.3

Index Parameters with Depth in Basin 3 (September 19, 2006)

Basin 3 9/19/2006

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	2:32 PM	0.5	2696	11.25	134.7	24.0
	2:32 PM	1.0	2705	11.46	136.2	23.4
	2:32 PM	2.0	2703	11.44	135.1	23.4
	2:32 PM	3.0	2705	11.36	134.5	23.3
	2:32 PM	4.0	2708	11.39	130.9	23.2
	2:32 PM	4.4	2708	0.26	3.1	22.9

Index Parameters with Depth in Basin 1 (October 11, 2006)

Basin 1 10/11/2006

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	2:07 PM	0.5	9440	11.54	144.0	22.1
	2:07 PM	1.0	10030	12.22	148.5	22.2
	2:07 PM	2.0	13490	13.75	165.1	22.3
	2:07 PM	3.0	35710	16.50	197.4	22.5
	2:07 PM	4.0	40800	15.23	186.7	22.6
	2:07 PM	5.0	41980	3.56	42.9	22.1
2	1:12 PM	0.5	15330	12.82	153.2	21.1
	1:12 PM	1.0	15530	13.67	161.4	21.2
	1:12 PM	1.5	15930	14.65	171.6	20.7
	1:12 PM	2.1	30960	16.25	197.5	21.9
3	12:45 PM	0.5	19220	16.77	207.7	21.4
	12:45 PM	1.0	20370	19.43	239.9	21.6
	12:45 PM	1.5	28620	18.64	232.2	22.4
	12:45 PM	2.0	35280	17.67	223.6	22.2
	12:45 PM	2.5	36560	22.47	285.1	22.4
	12:45 PM	3.0	40400	18.89	241.4	23.0
4	12:12 PM	0.5	33940	14.15	184.4	22.4
	12:12 PM	1.0	37420	12.14	156.4	21.8
	12:12 PM	1.5	38040	12.07	157.7	21.7
	12:12 PM	2.0	38220	13.42	155.2	21.6
	12:12 PM	2.2	38370	11.44	148.4	21.6
5	11:30 AM	0.5	36080	8.74	119.6	20.9
	11:30 AM	1.0	37260	8.79	119.7	20.9
	11:30 AM	1.5	37540	8.73	118.9	20.9
	11:30 AM	2.0	37180	8.79	120.0	20.9
	11:30 AM	2.1	37370	0.38	5.0	21.0

Index Parameters with Depth in Basin 3 (October 11, 2006)

Basin 3 10/11/2006

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	2:46 PM	0.5	2508	11.47	129.7	20.8
	2:46 PM	1.0	2793	11.61	130.8	20.8
	2:46 PM	2.0	2595	11.69	131.6	20.8
	2:46 PM	3.0	2792	11.71	129.6	20.6
	2:46 PM	4.0	2792	11.66	130.3	20.5
	2:46 PM	4.4	2792	3.49	39.6	20.5

Index Parameters with Depth in Pre-basin (October 29, 2006)

Pre-basin 10/29/2006

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	12:55 PM	0.5	7680	10.71	132.8	19.8
	12:55 PM	1.0	8700	9.57	117.0	19.4
	12:55 PM	2.0	31930	9.00	63.3	20.3
	12:55 PM	3.0	36630	4.06	51.2	20.6
	12:55 PM	4.0	38210	4.98	63.8	20.9
	12:55 PM	5.0	38560	5.32	67.7	21.0
	12:55 PM	6.0	38980	5.00	63.8	21.0
	12:55 PM	7.0	39160	4.85	61.5	21.1
	12:55 PM	7.6	36160	0.07	1.0	21.1
2	1:45 PM	0.5	10920	10.13	125.8	19.4
	1:45 PM	1.0	11020	8.27	105.1	19.5
	1:45 PM	2.0	33590	8.38	109.3	20.7
	1:45 PM	3.0	36880	8.62	110.3	20.9
	1:45 PM	4.0	38980	8.01	104.4	21.0
	1:45 PM	5.0	40470	7.03	90.8	21.2
	1:45 PM	6.0	40890	3.44	45.3	21.3
	1:45 PM	6.2	41030	0.05	0.7	21.3
3	2:25 PM	0.5	13140	10.28	134.3	20.5
	2:25 PM	1.0	13670	10.67	143.1	20.5
	2:25 PM	2.0	34470	10.50	138.5	20.8
	2:25 PM	3.0	38270	8.91	117.1	20.9
	2:25 PM	4.0	40580	8.82	117.0	21.1
	2:25 PM	5.0	41560	6.46	83.8	21.2
	2:25 PM	6.0	42490	5.79	76.7	21.1
	2:25 PM	7.0	43620	5.57	73.1	21.1
	2:25 PM	8.0	44160	3.77	49.8	21.2
	2:25 PM	9.0	44760	4.05	53.4	21.3
	2:25 PM	10.0	44950	3.67	48.6	21.3
	2:25 PM	11.0	44980	3.53	46.6	21.3
	2:25 PM	12.0	45000	3.16	41.4	21.3
	2:25 PM	13.0	45010	3.00	39.8	21.3
	2:25 PM	13.5	44930	0.02	0.3	21.3
4	3:20 PM	0.5	19240	11.28	144.9	20.5
	3:20 PM	1.0	19740	12.76	166.6	20.7
	3:20 PM	2.0	35740	11.46	152.3	21.1
	3:20 PM	3.0	38890	9.31	123.1	21.3
	3:20 PM	4.0	40740	9.83	129.8	21.4
	3:20 PM	5.0	41950	7.80	103.0	21.4
	3:20 PM	6.0	43000	6.10	78.4	21.3
	3:20 PM	7.0	43700	5.36	70.3	21.2
	3:20 PM	7.3	43960	0.09	1.1	21.2

Index Parameters with Depth in Basin 2 (November 15, 2006)

Basin 2	11/15/2006					
Station	**Time**	**Depth (ft)**	**SC-TC (µS)**	**D.O. (mg/L)**	**D.O. (%)**	**Temp (ºC)**
1	12:14 PM	0.5	2425	9.65	104.4	19.8
	12:14 PM	1.0	2422	9.53	105.3	19.7
	12:14 PM	2.0	2388	8.80	96.6	19.3
	12:14 PM	3.0	2358	8.55	90.0	18.5
	12:14 PM	3.6	2609	0.12	1.4	17.8
2	11:08 AM	0.5	2496	10.21	113.7	19.7
	11:08 AM	1.0	2517	11.02	117.6	19.2
	11:08 AM	2.0	2547	9.36	99.0	17.7
	11:08 AM	3.0	2658	9.27	97.1	17.6
	11:08 AM	4.0	2718	9.01	94.7	17.4
	11:08 AM	4.9	2720	6.20	65.2	17.4
3	10:36 AM	0.5	2523	10.38	111.6	18.7
	10:36 AM	1.0	2525	10.52	113.0	18.4
	10:36 AM	2.0	2555	10.29	108.4	17.8
	10:36 AM	3.0	2567	9.26	98.0	17.3
	10:36 AM	4.0	2583	8.94	94.2	17.1
	10:36 AM	5.0	2618	8.80	92.6	17.0
	10:36 AM	6.0	2635	3.00	31.8	17.1

Index Parameters with Depth in Basin 1 (December 6, 2006)

Basin 1	12/6/2006					
Station	**Time**	**Depth (ft)**	**SC-TC (µS)**	**D.O. (mg/L)**	**D.O. (%)**	**Temp (ºC)**
1	1:54 PM	0.5	10230	10.56	106.1	12.8
	1:54 PM	1.0	11510	10.48	106.3	13.0
	1:54 PM	2.0	12950	10.80	109.1	13.0
	1:54 PM	3.0	31400	10.59	109.3	13.6
	1:54 PM	4.0	33660	11.66	120.0	14.0
	1:54 PM	5.0	36700	0.16	1.6	15.0
2	1:12 PM	0.5	8840	9.88	99.7	13.8
	1:12 PM	1.0	9870	10.13	102.8	13.5
	1:12 PM	1.5	15560	10.35	104.6	13.1
	1:12 PM	2.0	20570	10.61	106.6	13.4
	1:12 PM	2.3	33580	11.72	121.2	14.1
3	12:50 PM	0.5	6990	10.08	103.0	13.8
	12:50 PM	1.0	7230	10.33	105.2	13.5
	12:50 PM	2.0	31440	10.32	106.9	14.0
	12:50 PM	3.0	36880	12.76	131.4	14.3
	12:50 PM	3.6	37140	0.09	1.0	14.6
4	11:46 AM	0.5	6110	10.19	102.4	12.8
	11:46 AM	1.0	6270	10.08	100.6	12.9
	11:46 AM	1.5	8840	10.40	104.0	12.5
	11:46 AM	2.0	28120	8.97	92.5	13.1
	11:46 AM	2.5	36880	10.39	108.1	14.0
	11:46 AM	2.9	37550	9.84	102.8	14.3
5	11:03 AM	0.5	6430	9.83	96.7	12.0
	11:03 AM	1.0	6830	9.90	98.4	12.3
	11:03 AM	2.0	28690	8.90	91.2	12.9
	11:03 AM	3.0	38250	8.81	91.4	14.0
	11:03 AM	4.0	38930	10.82	112.4	14.7

Index Parameters with Depth in Pre-Basin (December 7, 2006)

Pre-Basin 12/7/2006

Station	Time	Depth (ft)	SC-TC (µS)	D.O. (mg/L)	D.O. (%)	Temp (ºC)
1	12:22 PM	0.5	22220	9.58	104.5	13.6
	12:22 PM	1.0	22420	9.49	103.2	13.6
	12:22 PM	2.0	25070	9.25	101.4	13.6
	12:22 PM	3.0	29650	8.52	93.4	13.9
	12:22 PM	4.0	36290	7.26	79.8	14.3
	12:22 PM	5.0	43390	6.68	74.4	14.8
	12:22 PM	6.1	44350	2.18	23.3	14.9
2	1:22 PM	0.5	23330	9.38	103.0	13.9
	1:22 PM	1.0	23120	9.27	102.2	13.9
	1:22 PM	2.0	24500	9.07	100.3	13.9
	1:22 PM	3.0	30620	7.66	85.5	14.1
	1:22 PM	4.0	43100	6.52	73.7	14.7
	1:22 PM	5.0	44670	5.34	60.3	14.9
	1:22 PM	5.3	44680	0.61	7.6	15.0
3	1:58 PM	0.5	23790	9.10	102.0	14.2
	1:58 PM	1.0	23870	9.03	101.3	14.1
	1:58 PM	2.0	30080	8.54	96.0	14.3
	1:58 PM	3.0	35160	7.80	87.9	14.4
	1:58 PM	4.0	42620	7.09	80.7	14.9
	1:58 PM	5.0	44770	6.64	74.9	15.0
	1:58 PM	6.0	45660	6.43	72.9	15.0
	1:58 PM	7.0	45910	6.15	70.3	15.0
	1:58 PM	8.0	45900	6.39	72.0	15.0
	1:58 PM	9.0	46090	5.95	68.3	15.1
	1:58 PM	10.0	46190	5.78	65.8	15.1
	1:58 PM	11.0	46230	4.96	56.4	15.1
	1:58 PM	11.3	45910	0.43	4.9	15.1
4	2:51 PM	0.5	24530	9.24	102.9	14.7
	2:51 PM	1.0	24470	9.00	101.6	14.6
	2:51 PM	2.0	25620	8.78	99.4	14.6
	2:51 PM	3.0	30650	7.83	88.0	14.5
	2:51 PM	4.0	43950	7.15	81.0	14.9
	2:51 PM	4.8	45050	0.05	0.6	15.1

Index Parameters with Depth in Basin 2 (December 12, 2006)

Basin 2	12/12/2006					
Station	**Time**	**Depth (ft)**	**SC-TC (µS)**	**D.O. (mg/L)**	**D.O. (%)**	**Temp (ºC)**
1	11:38 AM	0.5	1509	7.33	72.8	15.4
	11:38 AM	1.0	1575	6.87	68.0	15.4
	11:38 AM	2.0	1631	6.20	62.3	15.3
	11:38 AM	3.0	1768	6.13	60.5	15.2
	11:38 AM	4.0	2251	0.02	0.3	14.8
2	11:02 AM	0.5	1423	6.80	68.1	15.2
	11:02 AM	1.0	1421	6.55	65.3	15.2
	11:02 AM	2.0	1658	6.34	63.1	15.2
	11:02 AM	3.0	1829	6.54	64.8	14.8
	11:02 AM	4.0	1888	6.48	64.0	14.6
	11:02 AM	5.0	2120	0.27	2.8	14.9
3	10:45 AM	0.5	1439	7.13	71.8	15.7
	10:45 AM	1.0	1429	6.42	64.4	15.0
	10:45 AM	2.0	1589	6.01	59.7	14.9
	10:45 AM	3.0	1994	5.47	55.3	15.3
	10:45 AM	3.7	1997	0.05	0.6	15.3

Index Parameters with Depth in Basin 3 (December 12, 2006)

Basin 3	12/12/2007					
Station	**Time**	**Depth (ft)**	**SC-TC (µS)**	**D.O. (mg/L)**	**D.O. (%)**	**Temp (ºC)**
1	12:41 PM	0.5	1792	7.02	72.2	16.4
	12:41 PM	1.0	1797	6.33	65.8	16.3
	12:41 PM	2.0	1830	6.31	64.9	16.3
	12:41 PM	3.0	1873	6.22	62.9	16.3
	12:41 PM	4.0	1885	5.91	60.8	16.2
	12:41 PM	4.2	1888	5.52	56.4	16.2

Index Parameters with Depth in Pre-Basin (January 18, 2007)

Pre-Basin	1/18/2007					
Station	**Time**	**Depth (ft)**	**SC-TC (µS)**	**D.O. (mg/L)**	**D.O. (%)**	**Temp (ºC)**
1	12:02 PM	0.5	13890	11.12	109.4	10.3
	12:02 PM	1.0	14440	11.05	108.4	10.3
	12:02 PM	2.0	15750	10.93	107.7	10.3
	12:02 PM	3.0	16980	10.76	106.0	10.4
	12:02 PM	4.0	23190	10.51	103.7	10.5
	12:02 PM	5.0	34620	9.67	96.9	11.1
	12:02 PM	6.0	40450	6.41	69.1	11.2
3	1:31 PM	0.5	16460	10.71	112.5	11.1
	1:31 PM	1.0	17410	10.71	112.0	11.0
	1:31 PM	2.0	23320	10.41	108.5	11.0
	1:31 PM	3.0	32990	10.04	104.7	11.0
	1:31 PM	4.0	43460	9.49	100.3	11.5
	1:31 PM	5.0	44750	8.97	94.9	11.5
	1:31 PM	6.0	45130	8.79	92.7	11.5
	1:31 PM	7.0	45200	8.91	94.2	11.5
	1:31 PM	8.0	45300	8.96	94.1	11.4
	1:31 PM	9.0	45310	8.90	93.7	11.4
	1:31 PM	10.0	45390	8.70	92.0	11.4
	1:31 PM	11.0	45410	6.66	69.8	11.4

Index Parameters with Depth in Basin 3 (January 18, 2007)

Basin 3	1/18/2007					
Station	**Time**	**Depth (ft)**	**SC-TC (µS)**	**D.O. (mg/L)**	**D.O. (%)**	**Temp (ºC)**
1	3:18 PM	1.5	2384	13.15	124.4	12.7

Index Parameters with Depth in Basin 1 (February 1, 2007)

Basin 1	2/1/2007					
Station	**Time**	**Depth (ft)**	**SC-TC (µS)**	**D.O. (mg/L)**	**D.O. (%)**	**Temp (ºC)**
1	2:05 PM	0.5	6650	8.64	91.6	14.8
	2:05 PM	1.0	7620	8.56	90.8	14.8
	2:05 PM	2.0	8590	8.54	90.1	14.8
	2:05 PM	3.0	26660	9.03	93.3	14.5
	2:05 PM	4.0	28650	9.49	99.5	14.5
	2:05 PM	4.8	29030	7.59	78.3	14.5
2	1:45 PM	0.5	5930	8.55	90.3	15.2
	1:45 PM	1.0	6190	8.55	90.8	15.2
	1:45 PM	1.5	7370	8.54	90.3	15.1
	1:45 PM	2.0	24660	10.07	112.0	14.8
3	1:05 PM	0.5	3857	8.01	85.6	15.3
	1:05 PM	1.0	5550	8.13	85.6	15.2
	1:05 PM	1.5	10540	8.72	92.8	14.6
	1:05 PM	2.0	27630	8.73	92.3	14.5
	1:05 PM	2.5	31280	9.09	96.1	14.4
	1:05 PM	2.8	32240	8.82	94.5	14.6
4	12:31 PM	0.5	3127	8.61	90.2	14.3
	12:31 PM	1.0	3160	8.68	90.4	14.3
	12:31 PM	1.5	8140	9.32	96.3	14.2
	12:31 PM	2.0	26900	10.30	106.8	14.3
	12:31 PM	2.2	28950	12.64	133.3	14.4
5	12:07 PM	0.5	3232	8.59	91.4	14.3
	12:07 PM	1.0	3749	8.53	89.0	14.3
	12:07 PM	1.5	8880	8.68	90.9	14.1
	12:07 PM	2.0	17930	8.52	89.2	14.2
	12:07 PM	2.5	29870	10.88	112.4	14.3
	12:07 PM	2.9	33080	10.97	117.4	14.4

Chapter 6

Time Series Analysis of Nitrate and Selenium in Upper Newport Bay

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Prepared for
Santa Ana Regional Water Quality Control Board

by

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INTRODUCTION

Upper Newport Bay (UNB) is an estuarine environment and protected ecological preserve covering 752 acres of mud flats, salt marsh, and open waters in Orange County, California. It is home to over 200 species of birds as well as fish and other wildlife. San Diego Creek, which discharges directly into the bay just downstream of the bridge at Jamboree Road, is the primary source of freshwater flows to UNB. High levels of selenium and nitrate have been found in the surface waters of the creek and are of potential concern to water quality and the ecological health of UNB. A treatment wetland, the San Joaquin Marsh preserve, was constructed to address the problem of high nitrate concentrations in surface flows and has had the added benefit of also removing some selenium (see Chapter 4). However, selenium concentrations in surface flows downstream of the marsh have been found to occasionally exceed the USEPA freshwater quality criterion of 5 μg/L for selenium.

Selenium is a problematic contaminant for wildlife as it tends to bioaccumulate in the food chain. High levels of selenium have been found to cause reproductive effects and can adversely impact the population health of fish and birds. In 2000, the USEPA promulgated water quality criterion for selenium in the California Toxics Rule (CTR). USEPA adopted a freshwater chronic criterion of 5 μg/L (or parts per billion) and a saltwater chronic criterion of 71 μg/L. The U.S. Fish and Wildlife Service (USFWS) however, issued a biological opinion that for selenium (as well as several other constituents) the CTR criteria were not sufficiently protective of certain sensitive species. USEPA and USFWS agreed to revise the criteria based on USFWS' concerns and that process is currently underway. Presser and others (2004) argue for the adoption of a

sediment-based selenium criterion to protect wildlife. Generally, dry-weight concentrations less than 2 mg/kg Se present minimal ecological risk while concentrations greater than 4 mg/kg present substantial ecological risk.

Nitrate can lead to algal blooms and eutrophication. The Santa Ana Regional Water Quality Control Board is currently implementing TMDL standards for total nitrogen (TN) and total phosphorous (TP) in the watershed. This chapter will help to quantify the amount of nitrate and selenium that reach the bay and to better understand the chemical dynamics that influence their mobility and bioavailability within UNB.

METHODS

Four water-quality monitoring stations were established within UNB. Depth profiles including electrical conductivity (EC), pH, and dissolved oxygen (DO) were recorded on a monthly basis at each of these sites over a six-month period beginning October 2007 and ending March 2008. Additionally, water samples were collected from the top and bottom of the water column at each station to monitor water quality parameters such as the concentrations of nitrate and selenium. An expanded set of parameters was collected in January including total nitrate (TN), ammonia, total kjeldahl nitrogen (TKN), total phosphorous (TP) and selenium speciation. Twice during the six-month monitoring period, water quality parameters were collected in the Back Bay Channel (BBC) that flows around Middle Island (Figure 6.1). Sediments were also collected from four sites very near to water quality sites and analyzed for total selenium and selenium speciation.

End-member samples and index parameters were also collected at upstream and downstream locations each month in order to characterize upstream and marine sources. Initially the upstream end-member was taken from San Diego Creek just downstream of the bridge at Campus Drive above the intake for San Joaquin treatment wetland. In December 2007, the site for the upstream end-member was relocated to San Diego Creek at Highway 73 just before it discharges into the bay, well downstream of the San Joaquin marsh outlet. This relocation was necessary in order to properly constrain end-member values and permit the use of mass balance calculations to interpret mixing of upstream and marine sources in the bay. Unless otherwise noted, future reference to the upstream end member will pertain to the latter location (San Diego Creek at Hwy 73). The marine end-member was taken where waters from UNB flow under the Pacific Coast Highway into Lower Newport Bay.

Routine as well as expanded water quality data were collected during both dry-weather and wet-weather conditions, which permits a better understanding of marine-terrestrial mixing in the bay under different conditions. Precipitation data show that December through February were the wettest months, while October and November were relatively drier and March had no precipitation at all (Figures 6.2 and 6.3). Sampling in October and November took place during dry-weather conditions while sampling in December took place during wet-weather conditions. January sampling took place during both wet-weather and dry-weather conditions, while sampling during February and March took place during dry-weather conditions. Expanded parameters were collected during both wet-weather and dry-weather conditions in December and January. Sediment

samples were collected during low tide under dry-weather conditions in January and February.

Due to dredging operations in the bay coinciding with the monitoring period, Station 2 had to be relocated to a more downstream location during the month of December. Station 4 also had to be relocated due to heavy boat traffic. This resulted in observations taken in waters of varying depths. In order to determine the degree of variation in water quality parameters due to these relocations, we decided at this time to also vary the position of other stations within the vicinity of the original sampling site. As can be see in Appendix 6A and 6B, depth variability associated with these relocations resulted in minimal variability in select water quality parameters, which allows inter-comparison of data collected at slightly different locations during different months.

RESULTS AND DISCUSSION

Nitrate and Selenium

Water samples were analyzed for both total and dissolved selenium. However, these data must be interpreted with caution due to interferences in the analytical method that sometimes results in total selenium values that are lower than the amount of dissolved selenium. For the purposes of this report all selenium values will be reported as dissolved selenium unless otherwise noted.

The upstream end-member exhibited an average selenium concentration of 8.1 µg/L over the monitoring period, while the marine end-member exhibited average selenium concentrations of 1.2 µg/L. Average concentrations of selenium in UNB over the monitoring period were 2.5 times higher in top waters (avg = 3.5 µg/L) than in bottom

waters (avg = 1.4 µg/L). Surface waters at stations 1 and 2, which are closer to the mouth of San Diego Creek, exhibited higher selenium concentrations than at the more distal stations 3 and 4 (Figures 6.4 and 6.5; Appendix 6B). Selenium in surface waters at stations 1 and 2 slightly exceeded 5 µg/L during dry-weather conditions (Figure 6.4). Dry-weather data show that salinities at these two stations are 6 to 36% lower than those observed for the marine end-member, so an intermediate value between the saltwater (71 µg/L) and freshwater (5 µg/L) criteria would be the most appropriate standard to apply at these stations where there is a greater influence from terrestrial waters. Wet weather flows (December, second part of January) acted to dilute selenium concentrations in surface waters across the bay (Figures 6.6-6.9).

Selenium speciation data were collected under dry-weather conditions at the upstream end-member station and at stations 1 and 2 and show that Se (VI) dominates in upstream waters, making up 75% of total dissolved selenium (Table 6.1). These waters flow into the bay as a dilute lens riding on top of (and to some extent mixing with) a thick marine layer causing selenium to become dilute. As selenium enters the bay it shows some evidence for speciation whereby selenite increases by about 10% of the total dissolved selenium. In the upstream end-member, selenite makes up only about 25% of total dissolved selenium. As these waters flow into the bay, selenite becomes more dominant, comprising nearly 37% of total dissolved selenium. Selenium speciation data at stations 3 and 4 and at the marine end member were collected during wet-weather flows and show that virtually all of the dissolved selenium present is in the +6 oxidation state.

Selenite (IV) is thought to be more toxic to aquatic life forms than the more oxidized selenate (VI) (Thornton, 1983). However, the observed speciation is likely of minimal biologic concern (at least along aquatic pathways) as dissolved selenium concentrations in surface waters decrease as waters flow deeper into the bay. The observed decrease in selenium is most likely due to mixing between terrestrial waters with high selenium and marine waters with low selenium, resulting in dilution with low concentrations observed in top waters and the negligible concentrations observed in bottom waters. Another possible scenario that may explain progressively lower concentrations of selenium in the bay may be removal via flocculation at the freshwater-saltwater interface. This would result in selenium being sequestered in sediments, which is an alternative pathway of biological concern for selenium toxicity.

The upstream end-member exhibited average nitrate concentrations of 4.5 mg/L NO_3-N while the marine end member exhibited average values of 0.3 mg/L NO_3-N. Average concentrations of nitrate in UNB over the monitoring period were over 4 times higher in top water samples (avg = 1.4 mg/L NO_3-N) than in bottom waters (avg = 0.3 mg/L NO_3-N). The pattern of nitrate concentrations in the bay mimics those of selenium: higher in surface waters at stations 1 and 2 and lower at the more distal stations 3 and 4 (Figures 6.10 and 6.11). Whereas a dilution of selenium concentration in the surface water of the bay was observed during wet-weather, nitrate concentrations tend to increase in response to wet-weather flows (Figures 6.12-6.15).

Monitoring of water quality in the BBC took place twice during the monitoring period: once in December (wet month) and once in March (dry month). It is only accessible by boat during elevated tides. Sampling in December took place between high

and low tide while sampling in March took place at the peak of high tide. The channel is located between stations 3 and 4 (Figure 6.1). These stations exhibit very similar water quality parameters throughout the duration of the monitoring period. Thus we expected waters in the BBC to be very similar in composition to waters collected at stations 3 and 4.

The data show that selenium concentrations in the BBC fall roughly between surface water concentrations found at stations 3 and 4 during dry-weather (Figure 6.5). During wet-weather, selenium concentrations in the BBC are more dilute than in the top waters at either station 3 or 4. Inputs of direct channel precipitation and overland flow most likely account for this dilution. Nitrate concentrations in the BBC are, like surface waters in the bay, elevated during wet-weather conditions, but exhibit concentrations than are slightly more dilute than those found in the top waters at stations 3 and 4. This may be due to rapid mixing between residual waters in the BBC (i.e. those present before precipitation began with relatively dilute concentrations of nitrate) and surface runoff carrying high nitrate loads. Dry-weather data in the BBC support this interpretation, showing nitrate concentrations intermediate between those observed at stations 3 and 4 that are typical of the more dilute values that prevail without the influence of wet-weather.

Selenium and nitrate in the terrestrial system is primarily sourced from groundwater. San Diego Creek and its tributaries receive most of their dry-weather flows via groundwater baseflow and via direct discharge of groundwater to surface water from seeps, springs, leaky storm drains, and groundwater dewatering operations. Selenium is especially elevated in groundwaters that flow through the deposits of the historic “Swamp

of the Frogs" marsh while nitrate in groundwater is thought to be associated with fertilizer application in the historic orchards in the northern and eastern parts of the county.

Terrestrial surface waters are relatively dilute and therefore less dense than the marine end member with high salinity. This results in density stratification in the bay whereby relatively dilute waters, rich in nitrate and selenium, flow into the bay riding on top of a thick marine layer. Thus we observe much higher concentrations of nitrate and selenium in the surface waters of the bay than we observe in the bottom waters. Dissolved oxygen profiles show that bay waters are highly oxygenated throughout the water column (Figures 6.16-19), which discounts the role of redox processes in the removal of nitrate and selenium in the bottom waters of the bay. Marine waters exhibit very low concentrations of nitrate and selenium. Mixing between the terrestrial waters and marine waters causes the concentrations of these constituents to be diluted from their terrestrial concentrations, thus we observe much lower concentrations in surface waters of the bay farther from the mouth of San Diego Creek during dry-weather conditions.

Mixing dynamics in the bay are highly influenced by precipitation events. During wet-weather, terrestrial flows contain a larger component of flow from urban runoff. The bay itself also receives substantial amounts of surface runoff from the surrounding landscape as well as direct inputs from precipitation. This affects the size of the dilute lens both with respect to depth and longitudinal extent (Figures 6.20-25). Wet-weather appears to have minimal effect on the composition of bottom waters, however it has a dramatic effect on selenium and nitrate concentrations in surface waters of the bay.

Urban runoff contains very low levels of selenium. During wet-weather, stream discharge carries a larger component of flow from urban runoff, which acts to dilute selenium concentrations in surface flows. During the month of December, selenium concentrations in the upstream end-member were 4 times lower than dry-weather values (Appendix 6B). This dilution is also reflected in the surface waters of the bay, which exhibit much lower concentrations of selenium than dry-weather values (Figure 6.6-9). Nitrate in upstream source flows is more dilute during wet-weather, yet increases slightly in the surface waters of the bay. This is most likely due to increased inputs of nitrate from surface runoff from upland areas in the Upper Newport Bay Watershed. Wherever fertilizer applications or animal wastes remain on land surface, they have the potential to nitrify and be carried away as dissolved nitrate with overland flow.

Soils and Expanded Parameters

Soils collected from the upstream part of the basin (stations 1-3) have higher total selenium (avg = 1.1 mg/kg dry-weight) than the most downstream station (4) with total selenium content of 0.27 mg/kg. Background concentration for total selenium in soils not impacted by selenium is approximately 0.4 mg/kg whereas soils derived from Cretaceous rocks have higher total selenium in the range of 5 mg/kg (Thomas et al, 1998). Based on these values, the selenium data for bay soils at these locations indicate that these soils are not heavily impacted by selenium. These soils were collected at low tide from the mud-flats closest to the respective water quality monitoring site. Waterfowl are routinely observed feeding in these tidal flats. These limited data suggest that there is little risk of selenium toxicity associated with this pathway, where selenium levels in soils of the tidal

flats are well below recommended values (Presser and Luoma, 2004). However, other investigations have found highly variable quantities of selenium in bay sediments (Terry Reeder, personal communication).

Speciation data for the soils show that sediments from the downstream station (4) have non-detectable levels of inorganic selenium (IV or VI), whereas selenite makes up approximately 25% of total selenium in the 3 "upstream" sediments (Table 6.2). Selenite tends to adsorb strongly to mineral surfaces and organic matter (Ellis et al., 2003). Adsorption on sediments may remove marginal quantities of dissolved selenium. However, based on the available data it is difficult to say whether this fraction of selenium enters the bay already associated with solids or as a dissolved phase that subsequently adsorbs to available surfaces. It is very likely that both processes operate to some extent.

The fate of nutrients in the bay is also a concern. An expanded set of parameters collected from the upstream end-member and at stations 1 and 2 during dry-weather and from the marine end-member and stations 3 and 4 during wet-weather reveal the dominant forms of nitrogen and phosphorous in the bay under differing conditions. Despite varying weather conditions, nitrate makes up a significant portion of the total nitrogen concentration in all top water samples collected from the bay as well as in the two end-member samples (Figures 6.26, 6.27, 6.29, 6.31, 6.33, 6.35), while organic nitrogen makes up the dominant fraction of total nitrogen in most bottom water samples (Figures 6.28, 6.30, 6.32, 6.34). Surface waters also show detectable levels of organic nitrogen and, to a lesser extent, ammonia. Ortho-phosphate concentrations are consistently higher than total phosphorous, which is logistically impossible. Low values

for total phosphorous likely result from an analytical interference and must be discounted. For the purposes of this report we will assume that orthophosphate is the dominant form of phosphorous in these waters.

The upstream end-member exhibits 5.9 mg/L total nitrogen while the marine end-member exhibits only 0.47 mg/L total nitrogen. Total nitrogen in surface waters becomes progressively more dilute as water flows from station 1 to station 2 allowing for greater mixing between upstream and marine water. Stations 3 and 4 show elevated total nitrogen concentrations due to wet-weather flows, which act to enrich total nitrogen in the bay by increasing inputs of nitrate. There is some evidence to suggest that wet-weather flows may also increase the loading of orthophosphate in the surface waters of the bay (Figures 6.31 and 6.33).

Bottom waters are relatively unaffected by wet-weather flows and tend to have chemical composition similar to that of the marine end-member. Total nitrogen in bottom waters is highest at stations 1 and 2 (1.3 mg/L and 1.6 mg/L respectively), which are just downstream from where San Diego Creek discharges into the bay. Organic nitrogen makes up a greater fraction of total nitrogen at these sites (Figures 6.28 and 6.29). Total nitrogen is much lower in bottom waters at stations 3 and 4 (0.89 mg/L and 0.27 mg/L respectively), more closely resembling the composition of the marine end-member. Just as with stations 1 and 2, organic nitrogen makes up a significant fraction of total nitrogen in the bottom waters of stations 3 and 4 (Figures 6.32, 6.34). Organic nitrogen is most likely associated with the accumulation of organic detritus and decaying organic matter that collects on the basin floor. The data suggest that there is a greater accumulation of organic detritus in the vicinity of stations 1 and 2, which both show

elevated concentrations of organic nitrogen in the bottom waters (0.52 mg/L and 0.84 mg/L) respectively.

Orthophosphate in the upstream end-member exhibits a dry-weather value of 0.17 mg/L HPO_4-P, while the marine end-member shows a wet-weather value of 0.21 mg/L HPO_4-P (Figures 6.26, 6.35). Surface waters at stations 1 and 2 also exhibit low orthophoshpate concentrations on the order of 0.1 mg/L HPO_4-P. If we assume this trend is maintained at stations 3 and 4 during dry-weather conditions, then we can conclude that wet-weather flows contribute loading of HPO_4-P to the bay where elevated concentrations are observed in surface waters (0.56 mg/L HPO_4-P and 0.23 mg/L HPO_4-P respectively). Bottom waters at all stations except station 1 exhibit orthophosphate concentrations that are elevated relative to surface waters during dry weather (Figures 6.28, 6.30, 6.32, 6.34). This may result from anoxic conditions that can develop at the sediment-water interface. Iron-oxides will be reduced under anoxic conditions to soluble ferrous iron and any bound orthophosphate will be released to solution.

Salinity and Isotopes

Mixing dynamics between upstream and marine sources explain the observed patterns in nitrate and selenium in the bay and salinity data support these interpretations. As conservative anions, chloride and sulfate are well suited to track salinity patterns. Electrical conductivity (EC) is a semi-quantitative proxy for salinity. When used in conjunction with conservative constituents such as sulfate and chloride, a clear picture of upstream and marine mixing emerges.

Electrical conductivity data show that the bay demonstrated different mixing dynamics between the upstream and marine interface during wet and dry weather. Upstream waters show a dry-weather value of 2.92 mS while marine waters exhibit a much higher value of 49.87 mS. During dry weather (October), EC along the entire depth profile of stations 3 and 4 show negligible influence of upstream waters, with EC ranging from 49.2 to 49.46 mS (Figures 6.38, 6.39, 6.20). Salinities are more clearly stratified at station 1, which is closest to where San Diego Creek discharges into the bay, with EC ranging from 38.07 mS at the top of the water column to 46.48 at the bottom (Figure 6.36, Table 6.1). Upstream water from San Diego Creek acts to dilute marine salinity in the vicinity of station 1 where less dense terrestrial water mixes with marine bottom waters. A lens of dilute terrestrial water is observed in roughly the upper four feet of the profile (Figure 6.20). Station 2 is transitional between salinity stratification observed at stations 1 and 3. Salinities at station 2 exhibit less terrestrial mixing with EC ranging from 42.5 mS to 47.2 mS (Figures 6.36, 6.37 and Table 6.1). Below roughly four feet depth, waters exhibit salinities that are consistent with a marine source (Figure 6.20 and Figures 6.36-43).

During wet weather (December), water column profiles in UNB showed a heavy influence of terrestrial and marine water mixing. There were obvious differences between top and bottom water salinities due to heavy runoff in the urban catchment (Table 6.1). Greater dilution of surface waters was observed while salinities approach marine values (46.1 mS) with increasing depth (Figure 6.22). The most significant dilution effect was observed at station 1, where the EC ranged from ranged from 8.37 at the top of the water column to 45.0 mS at the bottom (Figure 6.40). This location was

much more affected by an increase in discharge from San Diego Creek during the rain event. EC data ranged from 17.1 mS to 43.21 mS; 24.2 mS to 44.4 mS; and 30.6 to 41.4 mS for stations 2, 3, and 4 respectively (Figure 6.41, 6.42, and 6.43). The higher salinities at more downstream locations indicate more marine influence in these waters, but also show that salinities have been somewhat diluted from marine values due to mixing with terrestrial discharge and overland flow. The thickness and longitudinal extent of the dilute lens increased due to the mixing of dilute runoff from the surrounding landscapes with water derived from marine sources (Figure 6.22).

Sulfate and chloride data support the dry-weather mixing patterns revealed by EC profiles. Marine waters exhibit elevated concentrations of chloride and sulfate (avg = 17,235 mg/L and avg = 2356 mg/L respectively) while upstream waters are relatively dilute with respect to these constituents (avg = 2280 mg/L and avg = 688 mg/L respectively). During dry weather, the stations most proximal to the Pacific Ocean (3 and 4) as well as bottom waters at all stations have sulfate and chloride values very close to that of marine water. Chloride and sulfate in the surface waters at stations 1 show a greater influence of dilution from upstream waters (avg = 10197 mg/L and 1637 mg/L respectively, Figure 6.44). Surface waters at station 2 exhibit values that are intermediate between values observed at stations 1 and 3 with average dry-weather chloride concentrations of 13957 mg/L and sulfate of 2056 mg/L.

During rain events, as was experienced in December 2007, chloride and sulfate concentrations tended to be relatively constant in bottom waters, while surface waters across the bay become more dilute with respect to these constituents due to increased inputs from terrestrial runoff and precipitation throughout UNB (Appendix 6C). Due to a

higher discharge from San Diego Creek during rain events, stations 1 and 2, which are closest to the creek, demonstrated a higher dilution factor than those further from the discharge point (Figure 6.45).

The conservative nature of sulfate and chloride is well suited to their application in mass balance calculations, which can be used to estimate the relative to contributions from upstream and marine sources to bay-water composition (Equation 6.1).

$$(UEM)(X) + (MEM)(1-X) = ST \qquad \text{Equation 6.1}$$

Where :

UEM = concentration of conservative constituent in the upstream end-member

MEM = concentration of conservative constituent in the marine end-member

ST = concentration of conservative at the station of interest

X = proportion of upstream water that comprises water in the station of interest.

Applying this equation to chloride concentrations during dry-weather flows (October and March) reveals that upstream waters comprise roughly 40% to 60% of the surface water at station 1, while it makes up only about 5% to 10% of the bottom waters at this station. Replacing sulfate concentrations for UEM, MEM and ST gives results that agree very well with those of the chloride mixing model. Likewise, sulfate and chloride mass balance reveal that upstream water comprises only about 20% to 30% of surface waters at station 2, whereas they still comprise nearly 10% of bottom waters at this station. The mixing model shows that surface waters at stations 3 and 4, farther from the mouth of San Diego Creek, are comprised of only 2% to 9% upstream flows, while

bottom waters at these stations are dominantly marine with less than 2% input from upstream sources.

Wet-weather mixing presents an entirely different story. It is difficult to apply the two-dimensional mixing model described in equation 6.1 to such a dynamic system like that operating during wet-weather conditions where inputs include more than just the terrestrial and marine end-members. Nevertheless, mass balance results for the month of December suggest that upstream waters have a stronger influence in the surface waters of the bay, making up 87% at station 1; 64% at station 2; 50 % at station 3; and 38% at station 4. Bottom waters also experience more influence from terrestrial mixing. Mass balance calculations show that upstream waters make up about 10% of bottom water composition throughout the bay during wet weather. These are only very rough approximations, as they do not take into account additional sources such as overland flow and direct precipitation.

Stable isotopes of water are very effective for tracking mixing of waters from distinct sources. Plotting δ^2H versus $\delta^{18}O$ we can observe where waters plot in relation to the global meteoric water line (GMWL). Figure 6.46 shows that marine waters have a dry weather isotopic signature close to zero for both δ^2H and $\delta^{18}O$, while upstream waters have a lighter isotopic signature in the range of –50 for δ^2H and –6 for $\delta^{18}O$. This figure also shows that, during dry weather, surface waters in the bay are a mixture of terrestrial and marine sources. Bay waters plot along a mixing line with top water samples from stations 1 and 2 plotting closer to the upstream end-member and top waters from stations 3 and 4 plotting closer to the marine end-member. Isotopic data for bottom waters shows

that they are most similar to marine waters across the bay, with very little influence from terrestrial sources (Figure 6.47).

During wet-weather, the isotopic signature of the upstream end-member plots very close to the GMWL, indicating that a large component of these flows is derived from precipitation. The isotopic signature of the marine end-member also shows a slight shift toward the GMWL. Surface waters tend to plot intermediate between these two wet-weather end-member values, though stations 2 and 3 show more influence of mixing with residual dry-weather waters (Figure 6.48). Bottom waters show very little influence from wet-weather flows, with samples from all stations plotting very near the dry-weather marine value (Figure 6.49). These results are consistent with salinity patterns and strongly support the model of wet-weather and dry-weather mixing in the bay that explains observed patterns of nitrate and selenium.

CONCLUSIONS

The concentrations of nitrate and selenium in the bay are strongly influenced by terrestrial-marine mixing dynamics, which vary in response to storm flows. Selenium and nitrate entering the bay are diluted by the twice-daily ebb and flow of the tides that bring in a constant flux of marine water with negligible concentrations of nitrate and selenium. Although high levels of nitrate and selenium are found in groundwaters that make up most of the terrestrial discharge from San Diego Creek during dry-weather, these constituents pose lower risk to wildlife in the bay than freshwater in surface streams of the San Diego Creek Watershed. This is especially true in light of the order of magnitude difference between the EPA criterion for selenium in freshwater (5 µg/L)

versus saltwater (71 μg/L). Some value intermediate between these two criteria would best be applied to bay-waters closest to the mouth of San Diego Creek, while the latter value (71 μg/L) will most likely apply throughout the rest of UNB. Rainwaters also act to further dilute selenium concentrations in the bay, however wet-weather flows also increase the loading of nitrate to the bay due to surface leaching of nitrate via overland flow and urban runoff. Bottom waters are largely unaffected by wet-weather flows and maintain a composition very close to that of marine waters with very low levels of nitrate and selenium. Salinity and stable isotope results are consistent with the interpretations that explain observed patterns of nitrate and selenium in the bay. At the locations sampled, the soils show no evidence for the accumulation and sequestration of selenium. The flux of marine water is the major contributor to the dilution of nitrate and selenium in Upper Newport Bay.

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Table 6.1: Selenium Speciation of Water Samples in Upper Newport Bay

Location	Date	Se (IV) (µg/L)	Se (VI) (µg /L)	Dissolved Se (µg /L)	% Se (VI) (µg /L)
Terrestrial End Member at 73	1/17/2008	2.32	7.023	9.34	75.2
Newport Bay Station 1- Top	1/17/2008	1.31	3.201	4.51	71.0
Newport Bay Station 2 - Top	1/17/2008	0.87	1.498	2.37	63.3
Newport Bay Station 3 - Top	1/25/2008	<0.4	1.779	1.78	100.0
Newport Bay Station 4 - Top	1/25/2008	<0.4	1.554	1.55	100.0
Newport Bay Station 1- Bottom	1/17/2008	0.54	1.003	1.54	65.0
Newport Bay Station 2 - Bottom	1/17/2008	<0.4	1.564	1.56	100.0
Newport Bay Station 3 - Bottom	1/25/2008	<0.4	0.814	0.81	100.0
Newport Bay Station 4 - Bottom	1/25/2008	<0.4	0.761	0.76	100.0
Marine End Member at PCH	1/25/2008	<0.4	0.996	1.00	100.0

Table 6.2 Selenium in Sediments of Upper Newport Bay

	Wet-weight (mg/kg)			%TS	Dry-weight (mg/kg)		
Station	Se (IV)	Se (VI)	Total Se		Se (IV)	Se (VI)	Total Se
1	0.171	ND (< 0.046)	0.695	61.31	0.279	ND	1.134
2	0.155	ND (< 0.046)	0.656	68.18	0.227	ND	0.962
3	0.195	ND (< 0.046)	0.712	59.22	0.329	ND	1.202
4	ND (< 0.020)	ND (< 0.046)	0.199	72.93	ND	ND	0.273

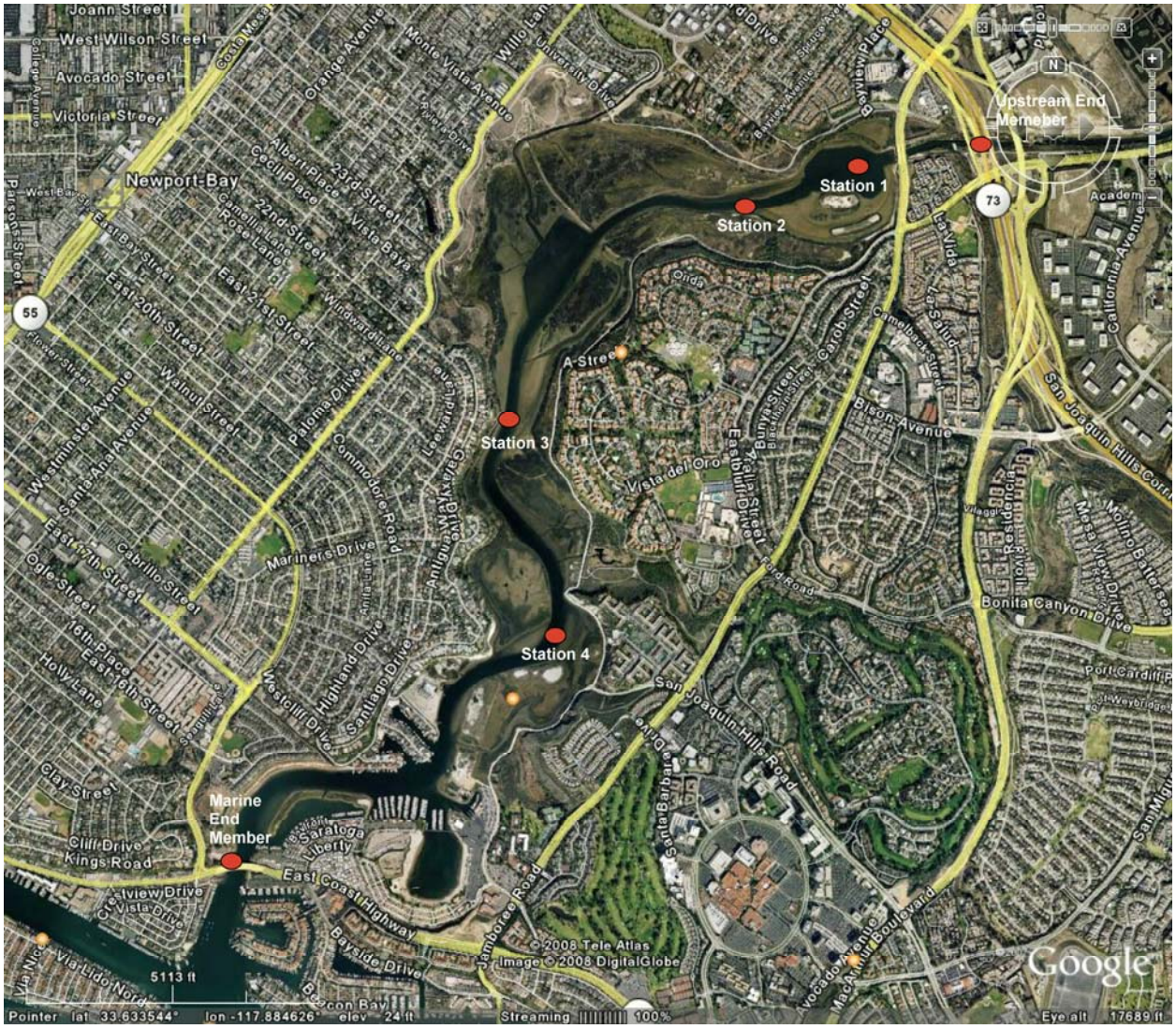

Figure 6.1. Upper Newport Bay and associated sampling stations.

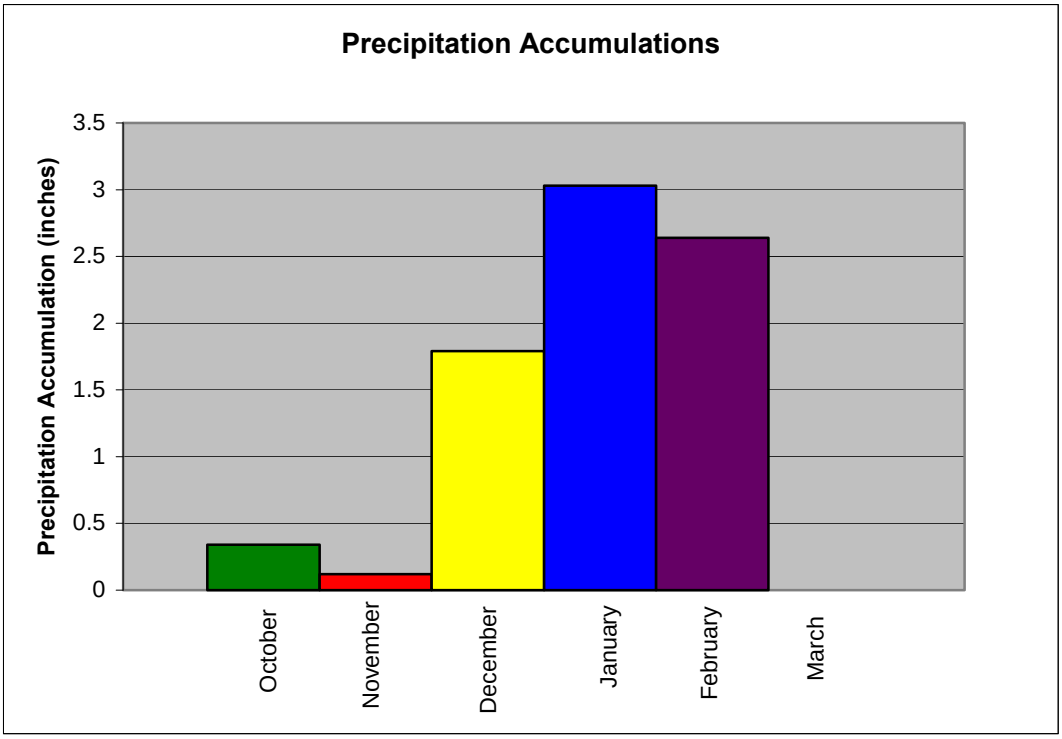

Figure 6.2. Precipitation accumulation per month during data collection period.

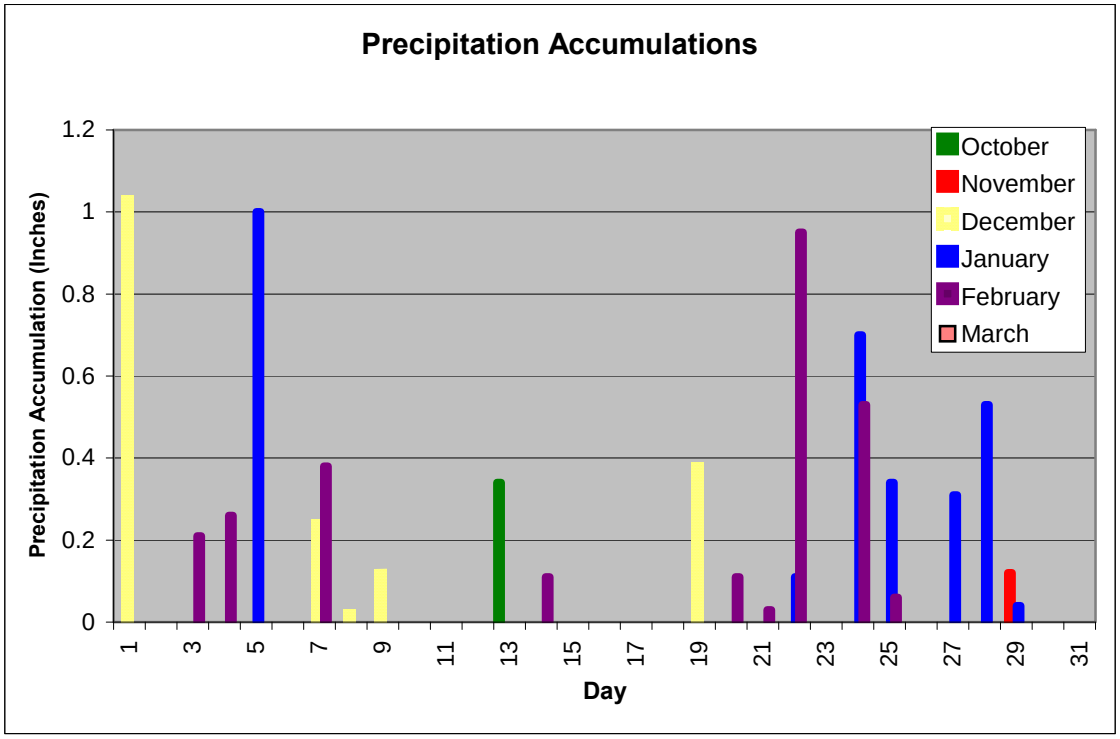

Figure 6.3. Precipitation accumulations per day for each month during data collection.

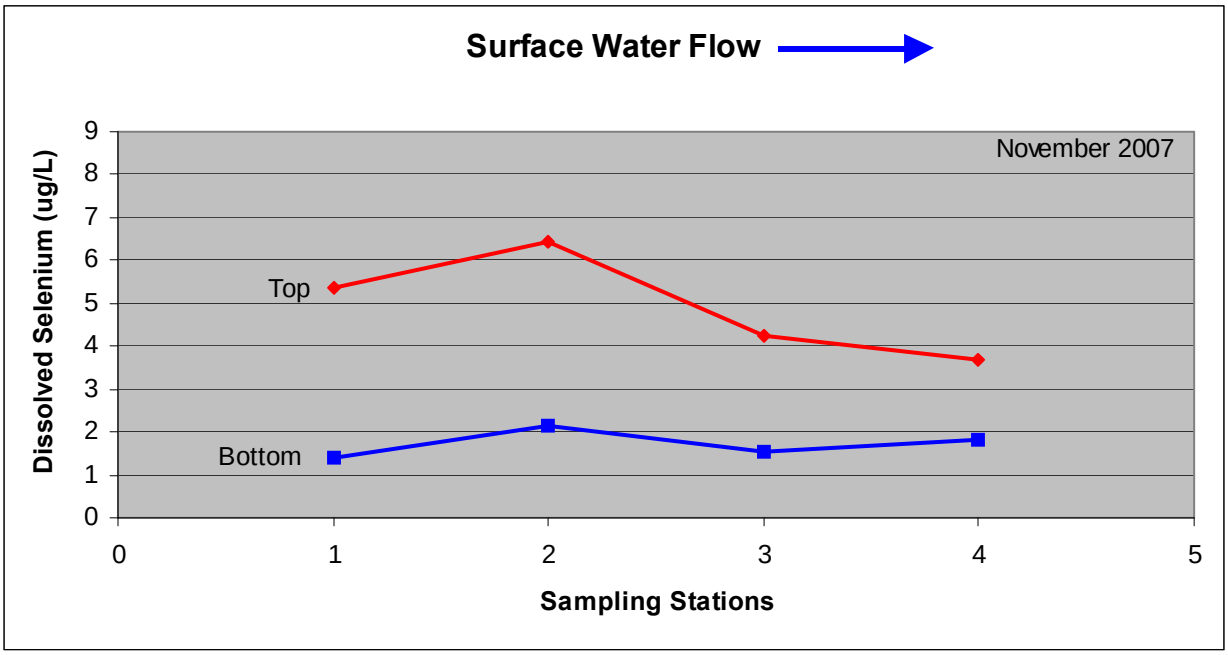

Figure 6.4. Dissolved selenium at each station during November 2007, a dry month.

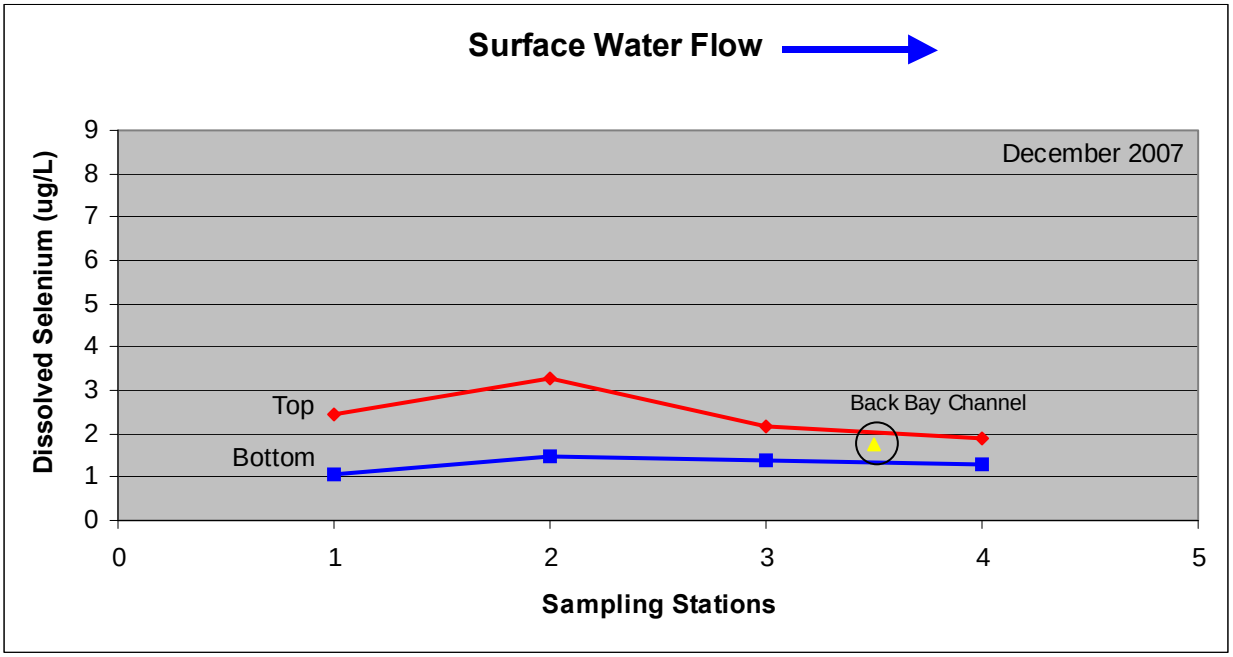

Figure 6.5. Dissolved selenium at each station during December 2007, a wet month.

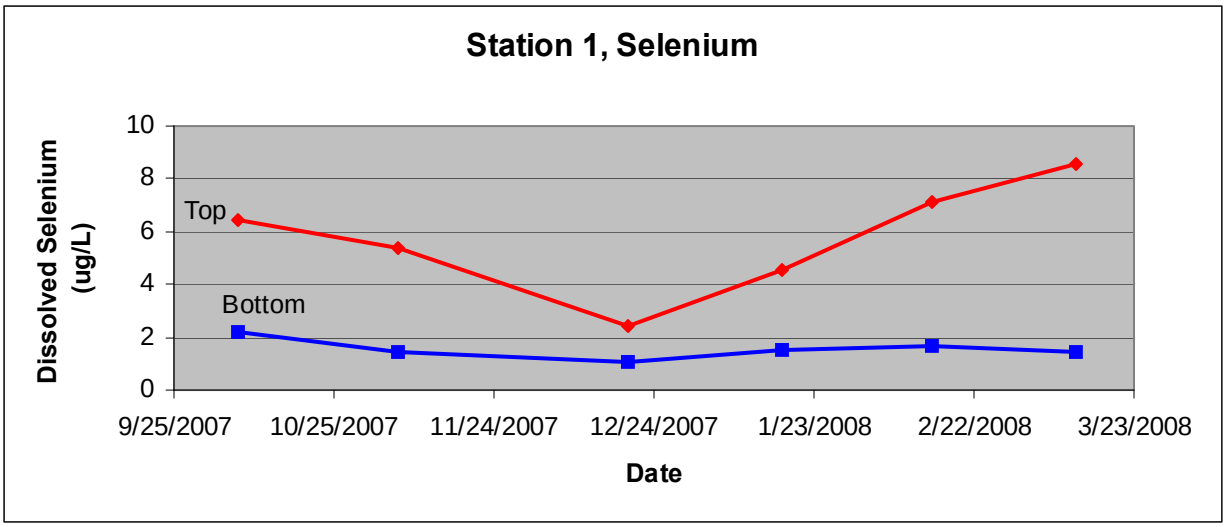

Figure 6.6. Dissolved selenium levels showing top and bottom of the water column at station 1 over a six-month period.

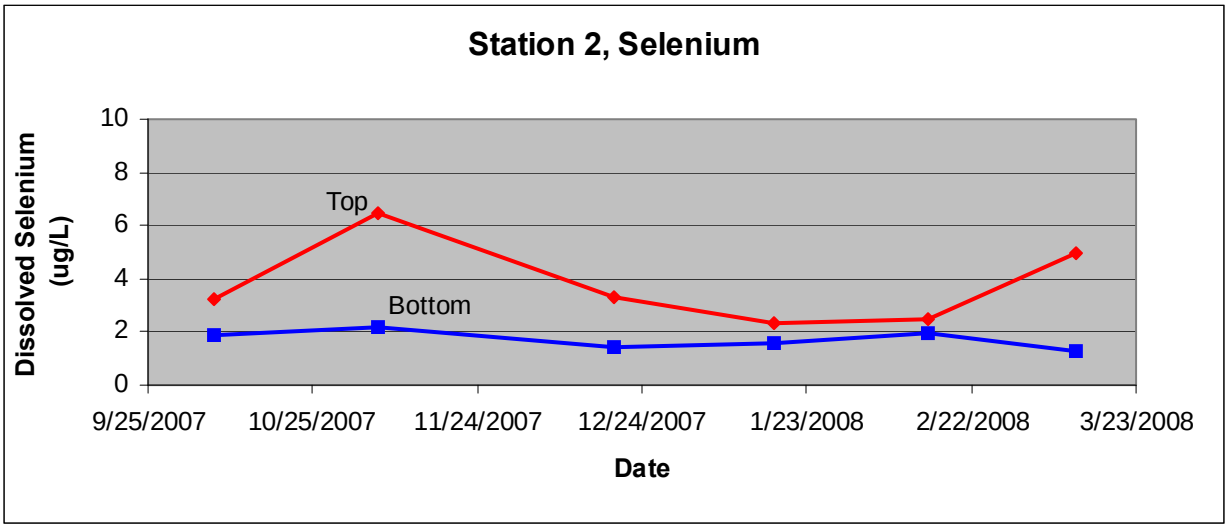

Figure 6.7. Dissolved selenium levels showing top and bottom of the water column at station 2 over a six-month period.

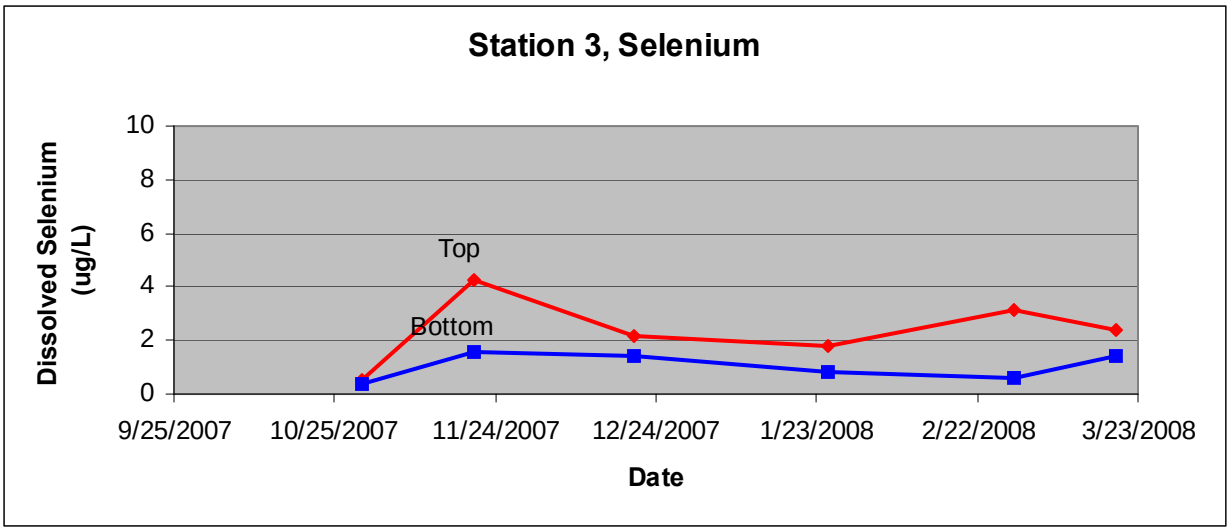

Figure 6.8. Dissolved selenium levels showing top and bottom of the water column at station 3 over a six-month period.

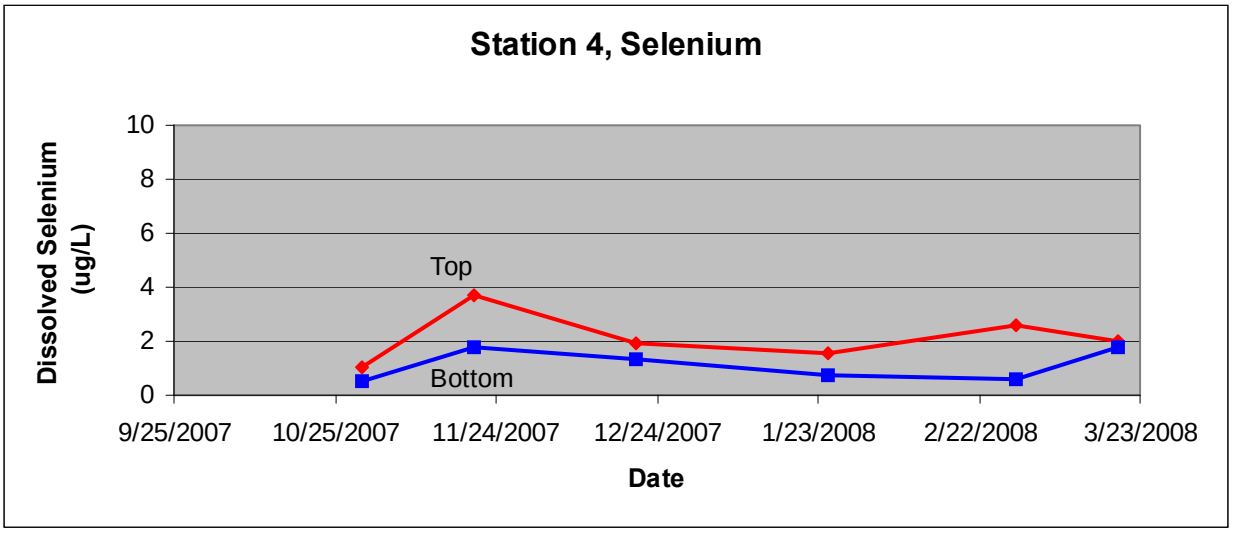

Figure 6.9. Dissolved selenium levels showing top and bottom of the water column at station 4 over a six-month period.

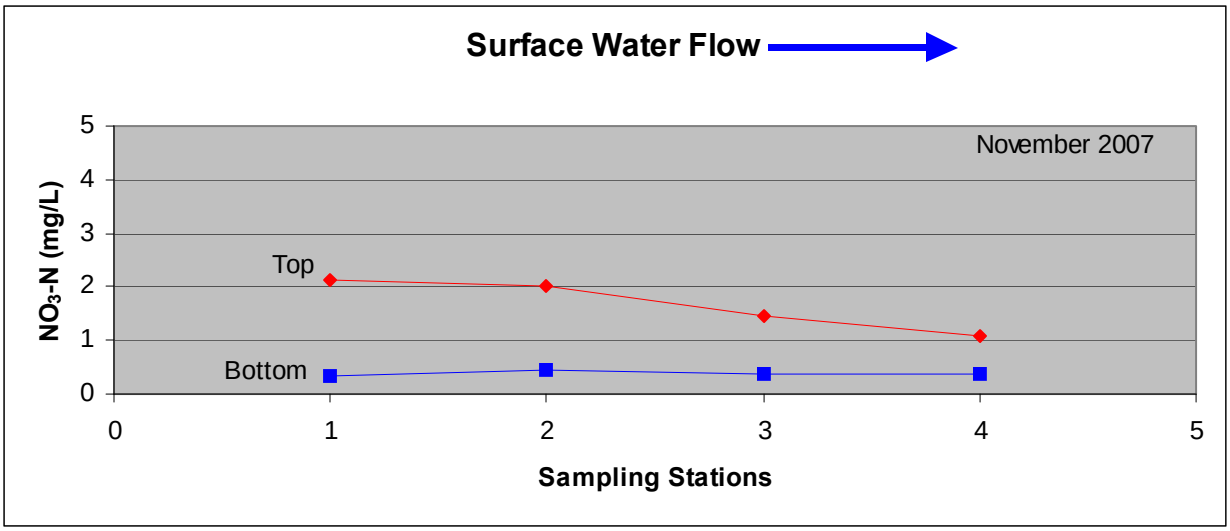

Figure 6.10. Nitrate as nitrogen at each station during November 2007, a dry month.

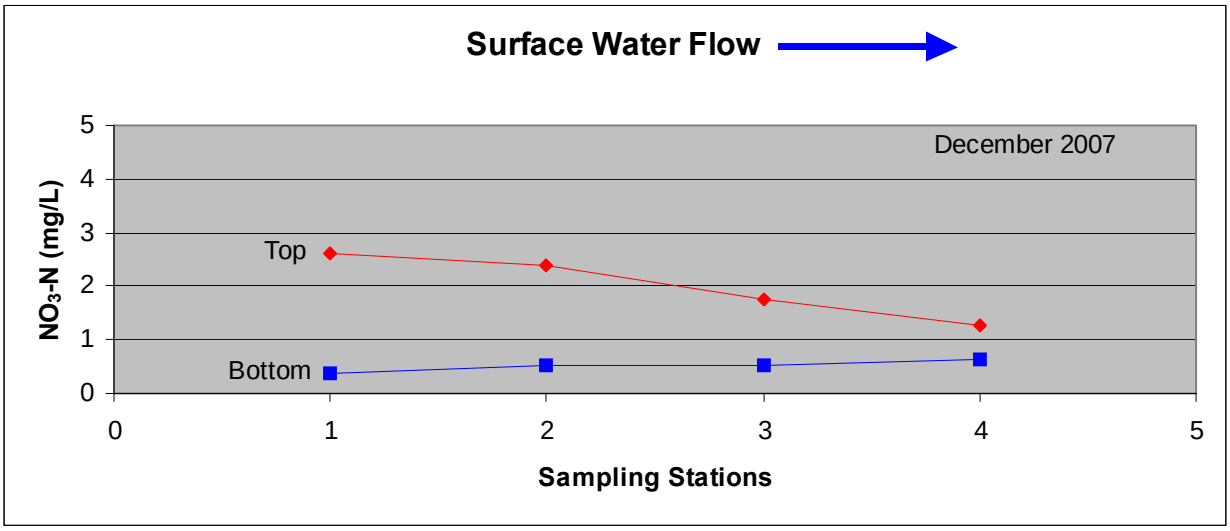

Figure 6.11. Nitrate as nitrogen as nitrogen at each station during December 2007, a wet month.

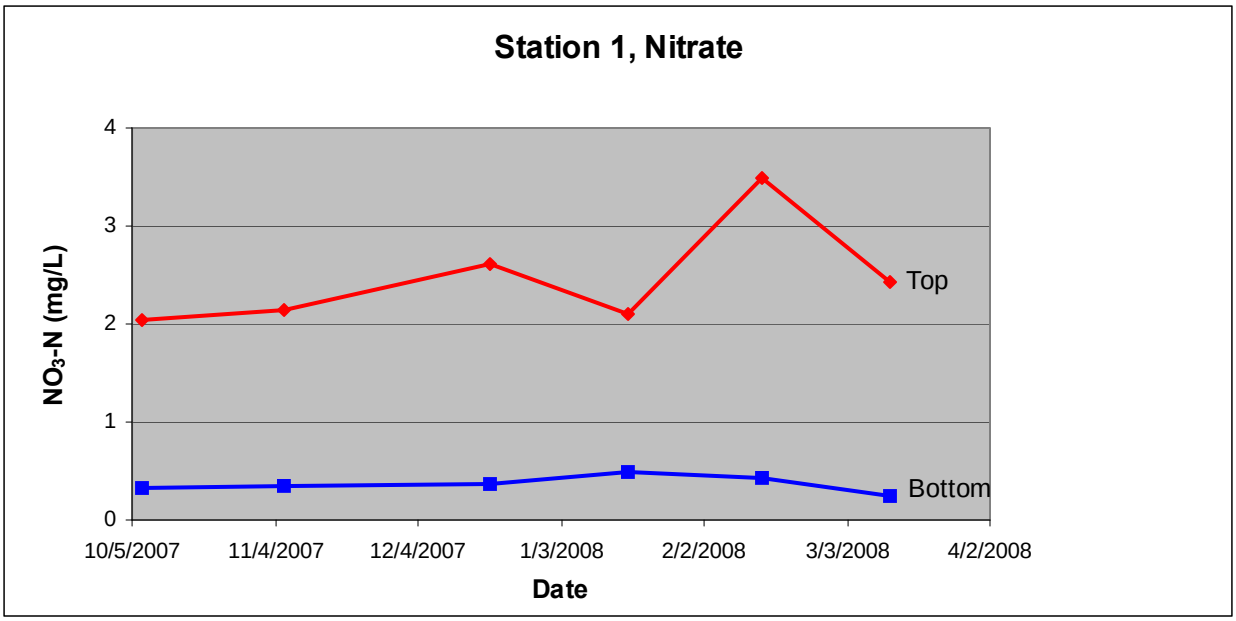

Figure 6.12. Nitrate as nitrogen levels shown at top and bottom of the water column at station 1 over a six-month period.

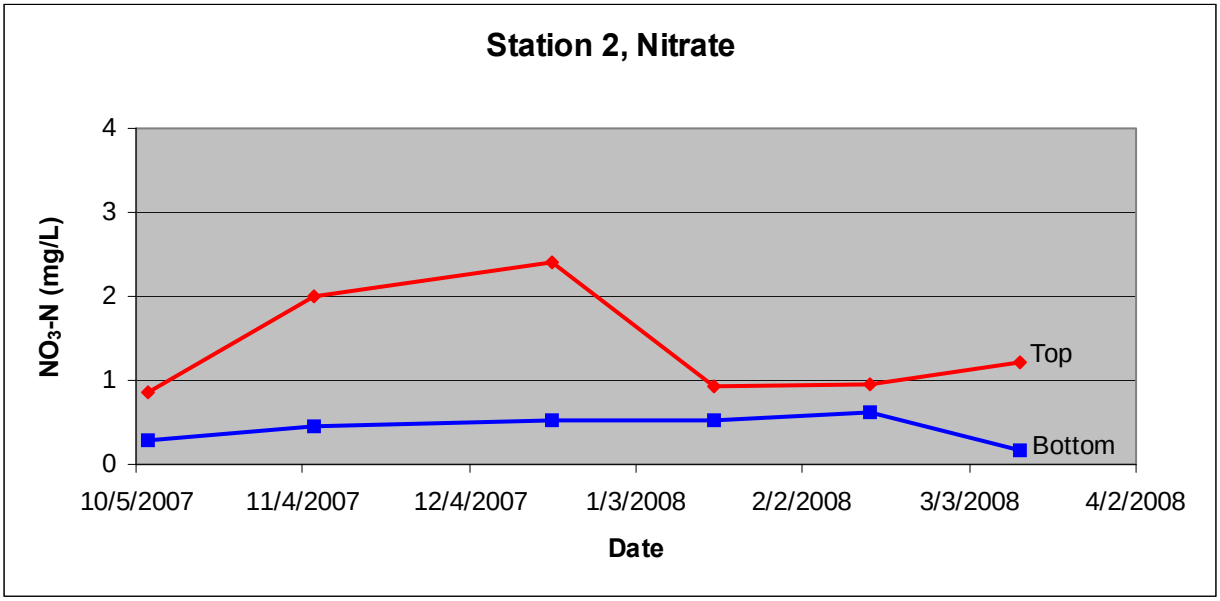

Figure 6.13. Nitrate as nitrogen levels shown at top and bottom of the water column at station 2 over a six-month period.

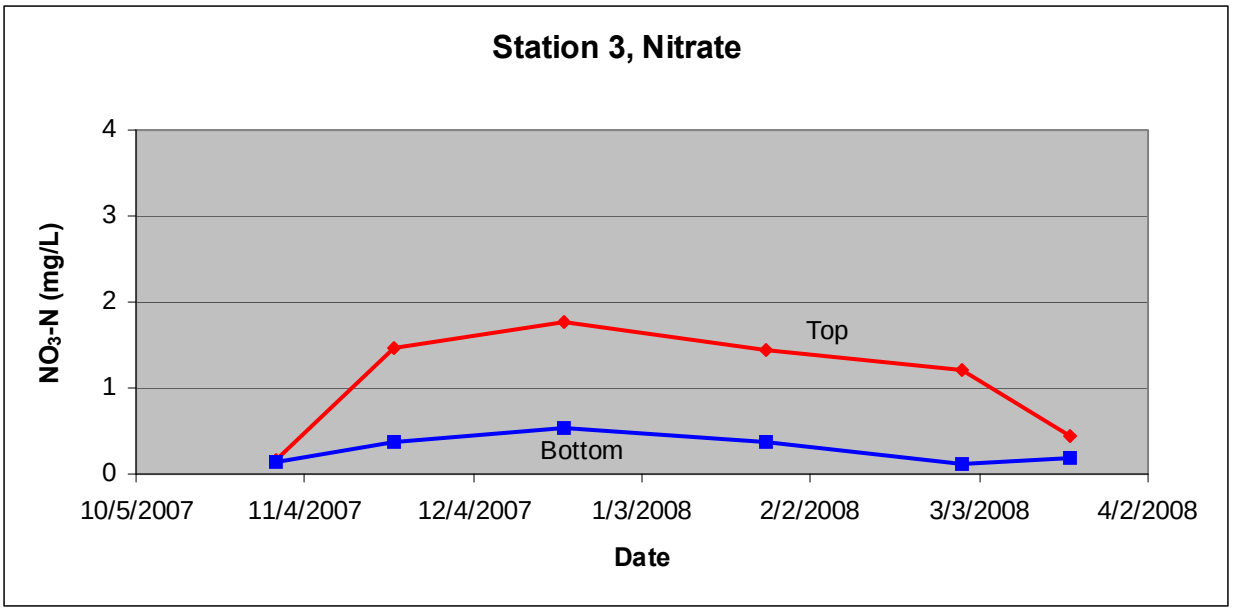

Figure 6.14. Nitrate as nitrogen levels shown at top and bottom of the water column at station 3 over a six-month period.

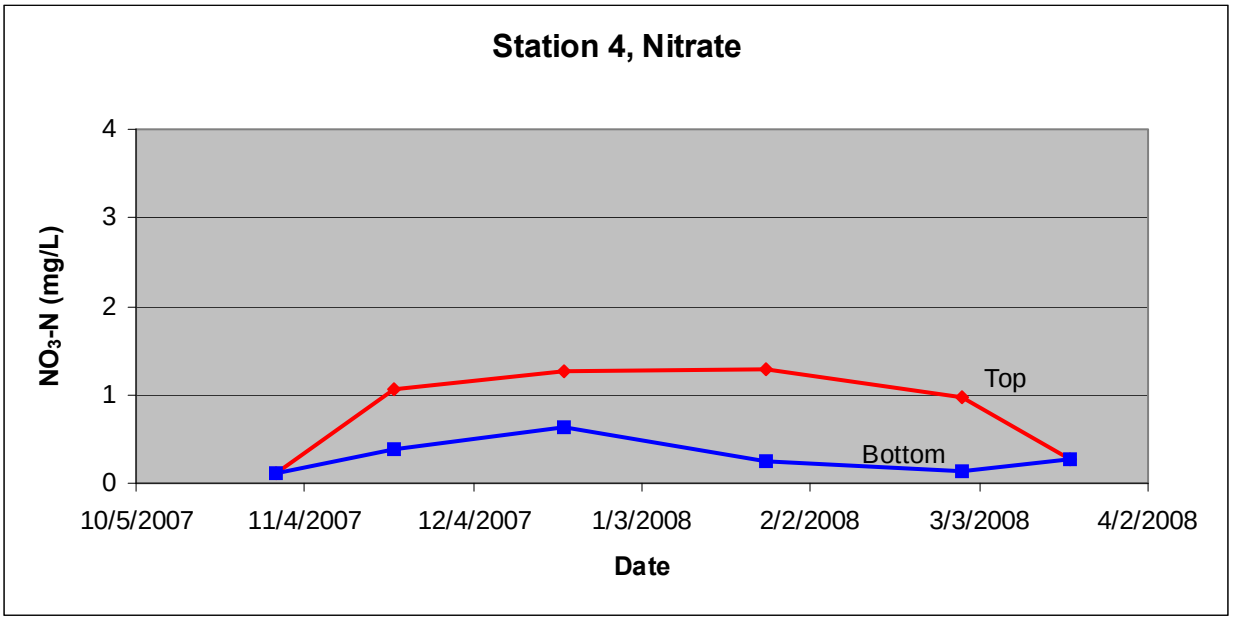

Figure 6.15. Nitrate as nitrogen levels shown at top and bottom of the water column at station 4 over a six-month period.

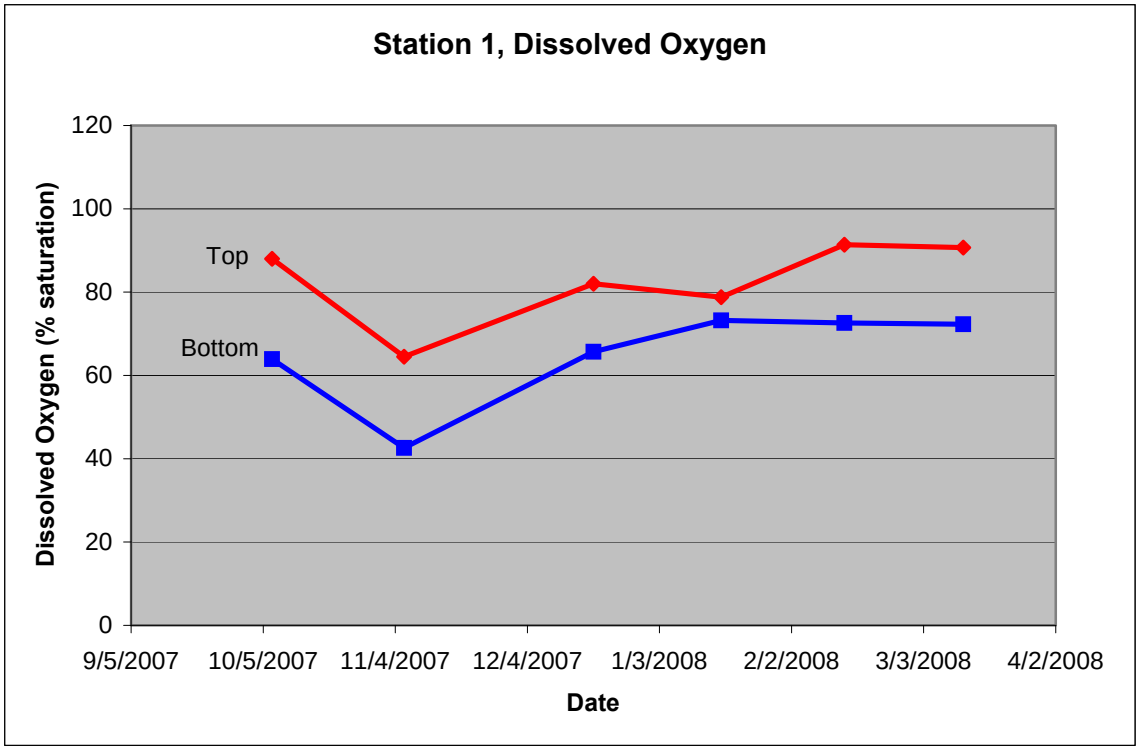

Figure 6.16. Percent saturation of dissolved oxygen over a six-month period at station 1.

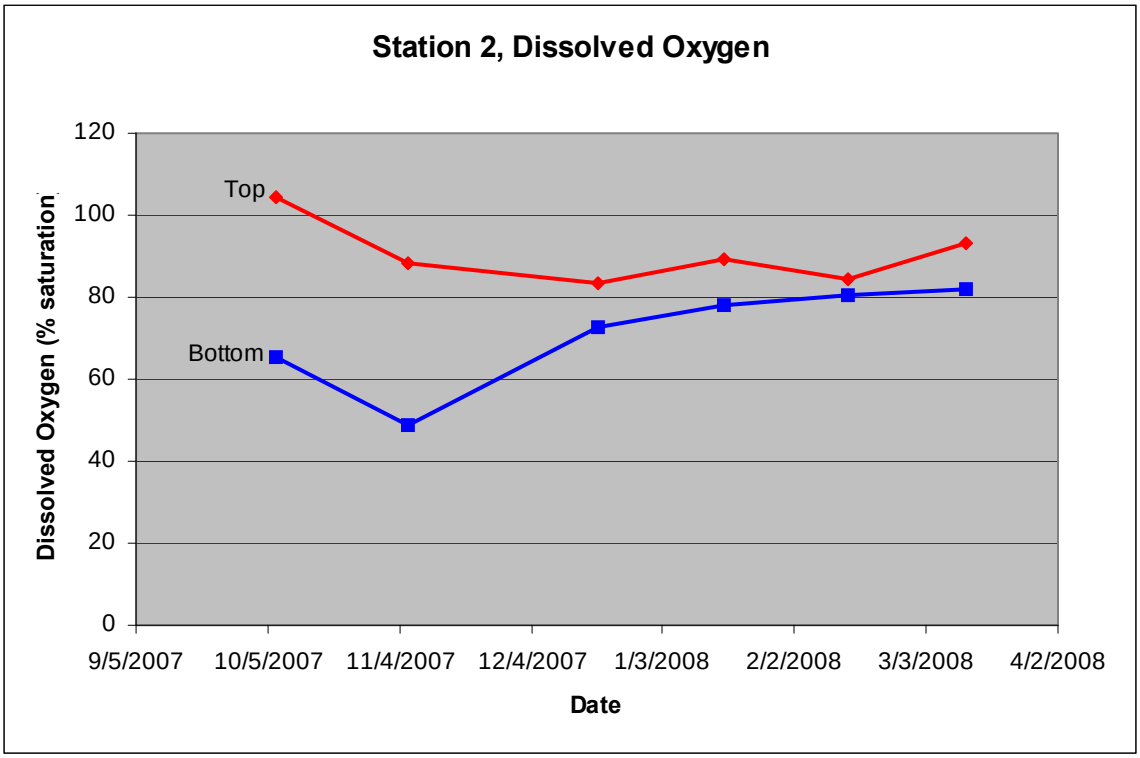

Figure 6.17. Percent saturation of dissolved oxygen over a six-month period at station 2.

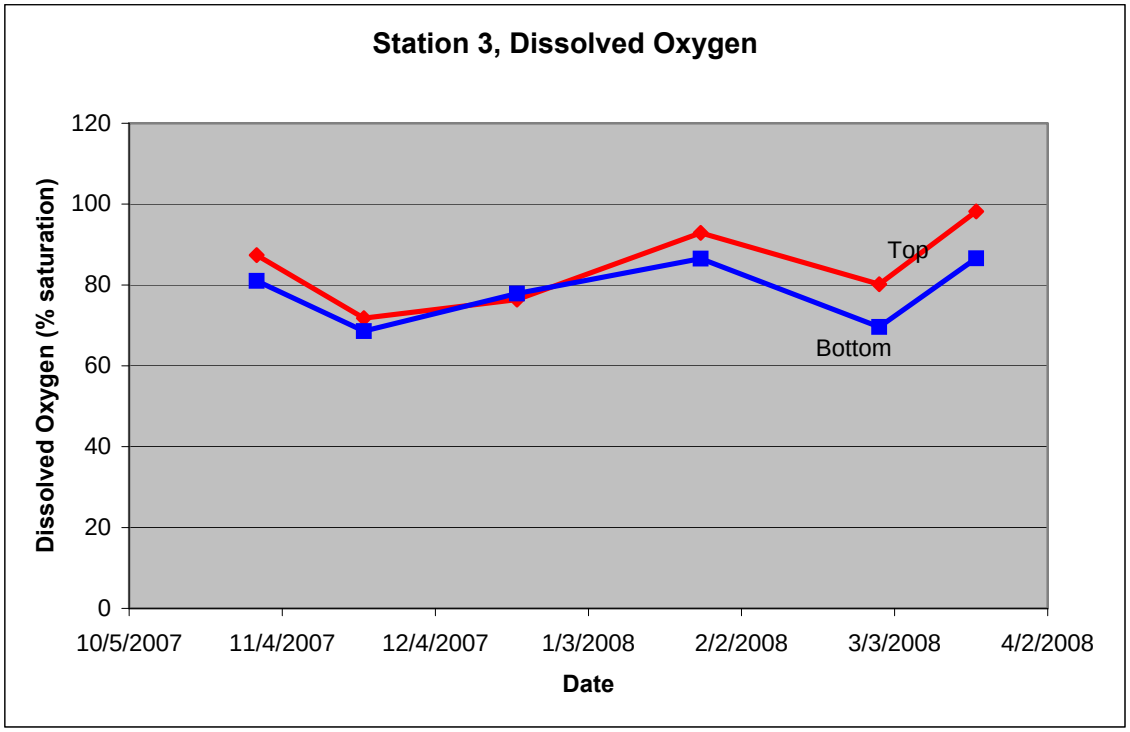

Figure 6.18. Percent saturation of dissolved oxygen over a six-month period at station 3.

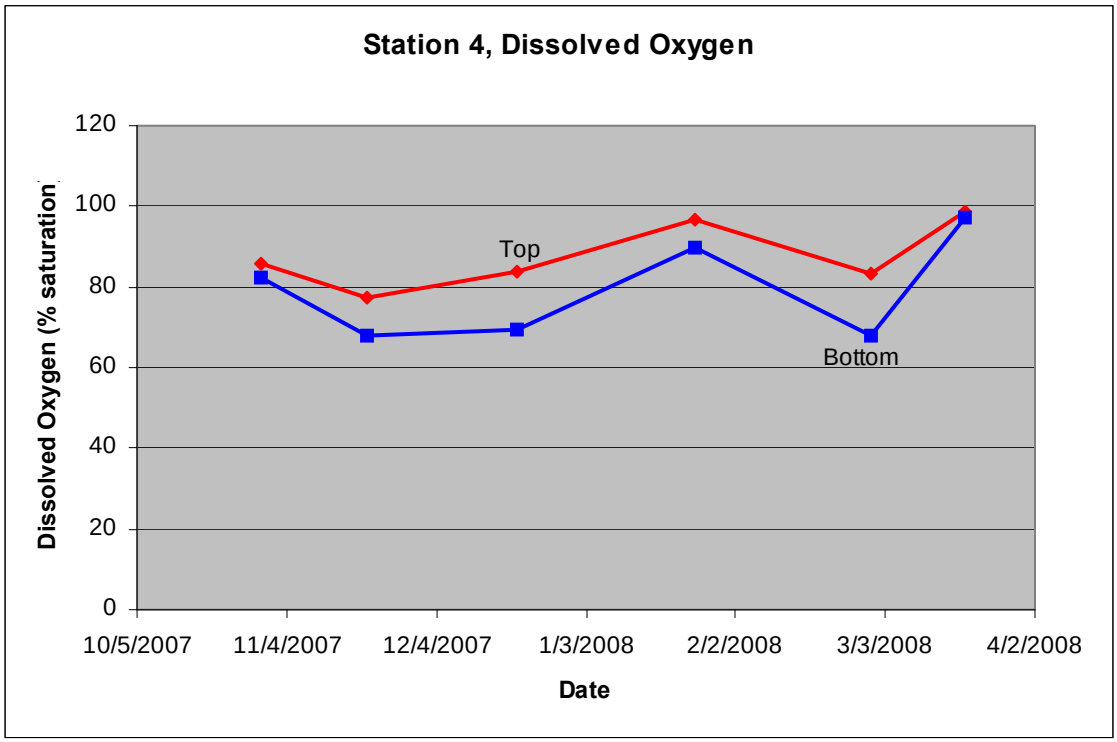

Figure 6.19. Percent saturation of dissolved oxygen over a six-month period at station 4.

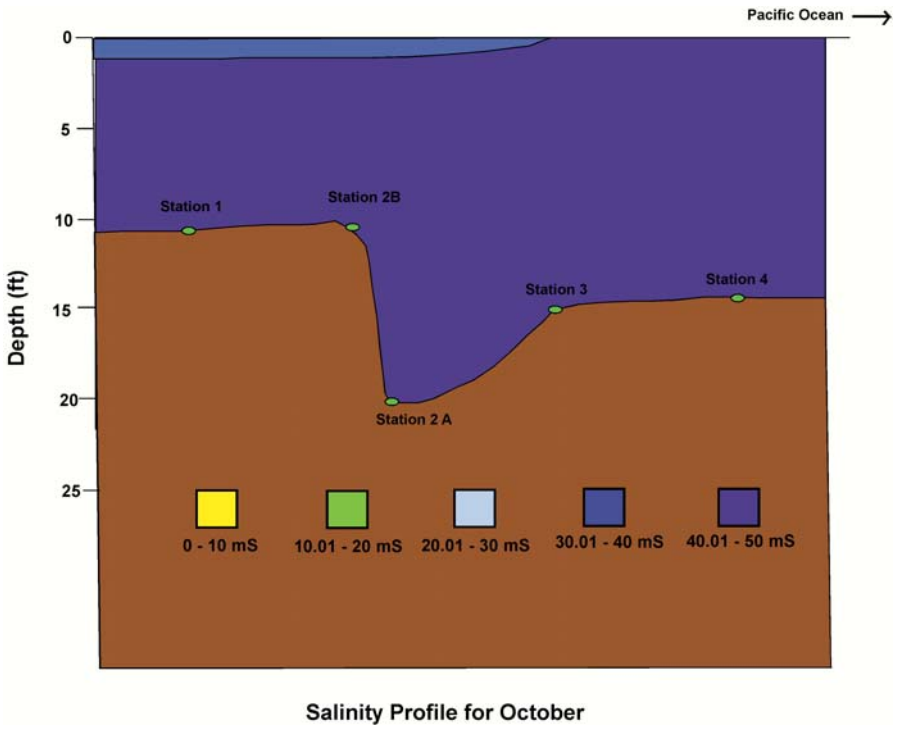

Figure 6.20. Salinity water column profile of stations located in the bay during October 2007, a dry month.

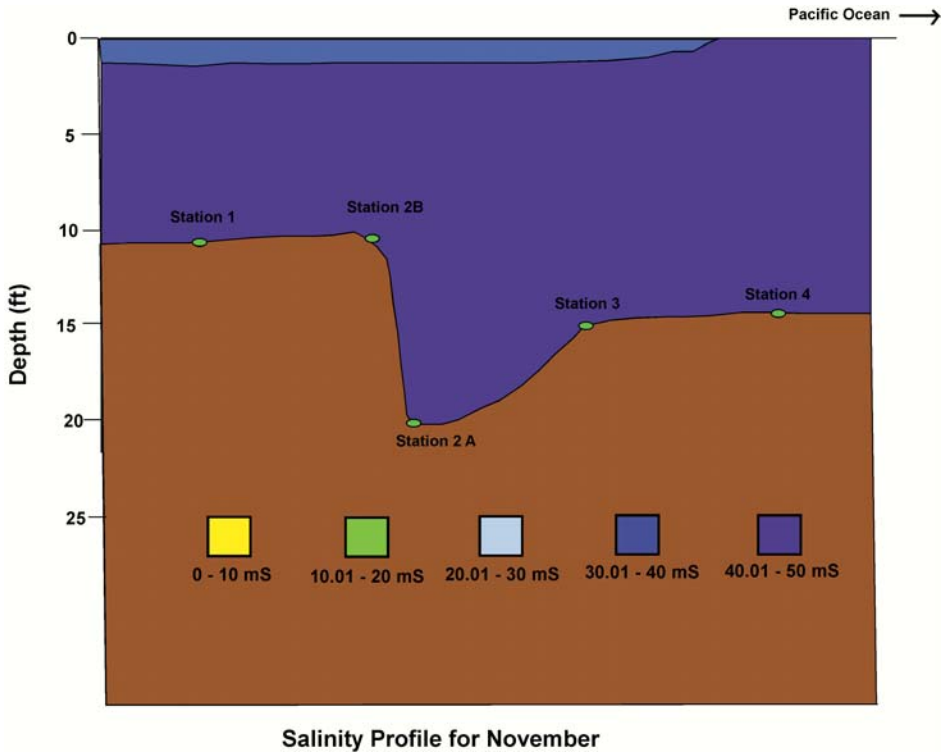

Figure 6.21. Salinity water column profile of stations located in the bay during November 2007, a dry month.

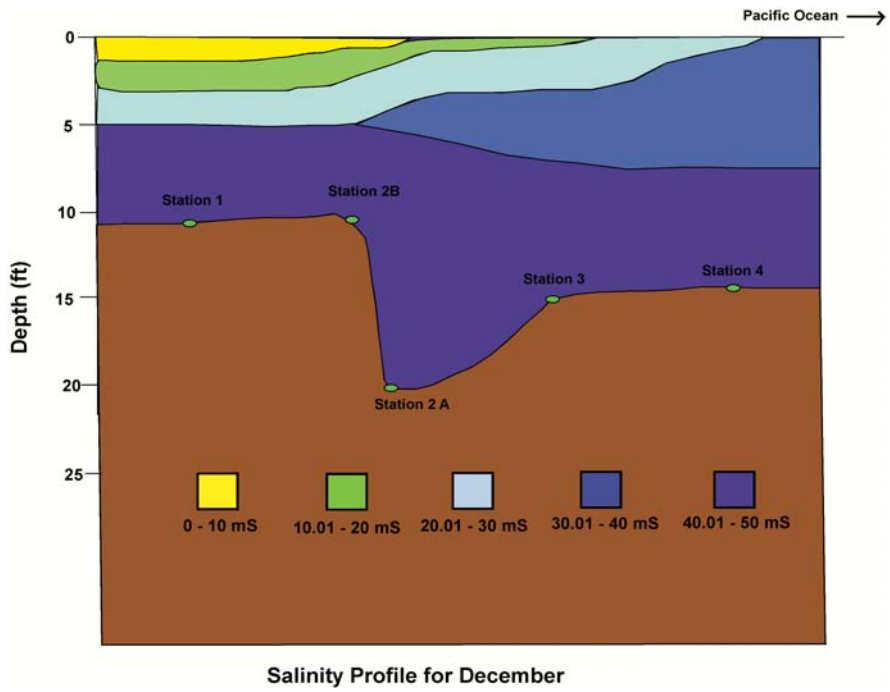

Figure 6.22. Salinity water column profile of stations located in the bay during December 2007, a wet month.

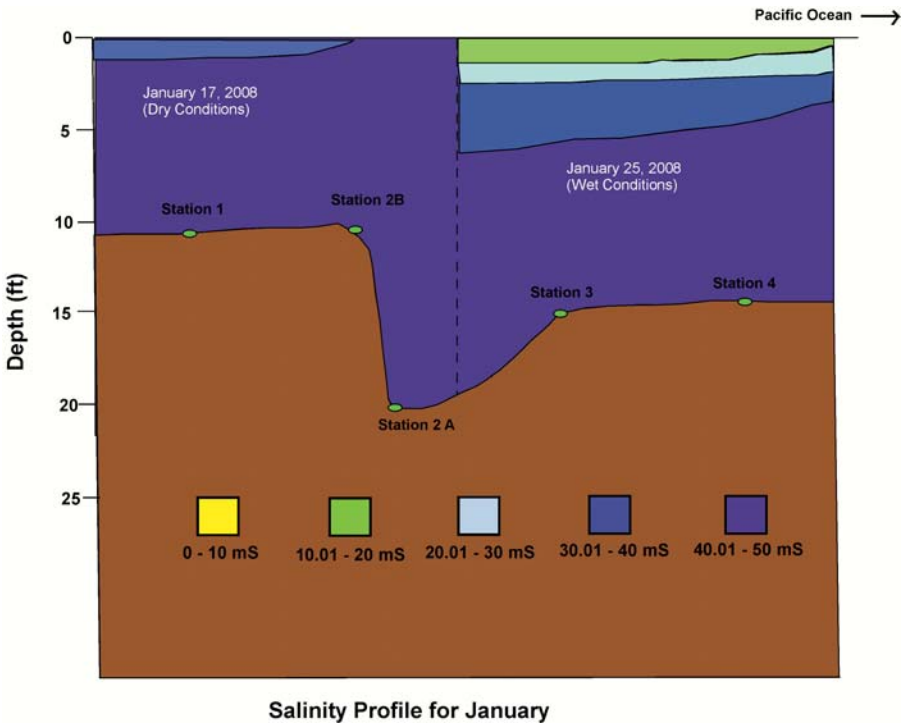

Figure 6.23. Salinity water column profile of stations located in the bay during January 2008. Data for stations 1 and 2 were collected during dry weather whereas data collected for stations 3 and 4 were during wet weather. Note the variation in fresh water lens between dry and wet weather.

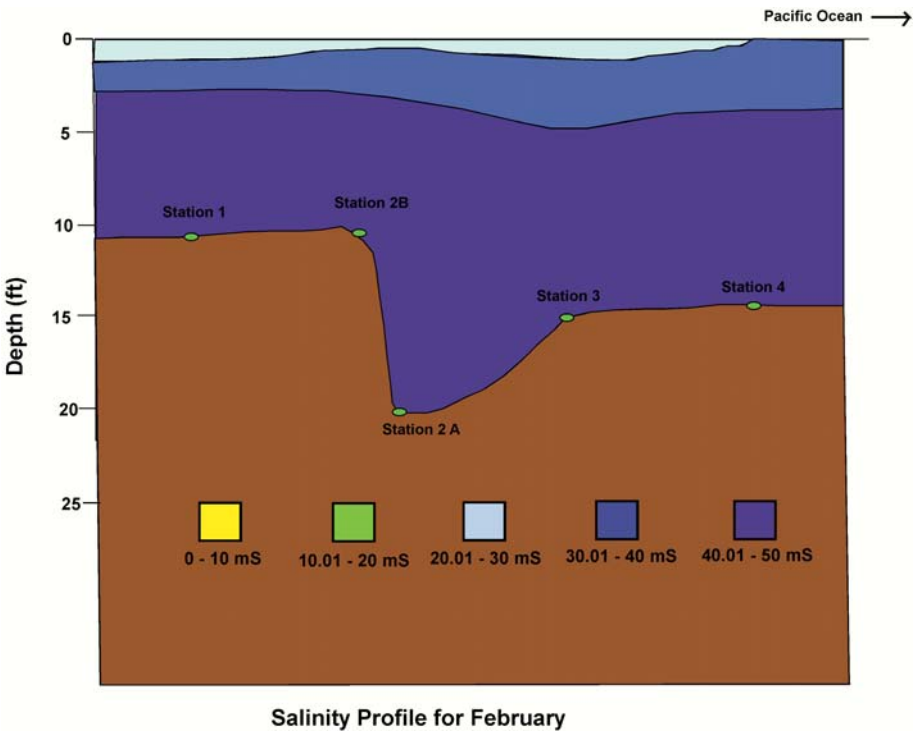

Figure 6.24. Salinity water column profile of stations located in the bay during February 2008, a wet month.

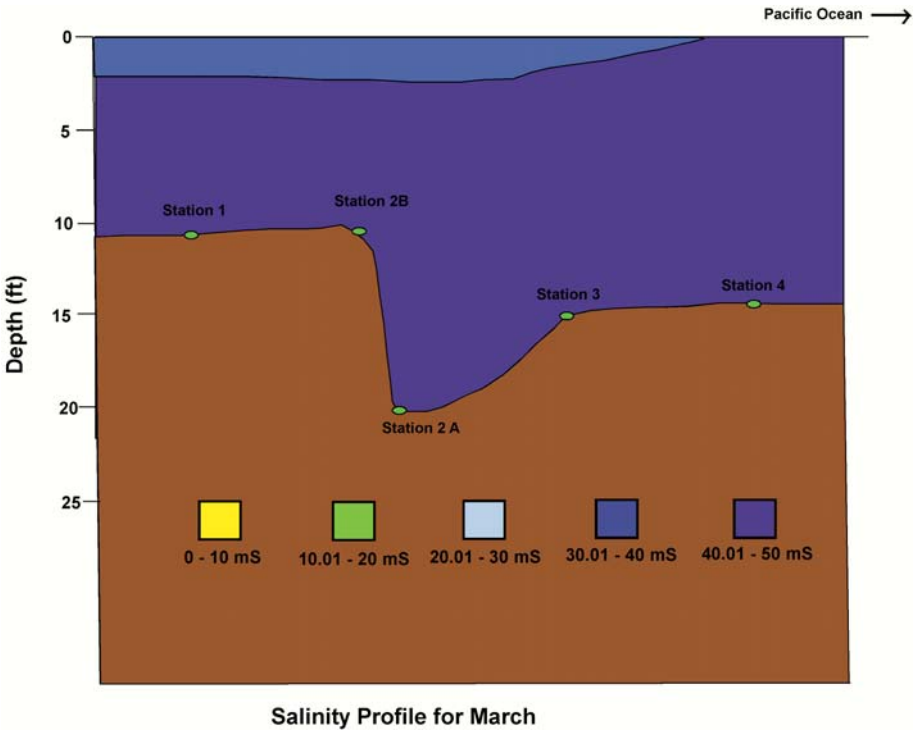

Figure 6.25. Salinity water column profile of stations located in the bay during March 2008, a dry month.

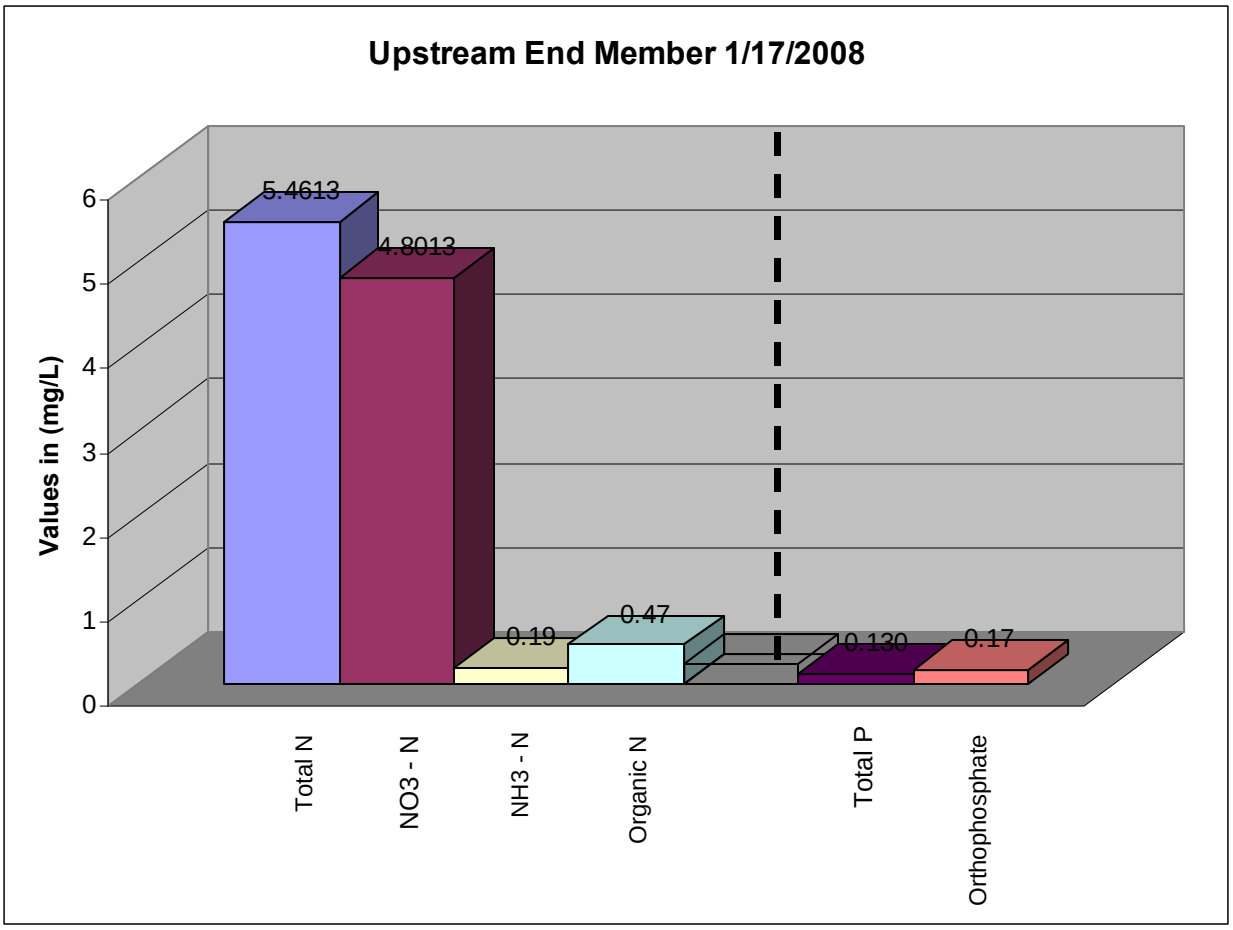

Figure 6.26. Expanded parameters: nitrogen and phosphorus at the upstream end member.

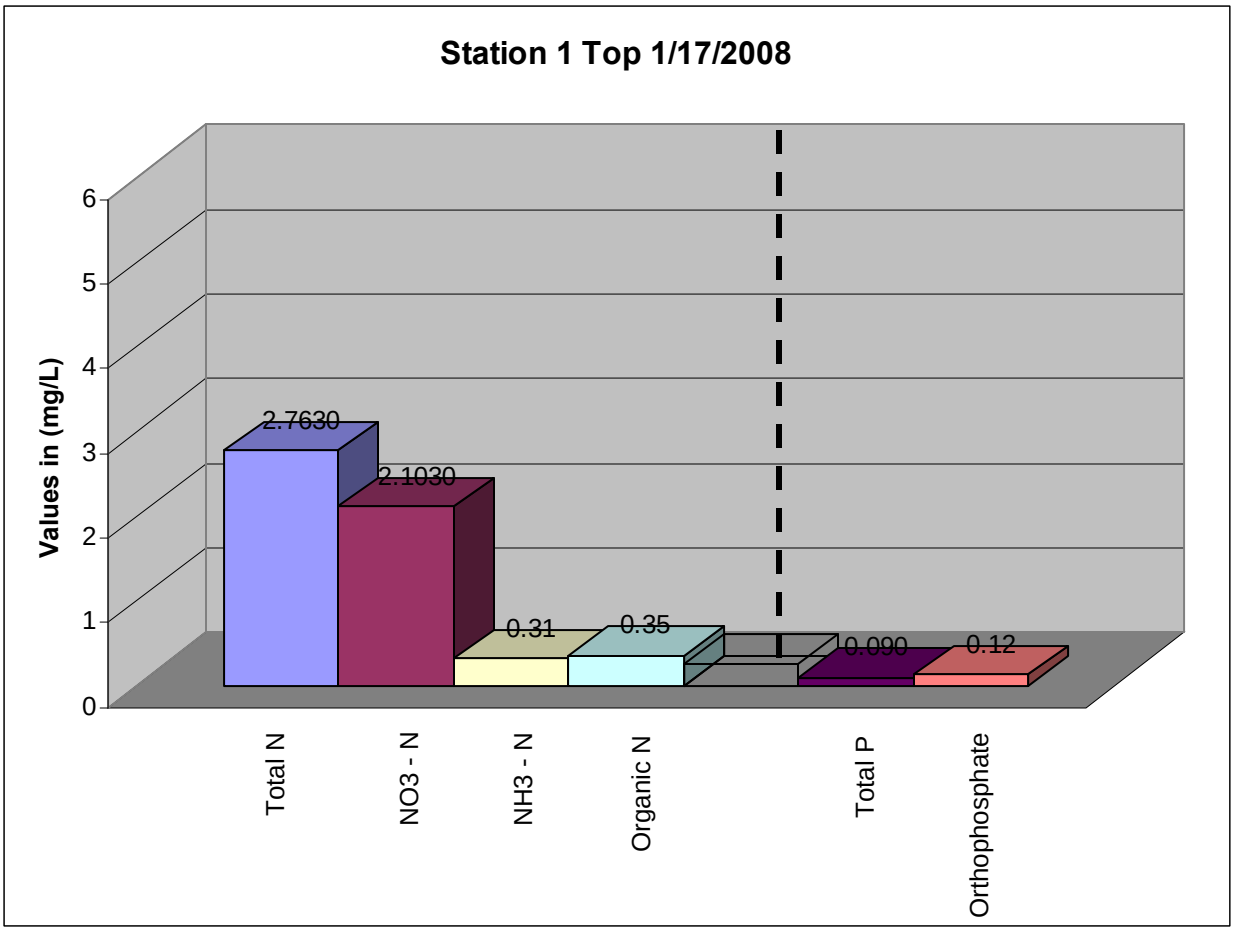

Figure 6.27. Expanded parameters: nitrogen and phosphorus of surface water at the station 1.

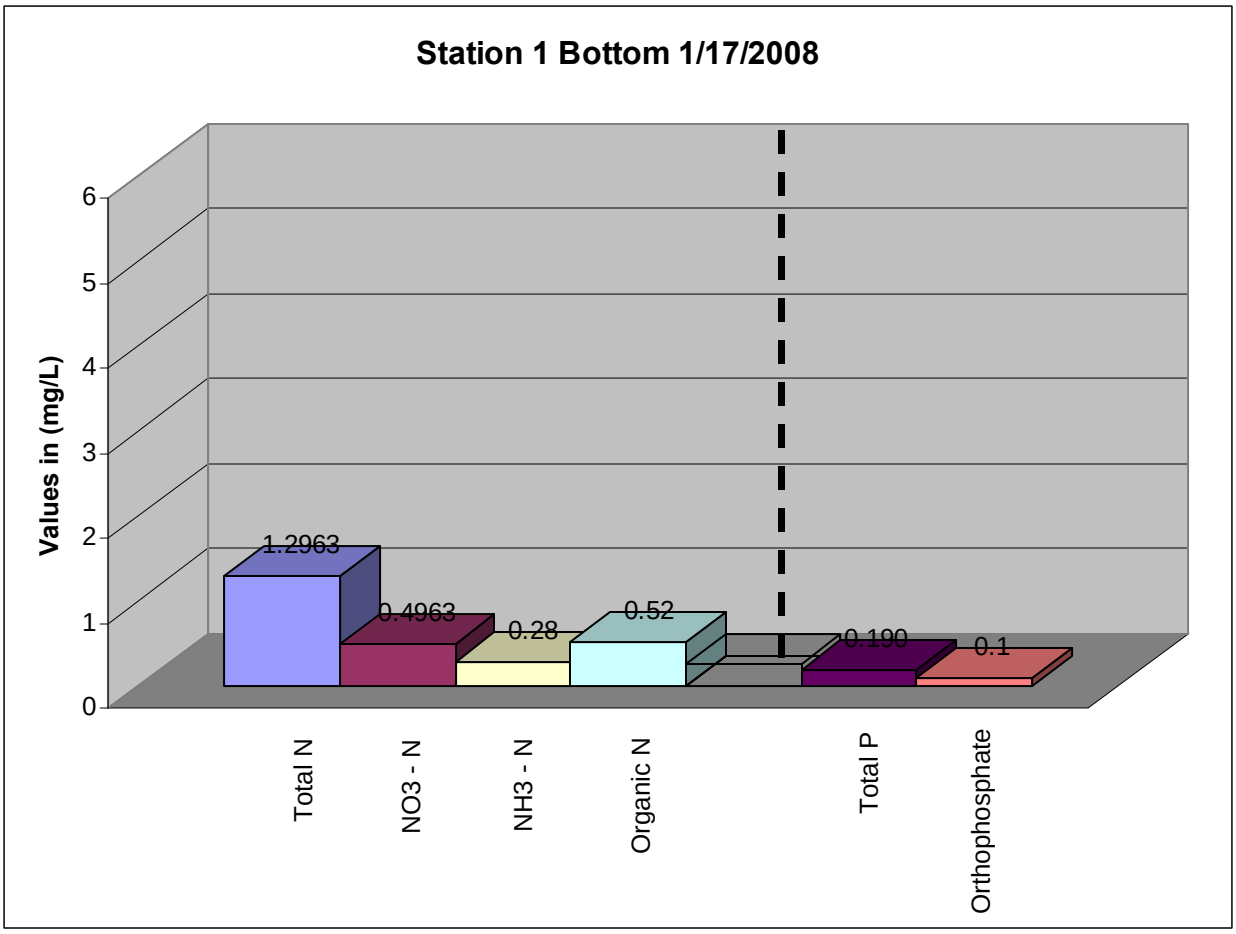

Figure 6.28. Expanded parameters: nitrogen and phosphorus of bottom water at the station 1.

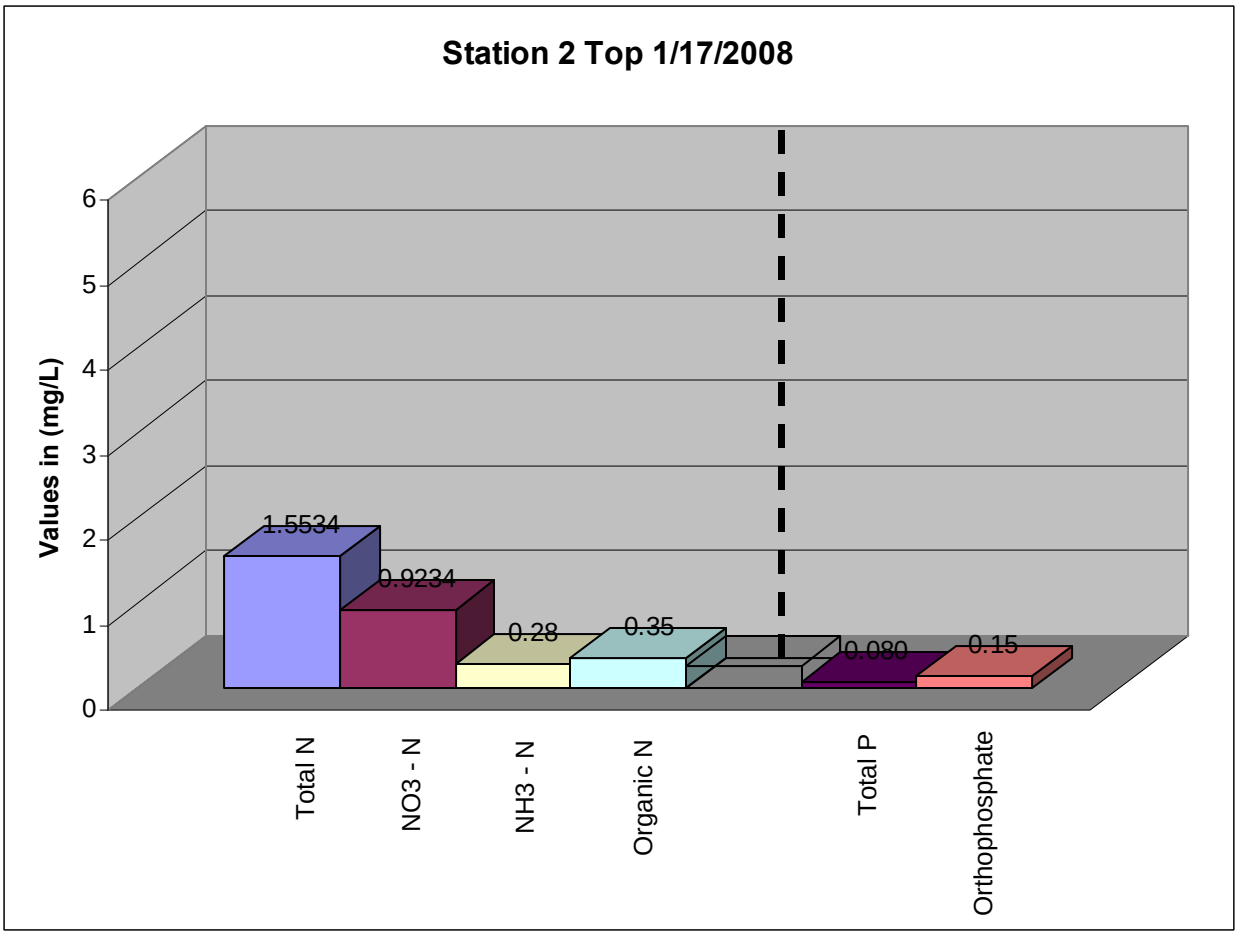

Figure 6.29. Expanded parameters: nitrogen and phosphorus of surface water at the station 2.

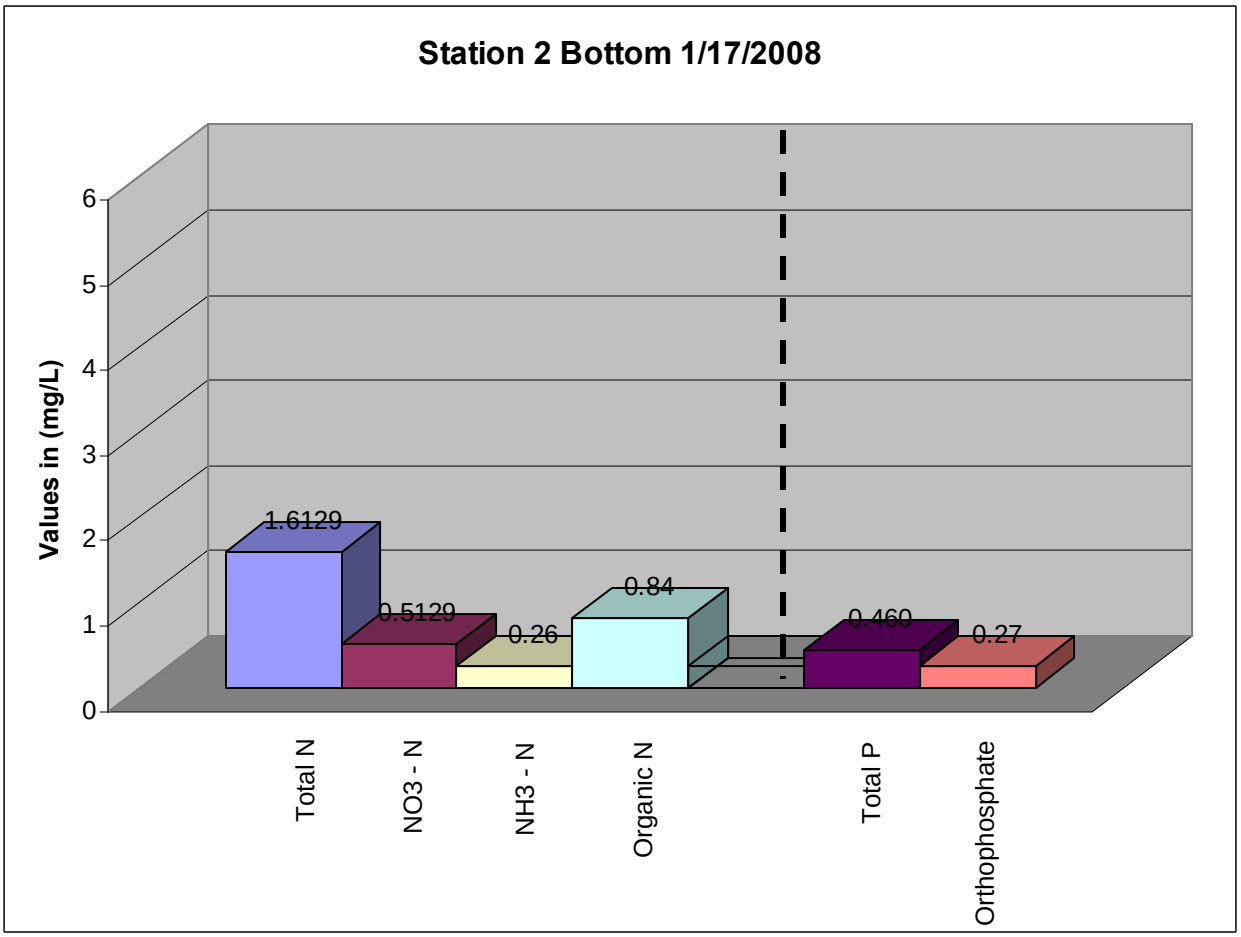

Figure 6.30. Expanded parameters: nitrogen and phosphorus of bottom water at the station 2.

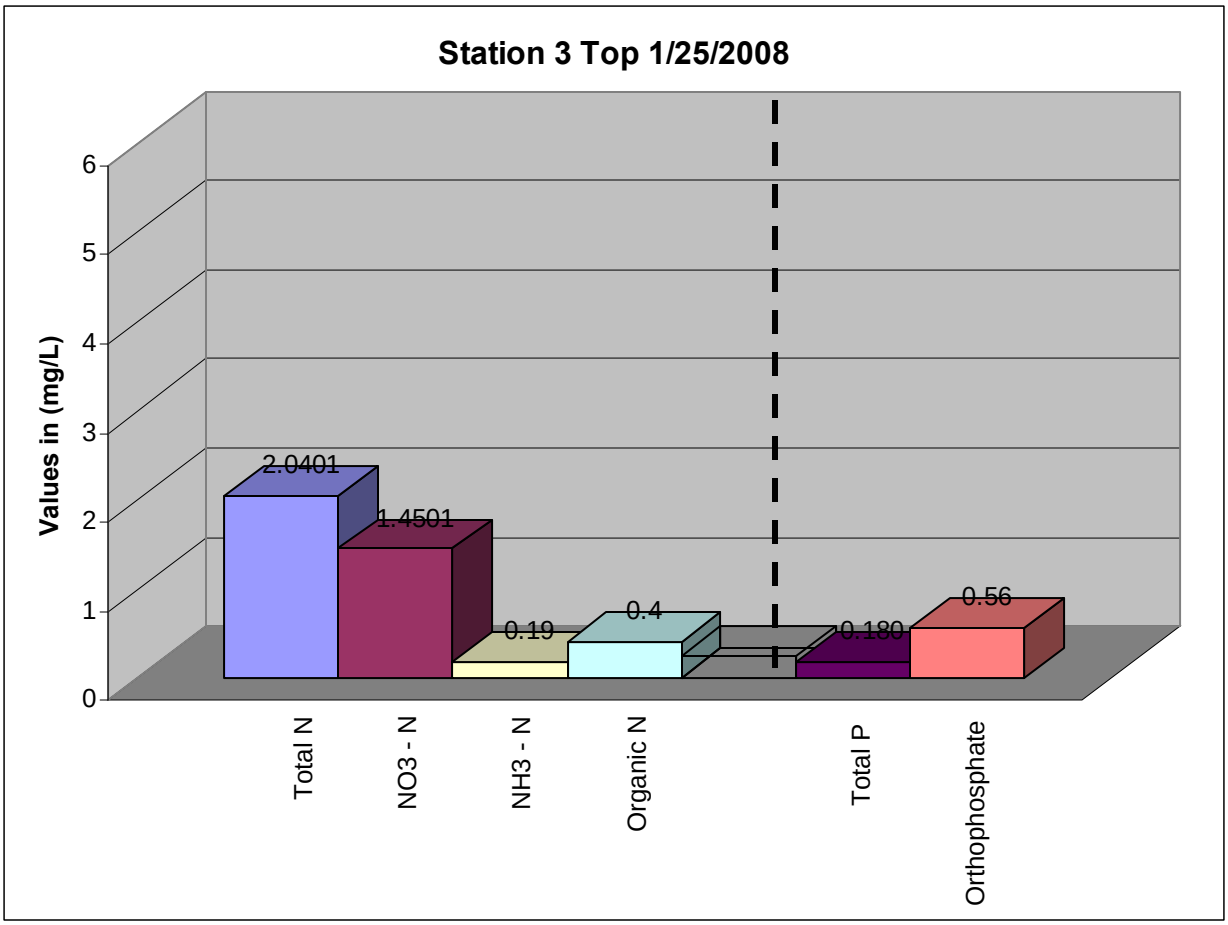

Figure 6.31. Expanded parameters: nitrogen and phosphorus of surface water at the station 3.

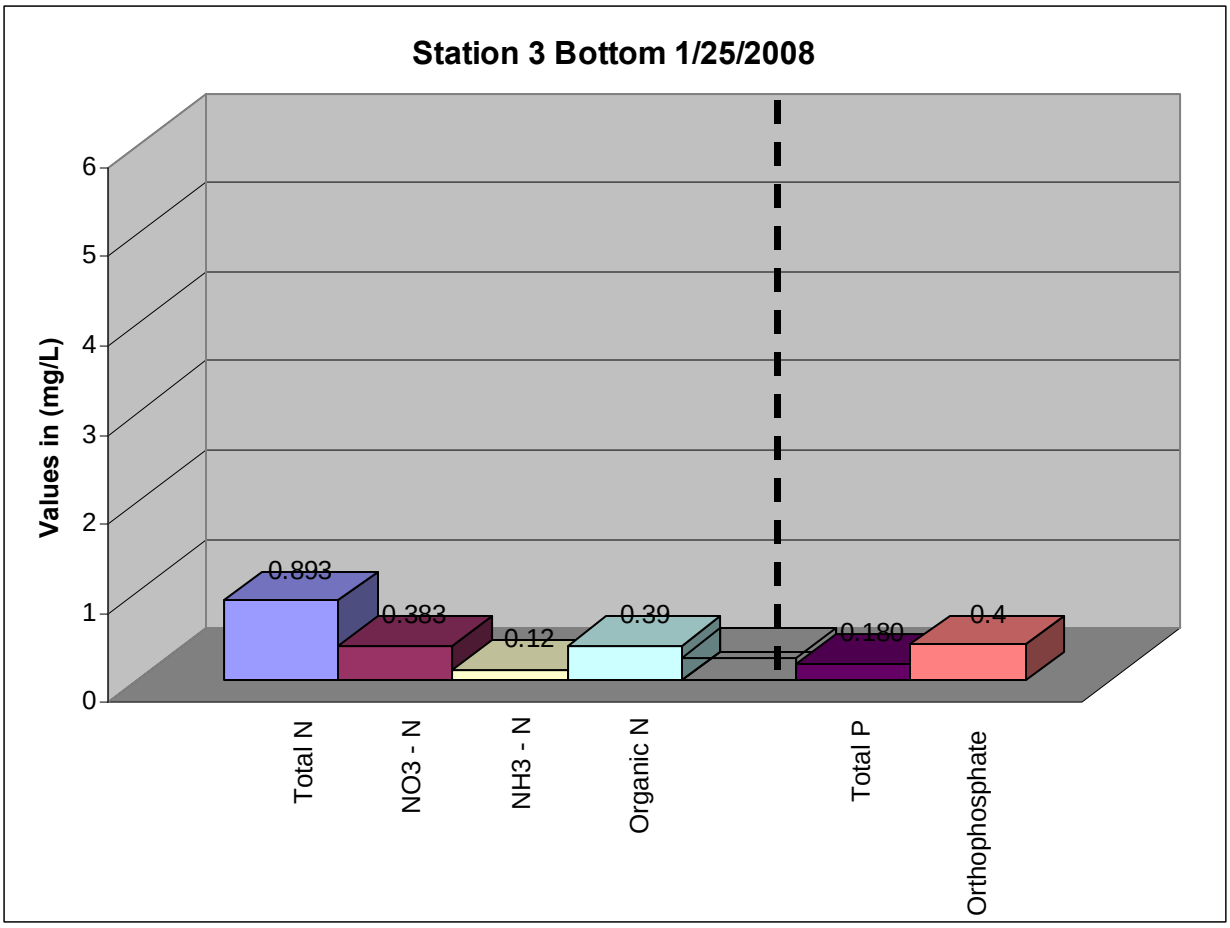

Figure 6.32. Expanded parameters: nitrogen and phosphorus of bottom water at the station 3.

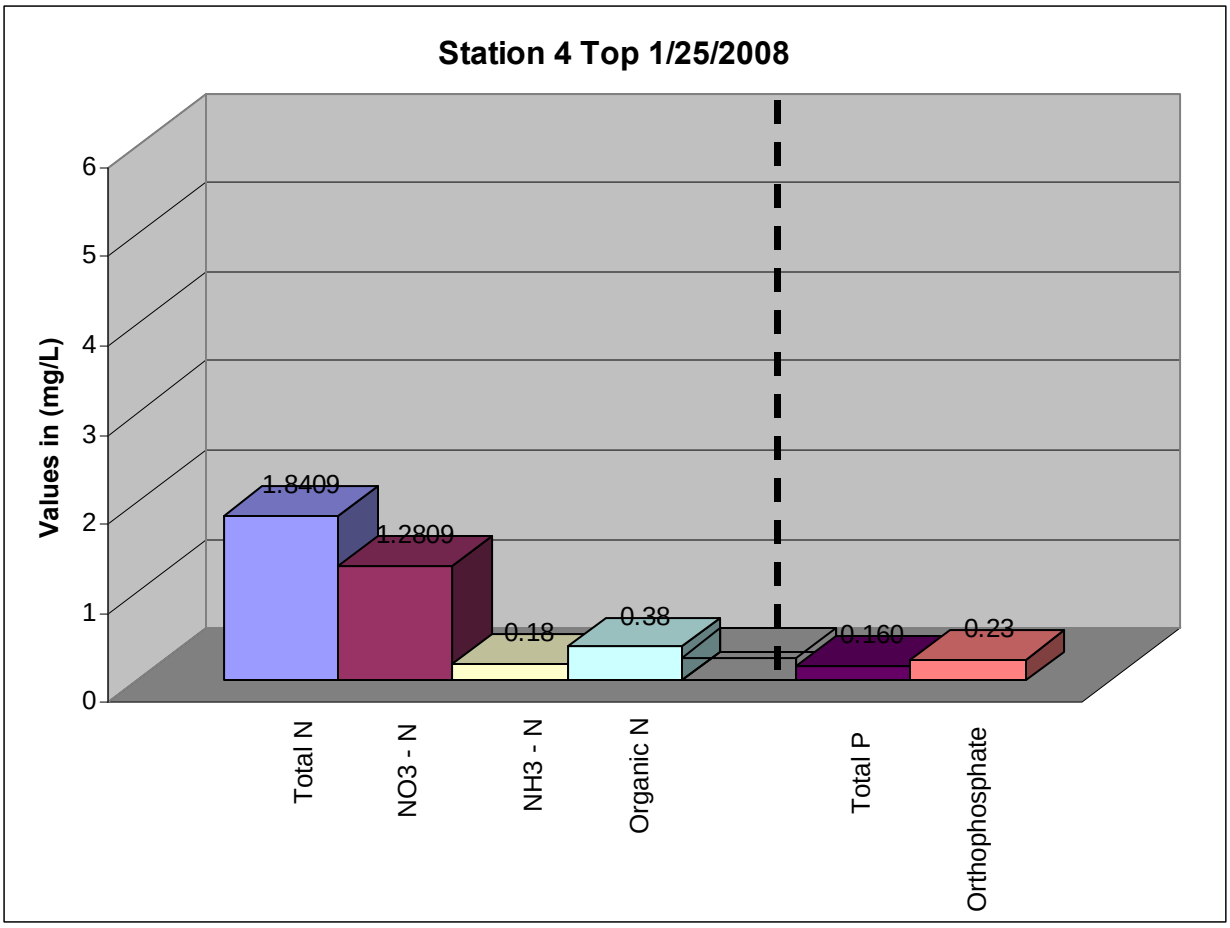

Figure 6.33. Expanded parameters: nitrogen and phosphorus of surface water at the station 4.

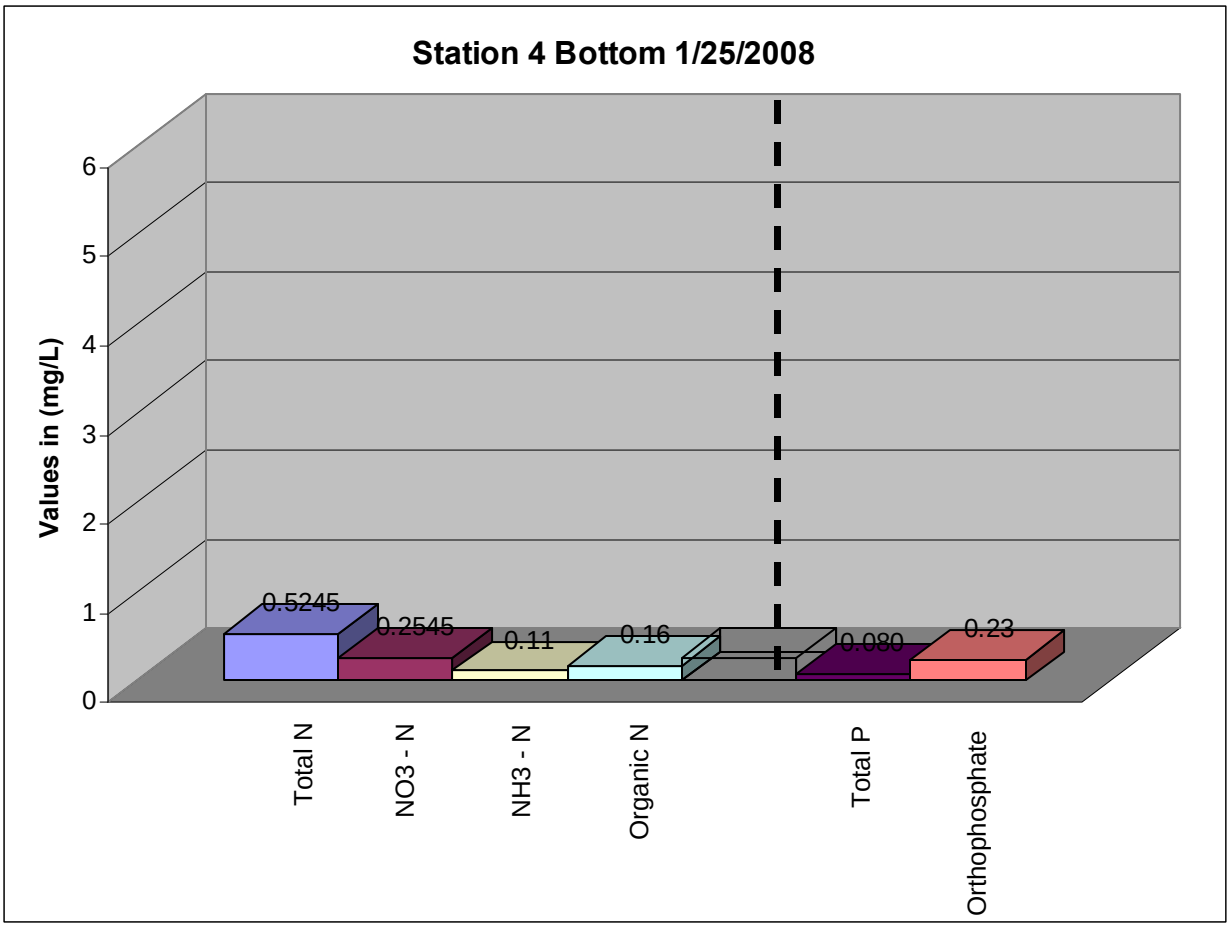

Figure 6.34. Expanded parameters: nitrogen and phosphorus of bottom water at the station 4.

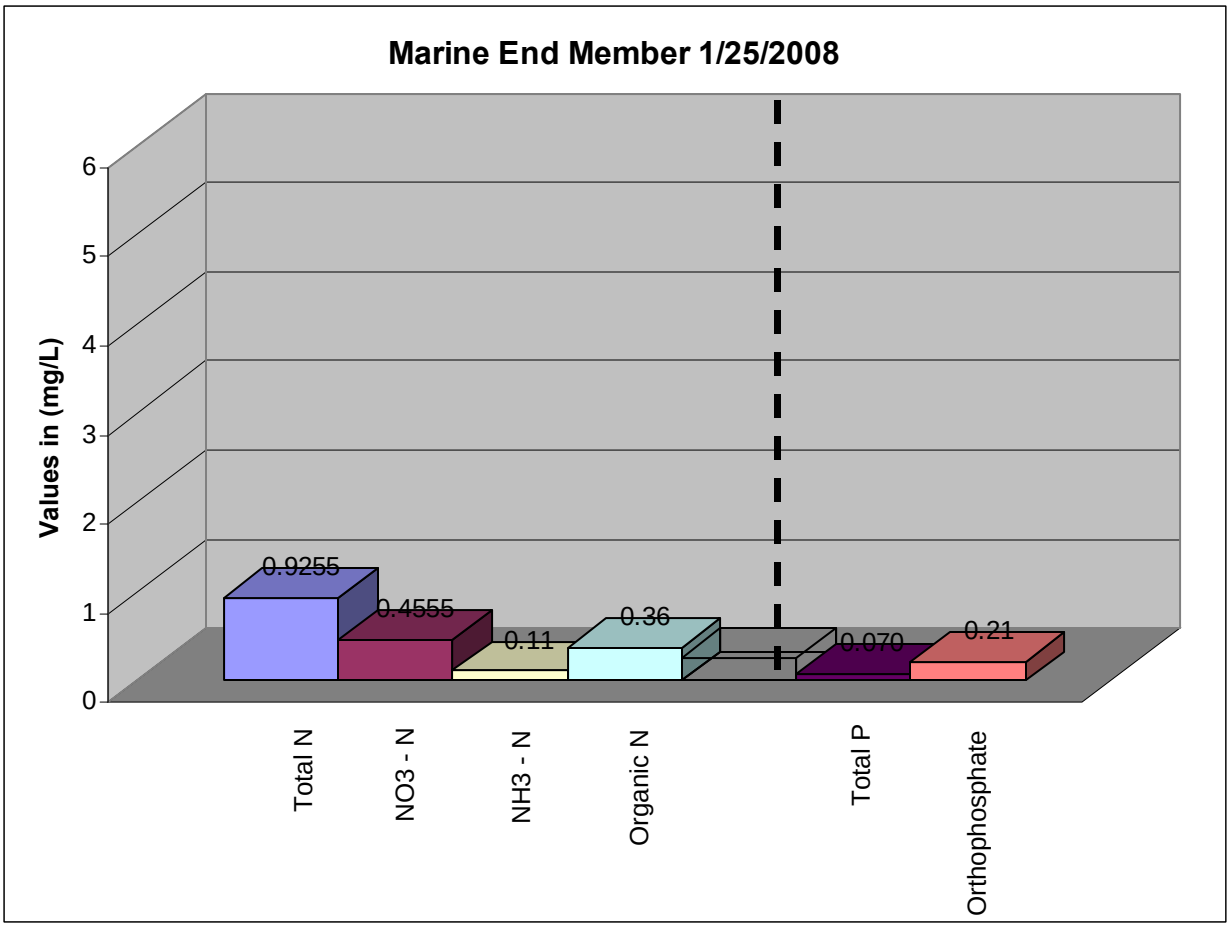

Figure 6.35. Expanded parameters: nitrogen and phosphorus at the marine end member.

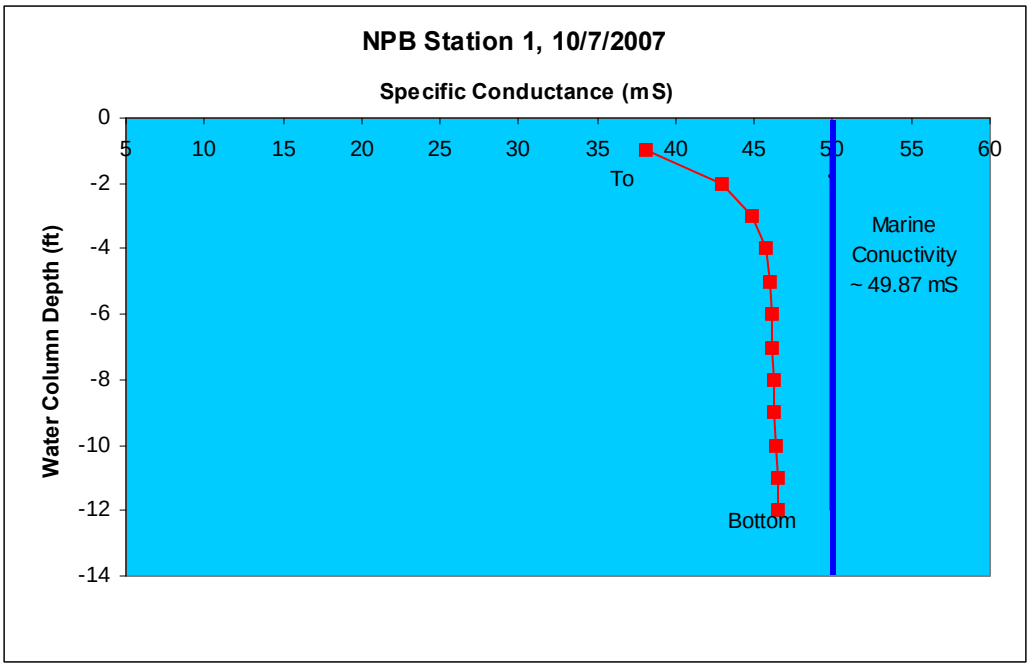

Figure 6.36. Electrical conductivity of water for station 1 during October. Salinity of the water column is near marine salinity values during dry months. Salinity at the top of water column deviates from marine salinity due to terrestrial discharge from San Diego Creek.

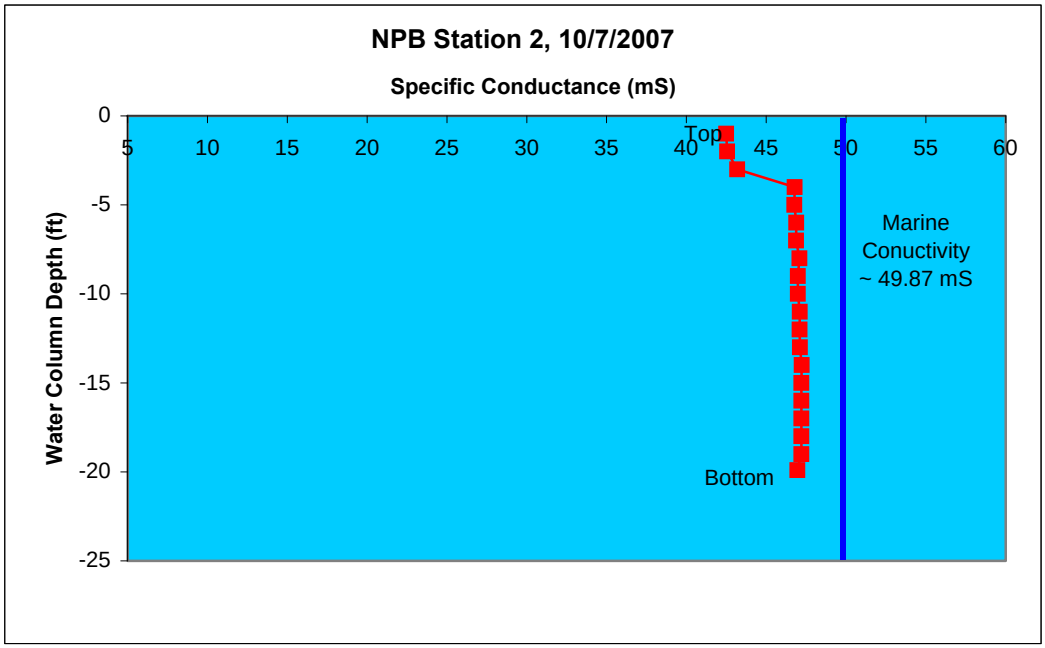

Figure 6.37. Electrical conductivity of water for station 2 during October. Salinity of the water column is near marine salinity values during dry months. Salinity at the top of water column deviates from marine salinity due to terrestrial discharge from San Diego Creek.

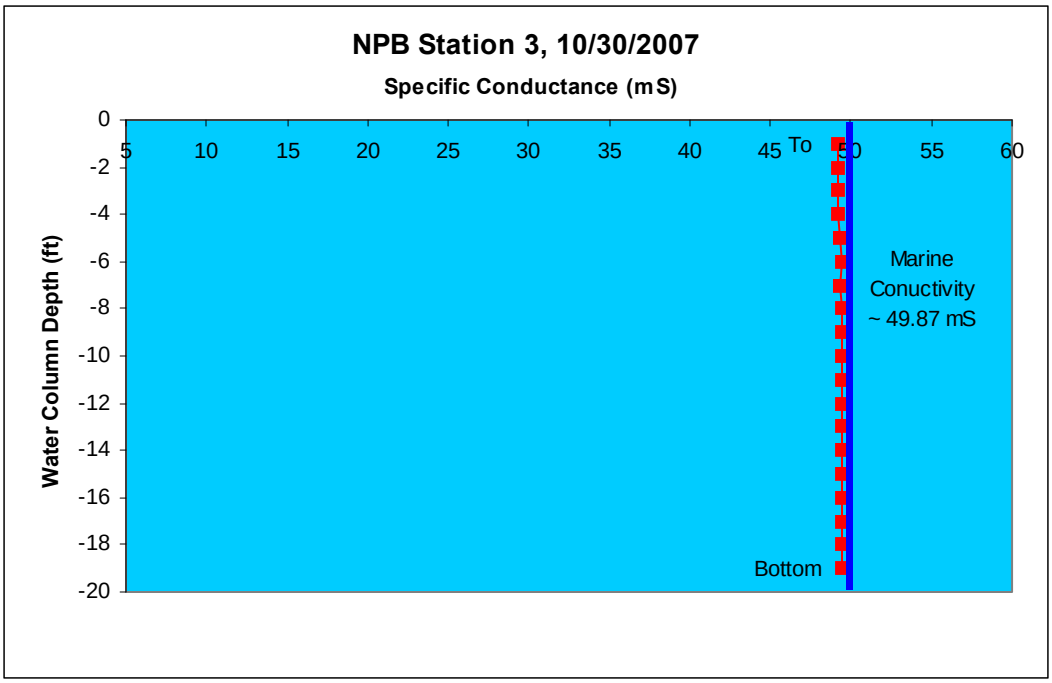

Figure 6.38. Electrical conductivity of water for station 3 during October. Salinity throughout the water column is very close to marine salinity value during dry months.

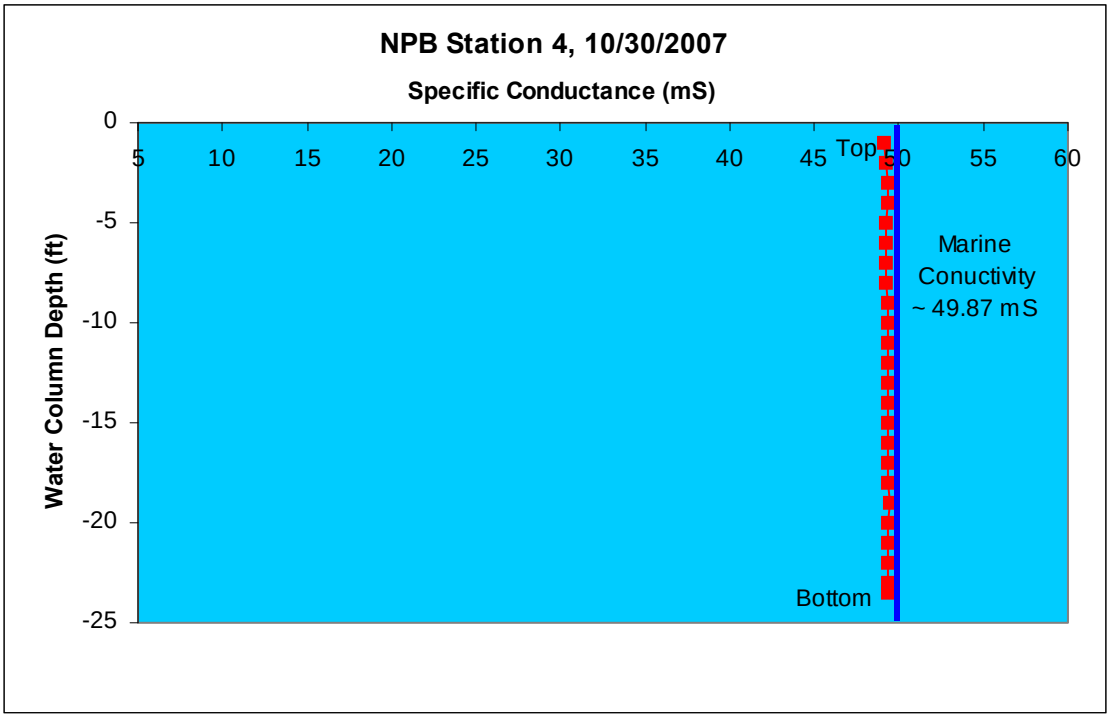

Figure 6.39. Electrical conductivity of water for station 4 during October. Salinity throughout the water column is very close to marine salinity value during dry months.

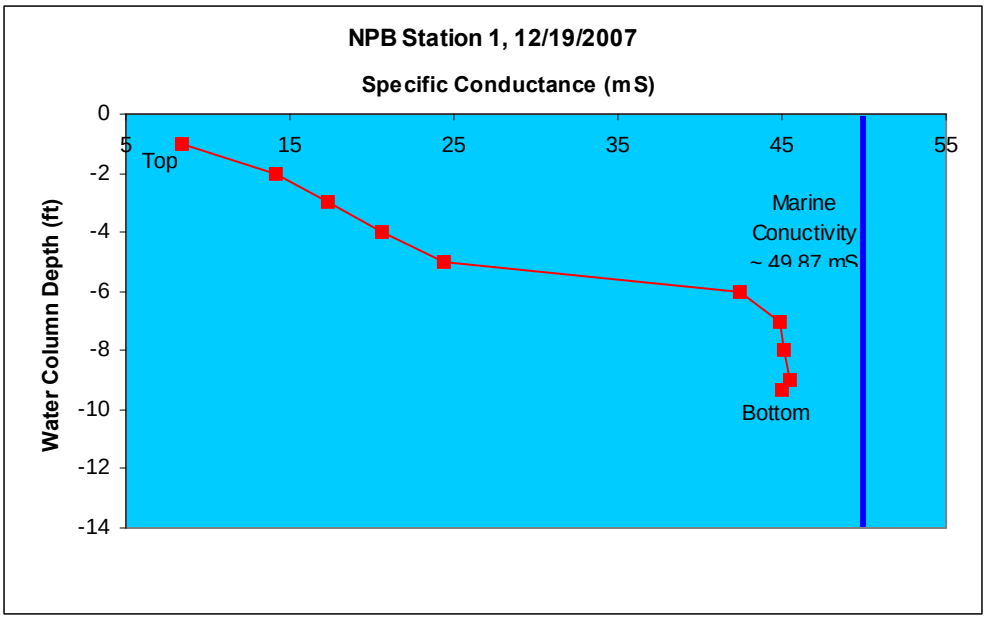

Figure 6.40. Electrical conductivity of water for station 1 during December. Salinity of the water column is diluted during wet months. Salinity at the top of water column strays from marine salinity due to rain events and increased terrestrial discharge from San Diego Creek. As depth increases, the salinity approaches marine values due to influx of tides.

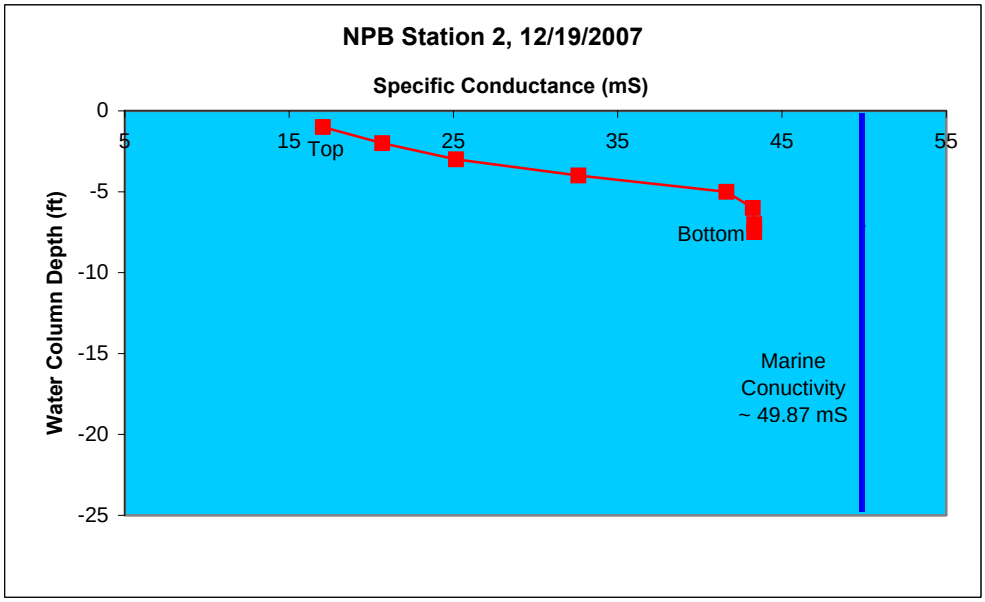

Figure 6.41. Electrical conductivity of water for station 2 during December. Salinity of the water column is diluted during wet months. Salinity at the top of water column strays from marine salinity due to rain events and increased terrestrial discharge from San Diego Creek. As depth increases, the salinity approaches marine values due to influx of tides.

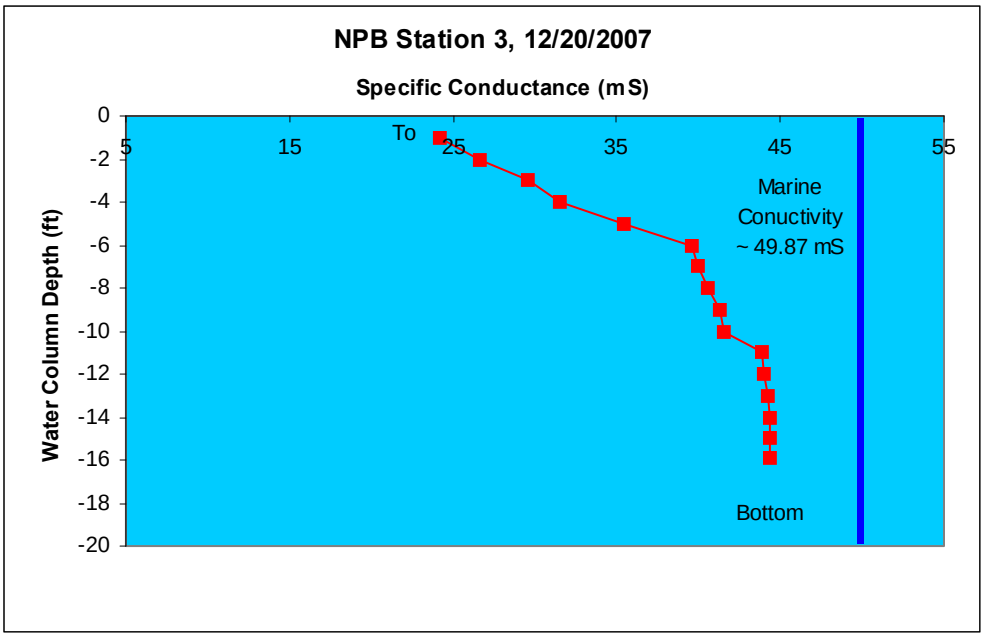

Figure 6.42. Electrical conductivity of water for station 3 during December. Salinity of the water column is diluted during wet months. Salinity at the top of water column deviates from marine salinity due to rain events and increase terrestrial discharge from San Diego Creek. As depth increases, the salinity approaches marine values due to influx of tides.

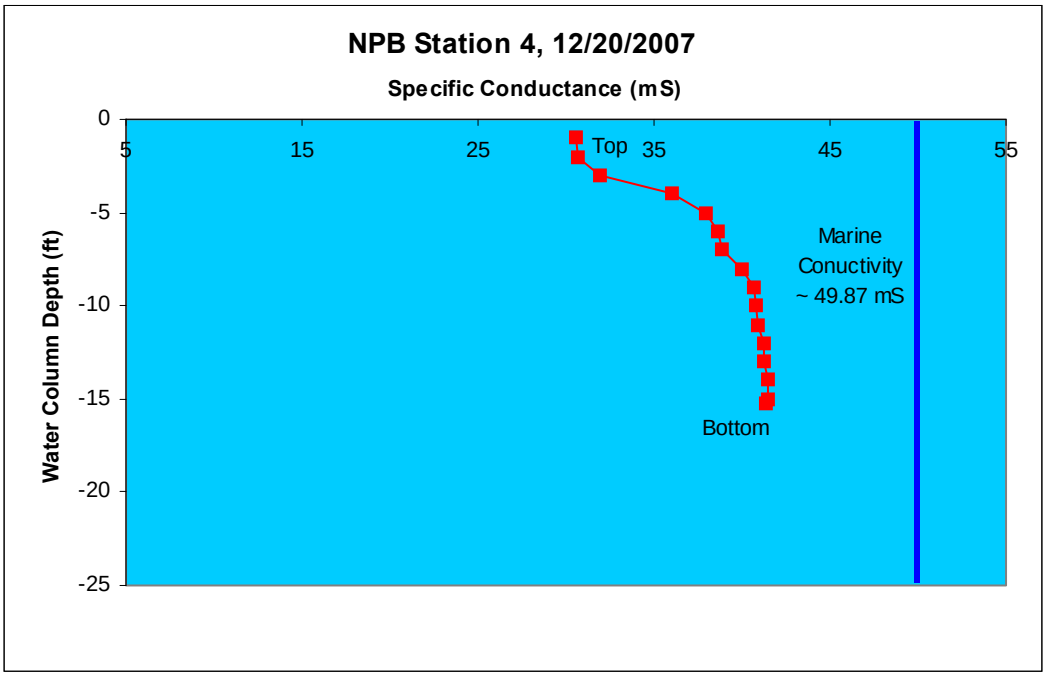

Figure 6.43. Electrical conductivity of water for station 4 during December. Salinity of the water column is diluted during wet months. Salinity at the top of water column digresses from marine salinity due to rain events and increase terrestrial discharge from San Diego Creek. As depth increases, the salinity approaches marine values due to influx of tides.

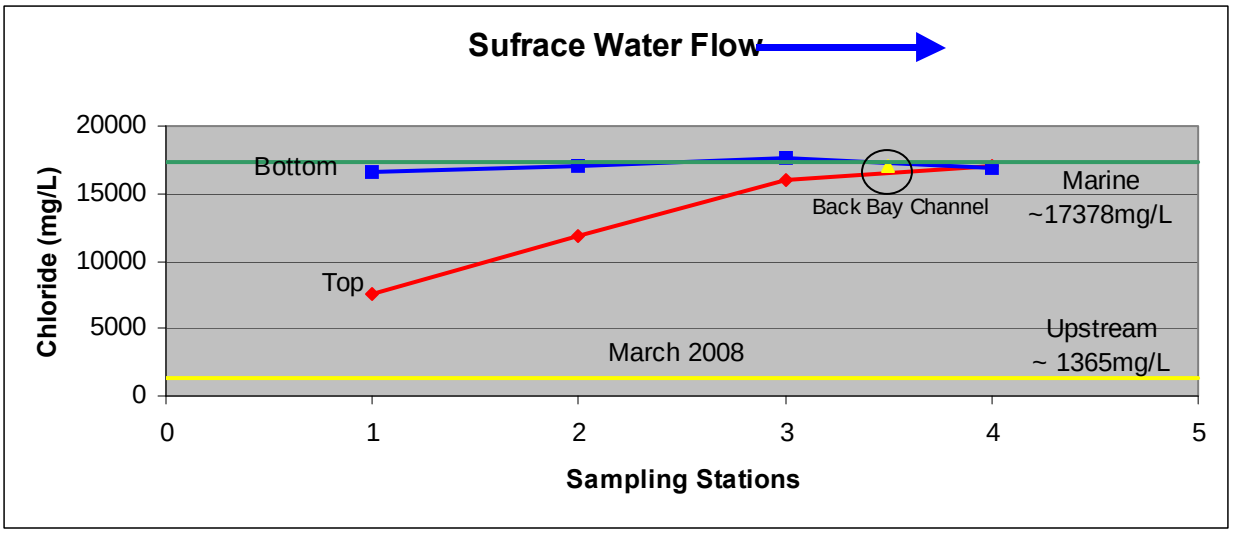

Figure 6.44. Chloride levels at each station during March 2008, a dry month.

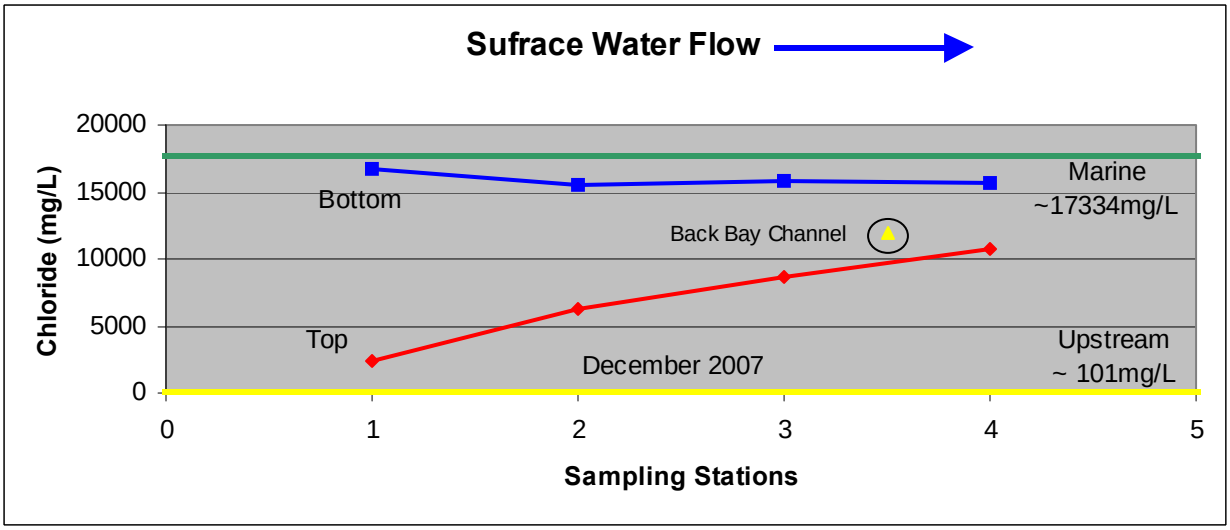

Figure 6.45. Chloride levels at each station during December 2007, a wet month.

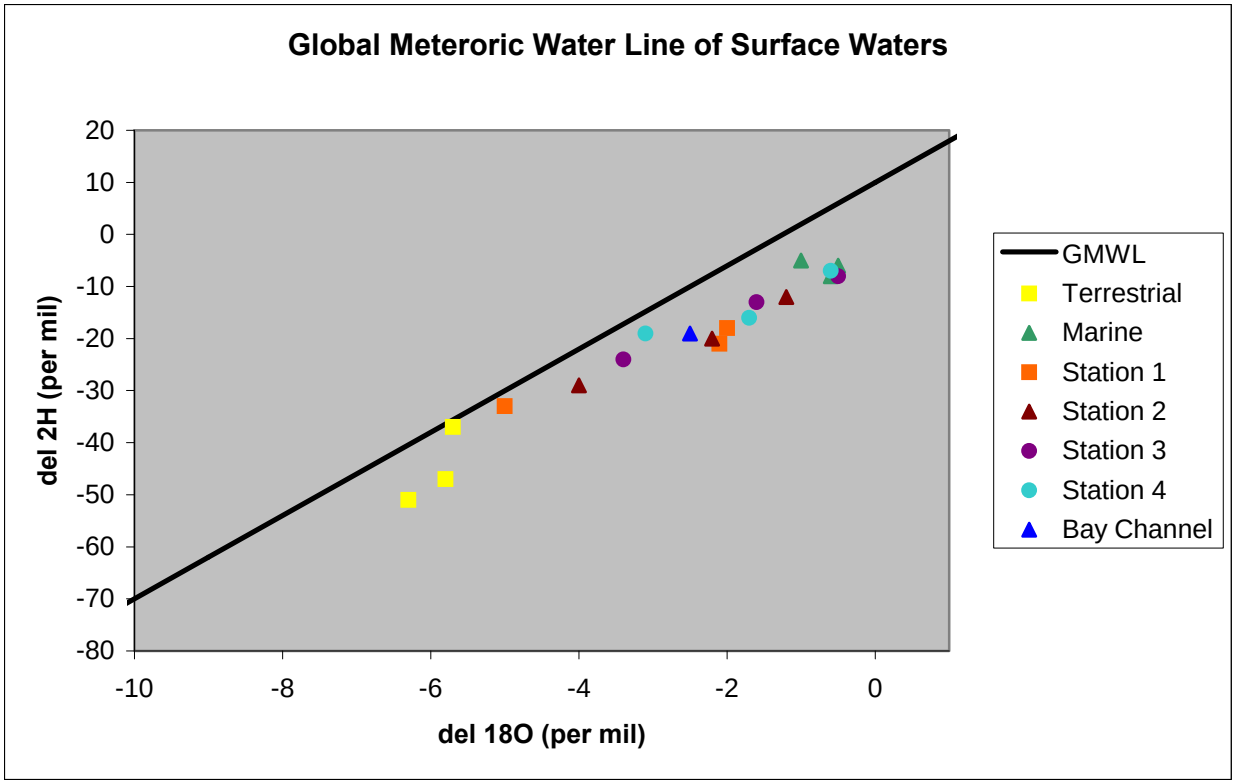

Figure 6.46. Isotopic signature of surface water plotted along Global Meteoric Water Line.

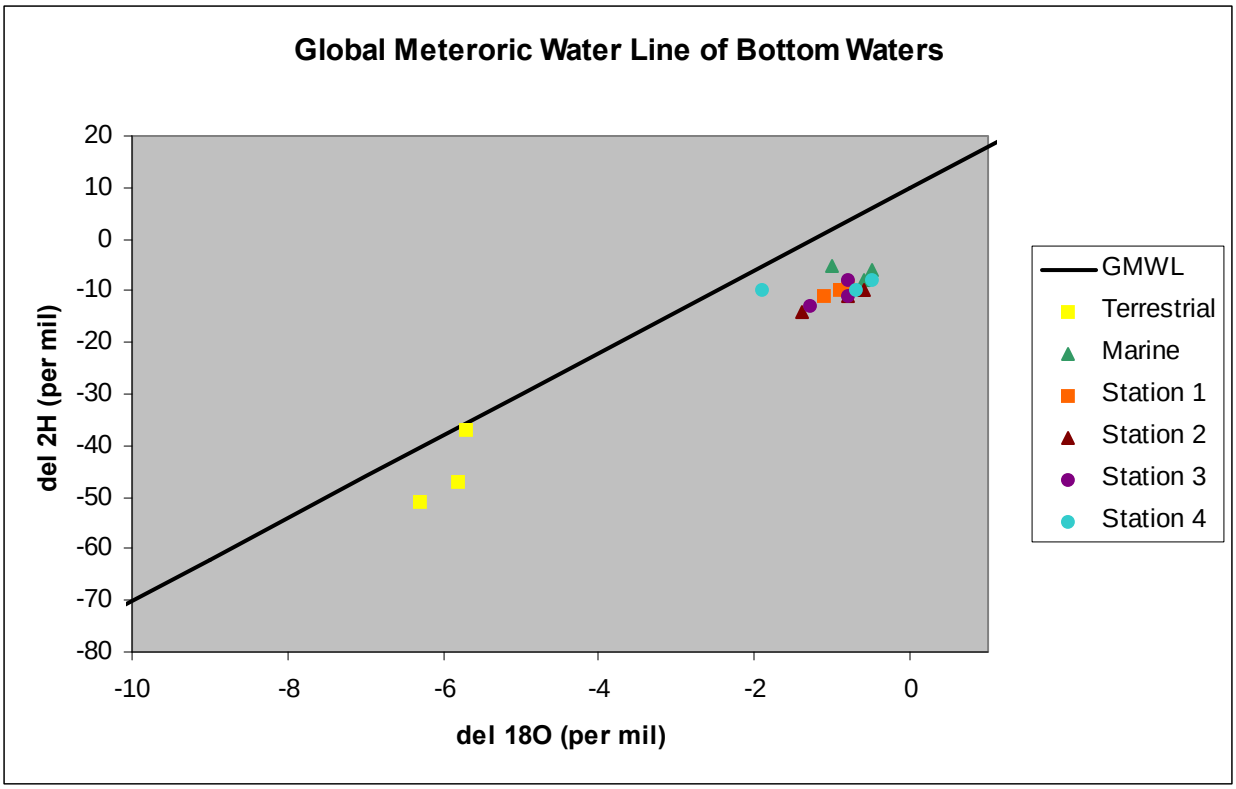

Figure 6.47. Isotopic signature of bottom water plotted along Global Meteoric Water Line.

APPENDIX 6A:

DEPTH PROFILES FOR INDEX PARAMETERS IN UPPER NEWPORT BAY

Electrical Conductivity, Dissolved Oxygen, Percentage of Dissolved Oxygen, and Temperature of Water Column in Upper Newport Bay

Station	Date	Time	Depth (ft)	SC-TC (mS)	D.O. (mg/L)	D.O. %	Temp (ºC)
Terrestrial End Member (IRWD)	10/7/2007	5:30 PM	1	2.922	8.21	95.7	22.9
1 Upper	10/7/2007	1:25 PM	1	38.07	6.71	88.00	21.70
			2	42.93	7.03	98.00	21.70
			3	44.87	5.43	72.10	21.40
			4	45.74	4.90	67.20	21.40
			5	46.03	4.31	58.90	21.20
			6	46.07	4.64	61.40	21.20
			7	46.17	4.69	61.40	21.10
			8	46.24	4.70	63.40	20.90
			9	46.29	4.74	64.20	20.80
			10	46.42	4.67	62.30	20.70
			11	46.47	4.72	63.90	20.70
			12	46.48	0.02	0.20	20.70
2 Mid-Upper	10/7/2007	2:47 PM	1	42.49	7.42	104.2	22.6
			2	42.55	7.37	102.4	22.6
			3	43.18	7.33	100.2	22.2
			4	46.78	7.03	97.8	21.1
			5	46.76	5.44	74.3	20.5
			6	46.88	5.12	69.5	20.4
			7	46.87	5.13	68.7	20.4
			8	47.08	5.11	68.2	20.4
			9	46.98	5.10	67.8	20.3
			10	46.98	5.04	68.0	20.2
			11	47.1	5.06	67.7	20.2
			12	47.09	5.00	67.1	20.2
			13	47.11	4.81	65.1	20.2
			14	47.22	4.91	65.8	20.1
			15	47.2	4.87	64.6	20.1
			16	47.2	4.93	64.7	20.2
			17	47.2	4.80	66.2	20.1
			18	47.2	4.91	65.3	20.1
			19	47.2	4.68	54.0	20.1
			19.9	42.57	Tide Out	Tide Out	20.1

Electrical Conductivity, Dissolved Oxygen, Percentage of Dissolved Oxygen, and Temperature of Water Column in Upper Newport Bay Continued

Station	Date	Time	Depth (ft)	SC-TC (mS)	D.O. (mg/L)	D.O. %	Temp (ºC)
3	10/30/2007	12:00 PM	1	49.2	6.70	87.4	18.7
Mid-Lower			2	49.17	6.72	87.2	18.6
			3	49.23	6.69	86.5	18.6
			4	49.25	6.63	85.8	18.4
			5	49.3	6.53	84.3	18.3
			6	49.39	6.51	83.9	18.3
			7	49.36	6.57	84.4	18.2
			8	49.45	6.46	83.1	18.1
			9	49.45	6.46	82.9	18.1
			10	49.45	6.45	82.9	18.1
			11	49.45	6.43	82.8	18.1
			12	49.44	6.46	83.2	18.1
			13	49.45	6.46	83.5	18.1
			14	49.44	6.47	83.5	18.1
			15	49.45	6.47	83.1	18.1
			16	49.45	6.42	82.7	18.1
			17	49.45	6.33	81.5	18.1
			18	49.45	6.24	80.2	18.1
			19	49.46	6.31	81.0	18.1

Electrical Conductivity, Dissolved Oxygen, Percentage of Dissolved Oxygen, and Temperature of Water Column in Upper Newport Bay Continued

4	10/30/2007	10:20 AM	1	49.16	6.67	85.9	18.2
Lower			2	49.21	6.60	84.8	18.1
			3	49.3	6.57	84.5	18.2
			4	49.3	6.56	84.2	18.1
			5	49.28	6.55	84.2	18.1
			6	49.28	6.53	84.0	18.1
			7	49.29	6.53	84.0	18.1
			8	49.29	6.51	83.7	18.1
			9	49.39	6.53	83.8	18.1
			10	49.3	6.52	84.0	18.0
			11	49.3	6.52	83.7	18.0
			12	49.3	6.48	83.3	18.1
			13	49.4	6.50	83.5	18.0
			14	49.3	6.51	83.6	18.1
			15	49.31	6.51	83.4	18.0
			16	49.3	6.48	83.2	18.1
			17	49.41	6.48	83.1	18.1
			18	49.41	6.50	83.3	18.0
			19	49.42	6.50	83.3	18.0
			20	49.4	6.50	83.4	18.0
			21	49.38	6.51	83.6	18.0
			22	49.38	6.51	83.6	18.0
			23	49.38	6.42	82.5	18.0
			23.5	49.38	6.25	80.0	18.0

Marine End Member	10/30/2007	1:45 PM	1	49.87	7.53	97.0	18.1

Electrical Conductivity, Dissolved Oxygen, Percentage of Dissolved Oxygen, and Temperature of Water Column in Upper Newport Bay Continued

Station	Date	Time	Depth (ft)	SC-TC (mS)	D.O. (mg/L)	D.O. %	Temp (ºC)
Terrestrial End Member (IRWD)	11/6/2007	2:15 PM	1	3.102	13.29	145.6	19.4
1	11/6/2007	10:40 PM	1	39.96	4.97	64.5	19.0
Upper			2	41.24	4.52	57.8	19.0
			3	44.77	4.53	58.6	19.1
			4	45.73	4.31	56.0	19.1
			5	46.19	4.10	52.9	19.0
			6	46.38	3.70	48.1	19.0
			7	46.57	4.00	51.8	19.3
			8	46.75	3.65	47.3	19.2
			9	46.79	3.57	46.5	19.3
			10	47.01	3.19	41.4	19.4
			11	47.15	3.29	42.6	19.3
			12	47.16	0.20	2.7	19.3
			13	47.16			19.3
2	11/6/2007	12:00 PM	1	37.13	6.84	88.2	18.8
Mid-Upper			2	40.12	5.87	75.8	19.1
			3	41.6	5.52	71.7	19.1
			4	44.84	5.25	68.1	19.2
			5	45.99	4.85	63.0	19.2
			6	46.24	4.48	58.1	19.3
			7	46.35	4.28	55.5	19.3
			8	46.38	4.23	54.8	19.3
			9	46.43	3.98	51.6	19.3
			10	46.47	3.96	51.4	19.3
			11	46.48	3.87	50.1	19.3
			12	46.5	3.87	50.2	19.3
			13	46.49	3.82	49.6	19.3
			14	46.51	3.82	49.6	19.3
			15	46.54	3.77	48.9	19.3
			16	46.54	3.76	48.9	19.3
			17	46.56	3.74	48.6	19.3
			18	46.58	3.76	48.8	19.3
			19	46.58	3.53	45.8	19.3

Electrical Conductivity, Dissolved Oxygen, Percentage of Dissolved Oxygen, and Temperature of Water Column in Upper Newport Bay Continued

Station	Date	Time	Depth (ft)	SC-TC (mS)	D.O. (mg/L)	D.O. %	Temp (ºC)
3	11/20/2007	10:10 AM	1	40.5	5.75	71.8	17.0
Mid-Lower			2	42.49	5.52	69.0	17.3
			3	43.74	5.58	69.7	17.5
			4	44.09	5.60	70.0	17.5
			5	44.32	5.38	67.7	17.5
			6	45.49	5.23	66.1	17.7
			7	45.9	5.27	66.4	17.8
			8	47.15	5.27	66.4	17.8
			9	47.35	5.40	68.1	17.8
			10	47.4	5.41	68.1	17.8
			11	47.57	5.43	68.3	17.8
			12	47.65	5.42	68.2	17.7
			13	47.73	5.41	68.1	17.7
			14	47.74	5.44	68.5	17.7
			15	47.72	5.45	68.6	17.7
			16	47.73	5.35	67.3	17.7
4	11/20/2007	11:40 AM	1	42.83	6.13	77.2	17.3
Lower			2	43.05	5.90	74.5	17.3
			3	44.21	5.79	73.0	17.5
			4	44.67	5.65	71.3	17.5
			5	46.52	5.58	70.6	17.7
			6	47.1	5.54	70.2	17.7
			7	47.35	5.54	70.1	17.7
			8	47.41	5.50	69.6	17.7
			9	47.45	5.47	69.2	17.7
			10	47.47	5.45	69.0	17.7
			11	47.5	5.42	68.5	17.7
			12	47.51	5.39	68.4	17.7
			13	47.52	5.36	67.8	17.7
			14	47.52	5.32	66.2	17.7
			14.5	47.51			17.7
Marine End Member	11/20/2007	2:45 PM	1	48.8	6.76	84.5	16.7

Electrical Conductivity, Dissolved Oxygen, Percentage of Dissolved Oxygen, and Temperature of Water Column in Upper Newport Bay Continued

Station	Date	Time	Depth (ft)	SC-TC (mS)	D.O. (mg/L)	D.O. %	Temp (ºC)
Terrestrial End Member (at 73)	12/19/2007	9:45 AM	1	0.724	8.85	87.3	14.9
1 Upper	12/19/2007	12:30 PM	1	8.37	7.83	82.0	14.7
			2	14.15	7.50	79.1	14.7
			3	17.3	7.39	77.6	14.7
			4	20.58	7.31	76.5	14.6
			5	24.36	6.83	71.9	14.6
			6	42.4	6.90	81.5	14.8
			7	44.91	6.19	73.1	14.8
			8	45.11	5.56	65.7	14.7
			9	45.44	0.29	3.5	14.7
			9.3	45.04	Tide out	Tide out	14.8
2 Mid-upper	12/19/2007	11:00 AM	1	17.06	7.90	83.6	15.1
			2	20.67	7.39	79.5	14.8
			3	25.16	7.17	77.2	14.7
			4	32.61	6.59	75.7	14.7
			5	41.62	6.36	73.2	14.7
			6	43.23	6.33	72.6	14.7
			7	43.31	0.42	5.0	14.7
			7.5	43.31	Tide out	Tide out	14.7

Electrical Conductivity, Dissolved Oxygen, Percentage of Dissolved Oxygen, and Temperature of Water Column in Upper Newport Bay Continued

Station	Date	Time	Depth (ft)	SC-TC (mS)	D.O. (mg/L)	D.O. %	Temp (ºC)
3	12/20/2007	11:00 AM	1	24.19	6.70	76.4	15.0
Mid-Lower			2	26.6	6.08	69.2	14.8
			3	29.57	5.97	67.9	14.7
			4	31.52	5.97	67.7	14.8
			5	35.45	5.99	68.0	14.8
			6	39.61	6.09	69.0	14.8
			7	39.92	6.18	70.0	14.8
			8	40.52	6.25	70.8	14.8
			9	41.33	6.66	75.4	14.8
			10	41.59	6.81	77.1	14.8
			11	43.84	6.87	77.7	14.7
			12	44.04	6.93	78.5	14.7
			13	44.23	6.86	77.9	14.7
			14	44.36	6.64	74.9	14.7
			15	44.37	Tide out	Tide out	14.7
			15.9	44.4	Tide out	Tide out	14.7
Back Bay Channel	12/20/2007	12:00 PM	1	34.57	7.64	87.3	15.3
			2	35.54	0.29	0.4	15.0
4	12/20/2007	1:00 PM	1	30.6	7.22	83.9	15.7
Lower			2	30.73	6.99	81.1	15.6
			3	31.95	6.65	76.3	15.6
			4	36	6.44	73.6	15.3
			5	37.93	6.42	73.3	15.1
			6	38.6	6.38	72.9	15.0
			7	38.89	6.39	73.0	14.9
			8	39.99	6.34	72.3	14.8
			9	40.71	6.22	70.8	14.8
			10	40.76	6.23	70.8	14.8
			11	40.87	6.16	70.1	14.8
			12	41.29	6.11	69.4	14.8
			13	41.28	6.12	69.8	14.8
			14	41.5	6.09	69.4	14.8
			15	41.43	3.40	38.8	14.8
			15.25	41.41	Tide out	Tide out	14.8
Marine End Member	12/20/2007	4:00 PM	1	46.1	7.47	88.9	15.0

Electrical Conductivity, Dissolved Oxygen, Percentage of Dissolved Oxygen, and Temperature of Water Column in Upper Newport Bay Continued

Station	Date	Time	Depth (ft)	SC-TC (mS)	D.O. (mg/L)	D.O. %	Temp (ºC)
Terrestrial End Member (at 73)	1/17/2008	9:45 AM	1	18.68	10.03	96.5	11.1
1	1/17/2008	10:50 AM	1	38.61	6.99	78.8	13.0
Upper			2	40.84	7.02	78.5	12.9
			3	41.68	7.64	85.6	12.7
			4	42.25	7.61	85.5	12.8
			5	42.88	7.38	83.0	13.1
			6	43.03	6.69	75.7	13.2
			7	43.35	6.74	76.4	13.3
			8	43.49	6.60	74.7	13.3
			9	43.57	6.46	73.2	13.3
			10	43.66	0.45	5.2	13.3
			10.2	43.51	Tide out	Tide out	13.3
2	1/17/2008	12:50 PM	1	40.34	7.84	89.4	13.9
Mid-upper			2	40.47	7.76	88.4	13.6
			3	40.73	7.71	87.0	13.6
			4	41.31	7.39	82.4	13.2
			5	41.88	7.18	80.0	12.8
			6	42.12	7.07	78.7	12.7
			7	42.42	7.08	78.9	12.7
			8	42.51	7.05	78.5	12.7
			9	42.6	7.04	78.5	12.7
			10	42.76	7.05	78.6	12.7
			11	42.68	7.07	78.8	12.7
			12	42.72	7.09	79.2	12.7
			13	42.73	7.08	78.8	12.6
			14	42.82	7.06	79.3	12.7
			15	42.96	7.01	78.3	12.7
			16	43.57	6.99	78.1	12.8
			17	43.62	7.03	78.9	12.8
			18	43.74	6.96	78.1	12.9
			19	43.78	0.48	5.6	12.9
			20	43.65	Tide out	Tide out	12.9
			21	38.91	Tide out	Tide out	12.9
			21.5	33.97	Tide out	Tide out	13.2

Electrical Conductivity, Dissolved Oxygen, Percentage of Dissolved Oxygen, and Temperature of Water Column in Upper Newport Bay Continued

Station	Date	Time	Depth (ft)	SC-TC (mS)	D.O. (mg/L)	D.O. %	Temp (ºC)
3	1/25/2008	10:30 AM	1	14.92	8.45	92.9	12.5
Mid-Lower			2	242.1	8.22	91.1	12.6
			3	32.82	8.07	89.1	12.7
			4	36.42	7.98	88.0	12.8
			5	36.43	7.98	88.2	12.8
			6	36.75	7.98	88.3	12.8
			7	41.06	7.93	87.7	12.8
			8	43.32	8.01	88.7	12.8
			9	43.43	7.97	88.2	12.9
			10	43.65	7.92	87.7	12.9
			11	43.71	7.88	87.4	12.9
			12	43.86	7.79	86.5	12.9
			13	44.04	0.38	4.3	12.9
			13.5	43.9	Tide out	Tide out	12.9
4	1/25/2008	11:55 AM	1	19.81	8.64	96.8	13.0
Lower			2	20.62	8.66	96.8	12.9
			3	31.71	8.57	95.2	12.7
			4	34.28	8.42	93.8	12.7
			5	40.09	8.37	93.3	12.8
			6	41.14	8.32	92.8	12.8
			7	41.3	8.27	92.1	12.9
			8	43.69	8.24	91.8	12.9
			9	44.11	8.18	91.1	12.9
			10	44.43	8.14	90.8	12.9
			11	44.24	8.14	90.7	12.9
			12	44.06	8.08	90.2	12.9
			13	44.13	8.07	90.0	12.9
			14	44.25	8.06	89.8	12.9
			15	44.28	7.84	87.1	12.9
			15.5	44.04	Tide out	Tide out	12.9
Marine End Member	1/25/2008	1:15 PM	1	41.15	8.76	98.8	13.5

Electrical Conductivity, Dissolved Oxygen, Percentage of Dissolved Oxygen, and Temperature of Water Column in Upper Newport Bay Continued

Station	Date	Time	Depth (ft)	SC-TC (mS)	D.O. (mg/L)	D.O. %	Temp (ºC)
Terrestrial End Member (at 73)	2/14/2008	9:40 AM	1	5.92	10.52	104.2	14.2
1	2/14/2008	10:30 AM	1	28.72	7.78	91.4	14.6
Upper			2	35.17	7.10	83.4	14.9
			3	41.99	6.83	80.1	15.1
			4	42.84	6.70	79.1	15.3
			5	43.23	6.74	79.2	15.3
			6	43.72	6.70	79.8	15.2
			7	43.91	6.52	76.9	15.1
			8	43.95	6.17	72.6	15.1
			9	44.16	1.81	21.4	15.1
			9.5	44.19	Tide out	Tide out	15.1
2	2/14/2008	11:45 AM	1	38.9	7.22	84.3	14.7
Mid-upper			2	37.98	7.08	82.2	14.7
			3	39.27	6.98	81.2	14.8
			4	40.14	6.94	81.0	14.8
			5	40.9	6.97	81.2	14.9
			6	41.26	6.87	80.3	14.9
			7	41.62	6.88	80.3	14.9
			8	41.74	6.90	80.5	14.9
			9	41.9	6.86	80.1	14.9
			10	42.22	6.90	80.6	15.0
			11	42.68	6.87	80.4	15.0
			12	43.24	6.88	80.6	15.0
			13	43.24	6.03	70.5	15.0
			13.5	43.3	Tide out	Tide out	15.0

Electrical Conductivity, Dissolved Oxygen, Percentage of Dissolved Oxygen, and Temperature of Water Column in Upper Newport Bay Continued

Station	Date	Time	Depth (ft)	SC-TC (mS)	D.O. (mg/L)	D.O. %	Temp (ºC)
3	2/29/2008	11:25 AM	1	28.4	6.73	80.2	16.1
Mid-Lower			2	32.27	6.59	78.8	16.2
			3	35.65	6.41	76.6	16.2
			4	37.61	6.46	76.9	16.0
			5	39.27	6.45	76.5	15.8
			6	41.42	6.45	76.0	15.5
			7	43.09	6.42	75.2	15.3
			8	45.22	6.41	74.9	15.1
			9	46.46	6.35	73.8	15.0
			10	46.93	6.46	75.0	14.9
			11	47.34	6.43	74.9	14.9
			12	47.81	6.42	74.5	14.9
			13	48.07	6.33	73.6	14.8
			14	48.15	6.18	72.0	14.8
			15	48.27	5.96	69.6	14.8
			15.25	Tide in	5.10	59.3	Tide in
4	2/29/2008	12:30 PM	1	30.79	6.86	83.3	16.3
Lower			2	32.43	6.61	80.2	16.4
			3	36.49	6.56	79.3	16.3
			4	38.41	6.42	77.2	16.0
			5	41.2	6.40	76.4	15.7
			6	43.02	6.44	76.5	15.4
			7	44.49	6.40	76.0	15.2
			8	44.68	6.41	75.8	15.2
			9	46.21	6.28	74.1	15.1
			10	47.6	6.34	74.6	14.9
			11	48.27	6.25	73.6	14.9
			12	48.6	5.76	67.8	14.8
			12.25	48.59	0.77	9.1	14.8
Marine End Member	2/29/2008	2:00 PM	1	39.14	7.37	87.3	16.1

Electrical Conductivity, Dissolved Oxygen, Percentage of Dissolved Oxygen, and Temperature of Water Column in Upper Newport Bay Continued

Station	Date	Time	Depth (ft)	SC-TC (mS)	D.O. (mg/L)	D.O. %	Temp (ºC)
Terrestrial End Member (at 73)	3/12/2008	1:15 PM	1	5.99	12.29	133.2	18.8
1	3/12/2008	10:45 AM	1	30.38	7.18	90.7	18.2
Upper			2	39.2	6.85	87.2	18.5
			3	42.31	6.77	85.8	18.5
			4	45.17	6.96	87.9	18.2
			5	45.85	6.80	85.5	18.0
			6	46.46	6.46	81.0	17.7
			7	46.52	6.29	78.7	17.6
			8	46.7	6.23	77.8	17.5
			9	46.72	5.83	72.3	17.5
			9.5	46.72	3.14	39.4	17.5
2	3/12/2008	11:45 AM	1	36.88	7.32	93.4	18.1
Mid-upper			2	39.32	7.11	89.9	18.1
			3	42.42	6.84	86.4	18.0
			4	44.43	6.72	84.4	17.8
			5	44.85	6.67	84.0	17.8
			6	45.47	6.73	84.6	17.8
			7	46.35	6.78	85.1	17.6
			8	46.56	6.79	85.2	17.6
			9	46.68	6.77	85.0	17.5
			10	46.76	6.68	83.7	17.5
			11	46.87	6.71	84.4	17.5
			12	47.2	6.65	83.2	17.4
			13	47.19	6.65	83.2	17.4
			14	47.37	6.69	83.8	17.3
			15	47.44	6.68	83.6	17.3
			16	47.42	6.64	83.0	17.3
			17	47.44	6.58	82.4	17.3
			18	47.51	6.53	81.6	17.3
			19	47.68	6.59	82.3	17.2
			20	47.68	6.56	81.9	17.2
			21	47.66	0.91	11.5	17.2

Electrical Conductivity, Dissolved Oxygen, Percentage of Dissolved Oxygen, and Temperature of Water Column in Upper Newport Bay Continued

Station	Date	Time	Depth (ft)	SC-TC (mS)	D.O. (mg/L)	D.O. %	Temp (ºC)
3	3/19/2008	11:00 AM	1	43.98	7.88	98.2	17.2
Mid-Lower			2	44.63	7.90	98.3	17.1
			3	44.64	7.89	98.2	17.0
			4	44.77	7.91	98.1	17.0
			5	44.84	7.90	98.0	16.9
			6	45.26	7.87	97.4	16.9
			7	45.21	7.45	91.3	16.6
			8	46.73	7.28	89.0	16.4
			9	48.15	7.26	88.8	16.3
			10	48.13	7.16	87.7	16.3
			11	48.13	7.09	86.6	16.3
			12	48.12	3.89	47.8	16.3
			12.5	48.23	Tide out	Tide out	16.3
Back Bay Channel	3/19/2008	11:45 AM	1	46.18	7.98	99.5	17.1
4	3/19/2008	12:30 PM	1	45.94	7.89	98.9	17.6
Lower			2	46.13	7.90	99.1	17.4
			3	46.29	7.92	99.6	17.3
			4	46.49	7.93	98.9	17.2
			5	46.31	7.96	98.9	17.3
			6	46.27	7.96	99.7	17.3
			7	46.33	7.96	99.4	17.3
			8	46.41	7.95	99.2	17.2
			9	46.29	7.96	99.4	17.3
			10	46.4	7.93	99.1	17.3
			11	46.86	7.87	98.1	17.1
			12	46.97	7.85	97.8	17.0
			13	46.99	7.81	97.3	16.9
			14	46.99	7.73	96.2	16.9
			15	46.99	Tide out	Tide out	16.9
			15.5	47	Tide out	Tide out	16.9
Marine End Member	3/19/2008	2:00 PM	1	47.55	7.63	94.8	17.0

APPENDIX 6B

WATER QUALITY (NITRATE AND SELENIUM) IN UPPER NEWPORT BAY

Total and Dissolved Selenium, and Total Nitrate
at Top and Bottom of the Water Column in Upper Newport Bay

Location	Date	Station	Depth (ft)	Diss. Se (µg/L)	Total Se (µg/L)	NO3 (mg/L)
Slab Sample at IRWD	10/7/2007	T.E.M.	0.5	21.08	21.33	43.55
Slab Sample at IRWD	11/6/2007	T.E.M.	0.5	22.15	22.59	44.39
Slab Sample at 73	12/19/2007	T.E.M.	0.5	3.00	2.72	12.97
Slab Sample at 73	1/17/2008	T.E.M.	0.5	9.34	9.24	21.25
Slab Sample at 73	2/14/2008	T.E.M.	0.5	11.96	12.27	26.88
Slab Sample at 73	3/12/2008	T.E.M.	0.5	13.83	14.06	19.34

Location	Date	Station	Depth (ft)	Diss. Se (µg/L)	Total Se (µg/L)	NO3 (mg/L)
Newport Bay Station 1- Top	10/7/2007	1	1	6.46	6.27	9.00
Newport Bay Station 1 - Bottom	10/7/2007	1	12	2.16	2.95	1.42
Newport Bay Station 2 - Top	10/7/2007	2	1	3.24	2.95	3.84
Newport Bay Station 2 - Bottom	10/7/2007	2	19	1.86	1.93	1.26
Newport Bay Station 3 - Top	10/30/2007	3	1	0.54	0.31	0.72
Newport Bay Station 3 - Bottom	10/30/2007	3	19	0.39	0.59	0.60
Newport Bay Station 4 - Top	10/30/2007	4	1	1.01	0.95	0.47
Newport Bay Station 4 - Bottom	10/30/2007	4	23.5	0.51	0.28	0.48
Newport Bay Station 1- Top	11/6/2007	1	1	5.35	5.18	9.48
Newport Bay Station 1 - Bottom	11/6/2007	1	13	1.41	1.83	1.57
Newport Bay Station 2 - Top	11/6/2007	2	1	6.45	5.83	8.84
Newport Bay Station 2 - Bottom	11/6/2007	2	19	2.16	2.57	2.05
Newport Bay Station 3 - Top	11/20/2007	3	1	4.25	4.28	6.50
Newport Bay Station 3 - Bottom	11/20/2007	3	14.5	1.55	1.8	1.69
Newport Bay Station 4 - Top	11/20/2007	4	1	3.70	3.55	4.74
Newport Bay Station 4 - Bottom	11/20/2007	4	16	1.8	1.46	1.72
Newport Bay Station 1- Top	12/19/2007	1	1	2.45	2.43	11.60
Newport Bay Station 1 - Bottom	12/19/2007	1	9.3	1.04	1.04	1.60
Newport Bay Station 2 - Top	12/19/2007	2	1	3.29	3.21	10.60
Newport Bay Station 2 - Bottom	12/19/2007	2	7.5	1.47	1.67	2.32
Newport Bay Station 3 - Top	12/20/2007	3	1	2.16	2.26	7.77
Newport Bay Station 3 - Bottom	12/20/2007	3	15.9	1.39	1.23	2.38
Newport Bay Station 4 - Top	12/20/2007	4	1	1.90	1.98	5.60
Newport Bay Station 4 - Bottom	12/20/2007	4	15.25	1.30	1.50	2.80

Total and Dissolved Selenium, and Total Nitrate
at Top and Bottom of the Water Column in Upper Newport Bay Continued

Location	Date	Station	Depth (ft)	Diss. Se (µg/L)	Total Se (µg/L)	NO3 (mg/L)
Newport Bay Station 1 - Top	1/17/2008	1	1	4.51	4.52	9.32
Newport Bay Station 1 - Bottom	1/17/2008	1	10.2	1.54	1.62	2.20
Newport Bay Station 2 - Top	1/17/2008	2	1	2.37	2.43	4.09
Newport Bay Station 2 - Bottom	1/17/2008	2	21.5	1.56	2.23	2.27
Newport Bay Station 3 - Top	1/25/2008	3	1	1.78	1.46	6.42
Newport Bay Station 3 - Bottom	1/25/2008	3	13.5	0.81	0.66	1.70
Newport Bay Station 4 - Top	1/25/2008	4	1	1.55	1.59	5.67
Newport Bay Station 4 - Bottom	1/25/2008	4	15.25	0.76	0.78	1.13
Newport Bay Station 1- Top	2/14/2008	1	1	7.1	7.73	15.42
Newport Bay Station 1 - Bottom	2/14/2008	1	9.5	1.69	1.53	1.94
Newport Bay Station 2 - Top	2/14/2008	2	1	2.48	2.51	4.17
Newport Bay Station 2 - Bottom	2/14/2008	2	13.5	1.92	2.01	2.74
Newport Bay Station 3 - Top	2/29/2008	3	1	3.17	2.79	5.36
Newport Bay Station 3 - Bottom	2/29/2008	3	15.25	0.57	0.83	0.49
Newport Bay Station 4 - Top	2/29/2008	4	1	2.6	2.23	4.31
Newport Bay Station 4 - Bottom	2/29/2008	4	12.25	0.57	0.5	0.61
Newport Bay Station 1- Top	3/12/2008	1	1	8.53	8.4	10.75
Newport Bay Station 1 - Bottom	3/12/2008	1	9.5	1.45	1.11	1.06
Newport Bay Station 2 - Top	3/12/2008	2	1	4.94	4.62	5.42
Newport Bay Station 2 - Bottom	3/12/2008	2	20.9	1.3	1.56	0.71
Newport Bay Station 3 - Top	3/19/2008	3	1	2.37	2.34	1.93
Newport Bay Station 3 - Bottom	3/19/2008	3	12.25	1.38	1.65	0.81
Newport Bay Station 4 - Top	3/19/2008	4	1	1.97	1.96	1.24
Newport Bay Station 4 - Bottom	3/19/2008	4	15.5	1.77	1.73	1.19
Newport Bay Back Bay Channel	12/20/2007	3.5	0.5	1.76	1.82	4.91
Newport Bay Back Bay Channel	3/19/2008	3.5	0.5	2.03	1.91	1.33

Location	Date	Station	Depth (ft)	Diss. Se (µg/L)	Total Se (µg/L)	NO3 (mg/L)
PCH Grab Sample	10/30/2007	M.E.M.	0.5	0.73	0.64	0.39
PCH Grab Sample	11/20/2007	M.E.M.	0.5	1.41	1.11	0.96
PCH Grab Sample	12/20/2007	M.E.M.	0.5	0.75	0.67	1.32
PCH Grab Sample	1/25/2008	M.E.M.	0.5	1.00	1.10	2.02
PCH Grab Sample	2/29/2008	M.E.M.	0.5	1.3	1.28	1.61
PCH Grab Sample	3/19/2008	M.E.M.	0.5	1.97	2.04	0.84

APPENDIC 6C

SULFATE AND CHLORIDE IN UPPER NEWPORT BAY

Chloride and Sulfate Values for Top and Bottom of the Water Column in Upper Newport Bay			
Location	**Date**	**Cl (mg/L)**	**SO4 (mg/L)**
Slab Sample at IRWD	10/7/2007	326.91	814.57
Newport Bay Station 1- Top	10/7/2007	12593.45	1938.99
Newport Bay Station 1- Bottom	10/7/2007	17741.63	2466.25
Newport Bay Station 2 - Top	10/7/2007	15887.32	2283.77
Newport Bay Station 2 Bottom	10/7/2007	17772.23	2471.48
Newport Bay Station 3 - Top	10/31/2007	19082.46	2568.55
Newport Bay Station 3 - Bottom	10/31/2007	19251.70	2653.85
Newport Bay Station 4 - Top	10/30/2007	18981.98	2628.09
Newport Bay Station 4 - Bottom	10/31/2007	19170.02	2643.69
PCH Grab Sample	10/31/2007	19383.00	2681.78
Slab Sample at IRWD	11/6/2007	337.27	950.89
Newport Bay Station 1- Top	11/6/2007	13667.85	2076.39
Newport Bay Station 1- Bottom	11/6/2007	17945.63	2493.58
Newport Bay Station 2 - Top	11/6/2007	13843.13	2061.32
Newport Bay Station 2 Bottom	11/6/2007	17977.26	2466.81
Newport Bay Station 3 - Top	11/20/2007	15301.67	2246.39
Newport Bay Station 3 - Bottom	11/20/2007	18156.63	2525.92
Newport Bay Station 4 - Top	11/20/2007	16257.20	2328.77
Newport Bay Station 4 - Bottom	11/20/2007	18478.98	2527.43
PCH Grab Sample	11/20/2007	19111.49	2599.36
Slab Sample at 73	12/19/2007	100.88	133.50
Newport Bay Station 1- Top	12/19/2007	2396.01	457.17
Newport Bay Station 1- Bottom	12/19/2007	16712.12	2352.00
Newport Bay Station 2 - Top	12/19/2007	6246.71	984.09
Newport Bay Station 2 Bottom	12/19/2007	15501.55	2242.59
Newport Bay Station 3 - Top	12/20/2007	8665.55	1268.01
Newport Bay Station 3 - Bottom	12/20/2007	15854.42	2235.33
Newport Bay Back Bay Channel	12/20/2007	11932.26	1718.24
Newport Bay Station 4 - Top	12/20/2007	10784.73	1587.59
Newport Bay Station 4 - Bottom	12/20/2007	15605.57	2188.90
PCH Grab Sample	12/20/2007	17334.18	2426.87

Chloride and Sulfate Values for Top and Bottom of the Water Column in Upper Newport Bay Continued

Location	Date	Cl (mg/L)	SO4 (mg/L)
Slab Sample at 73	1/17/2008	6176.73	1202.56
Newport Bay Station 1- Top	1/17/2008	12093.96	1792.73
Newport Bay Station 1- Bottom	1/17/2008	16183.85	2223.11
Newport Bay Station 2 - Top	1/17/2008	14814.12	2077.89
Newport Bay Station 2 Bottom	1/17/2008	16375.58	2238.83
Newport Bay Station 3 - Top	1/25/2008	5112.62	758.59
Newport Bay Station 3 - Bottom	1/25/2008	16027.77	2148.75
Newport Bay Station 4 - Top	1/25/2008	6671.37	954.46
Newport Bay Station 4 - Bottom	1/25/2008	16933.69	2305.95
PCH Grab Sample	1/25/2008	15778.69	2056.52
Slab Sample at 73	2/14/2008	1478.05	673.01
Newport Bay Station 1- Top	2/14/2008	6962.57	1200.33
Newport Bay Station 1- Bottom	2/14/2008	15591.50	2191.78
Newport Bay Station 2 - Top	2/14/2008	14188.27	2026.43
Newport Bay Station 2 Bottom	2/14/2008	15210.50	2146.10
Newport Bay Station 3 - Top	2/29/2008	10413.83	1517.49
Newport Bay Station 3 - Bottom	2/29/2008	17971.28	2432.18
Newport Bay Station 4 - Top	2/29/2008	10664.36	1536.33
Newport Bay Station 4 - Bottom	2/29/2008	17805.49	2391.31
PCH Grab Sample	2/29/2008	14427.26	1979.14
Slab Sample at 73	3/12/2008	1365.49	741.58
Newport Bay Station 1- Top	3/12/2008	7566.55	1334.47
Newport Bay Station 1- Bottom	3/12/2008	16541.90	2332.73
Newport Bay Station 2 - Top	3/12/2008	11910.56	1853.14
Newport Bay Station 2 Bottom	3/12/2008	16998.85	2390.17
Newport Bay Station 3 - Top	3/19/2008	16003.80	2276.75
Newport Bay Station 3 - Bottom	3/19/2008	17691.85	2448.32
Newport Bay Back Bay Channel	3/19/2008	17084.18	2338.38
Newport Bay Station 4 - Top	3/19/2008	16972.49	2349.86
Newport Bay Station 4 - Bottom	3/19/2008	16868.59	2348.89
PCH Grab Sample	3/19/2008	17378.24	2393.40

Chapter 7

Nitrate and Selenium in Ephemeral Flows in Upstream Sediment Basins: San Diego Creek Watershed

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1 May 2008

Prepared for
Santa Ana Regional Water Quality Control Board

by

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INTRODUCTION

In order to characterize upstream sources of selenium and nitrate, surface waters were collected during wet weather flows in two upland canyons: Hicks Canyon Wash and Round Canyon (Figure 7.1). These ephemeral streams are dry throughout most of the year. Their physiographic position limits flow, which occurs exclusively in response to precipitation. Figure 7.1 shows the prevalent rock types outcropping along these two upland tributaries. It is thought that selenium is derived through the weathering and erosion of upland marine shales, especially those of Miocene age such as the Monterrey and Puente formations (Tracy, 1990). These formations consist of interbedded sandstones, siltstones and shales. Soil samples, assumed to have weathered from these geologic formations, were collected from the streambed in order to quantify the amount of selenium contained therein.

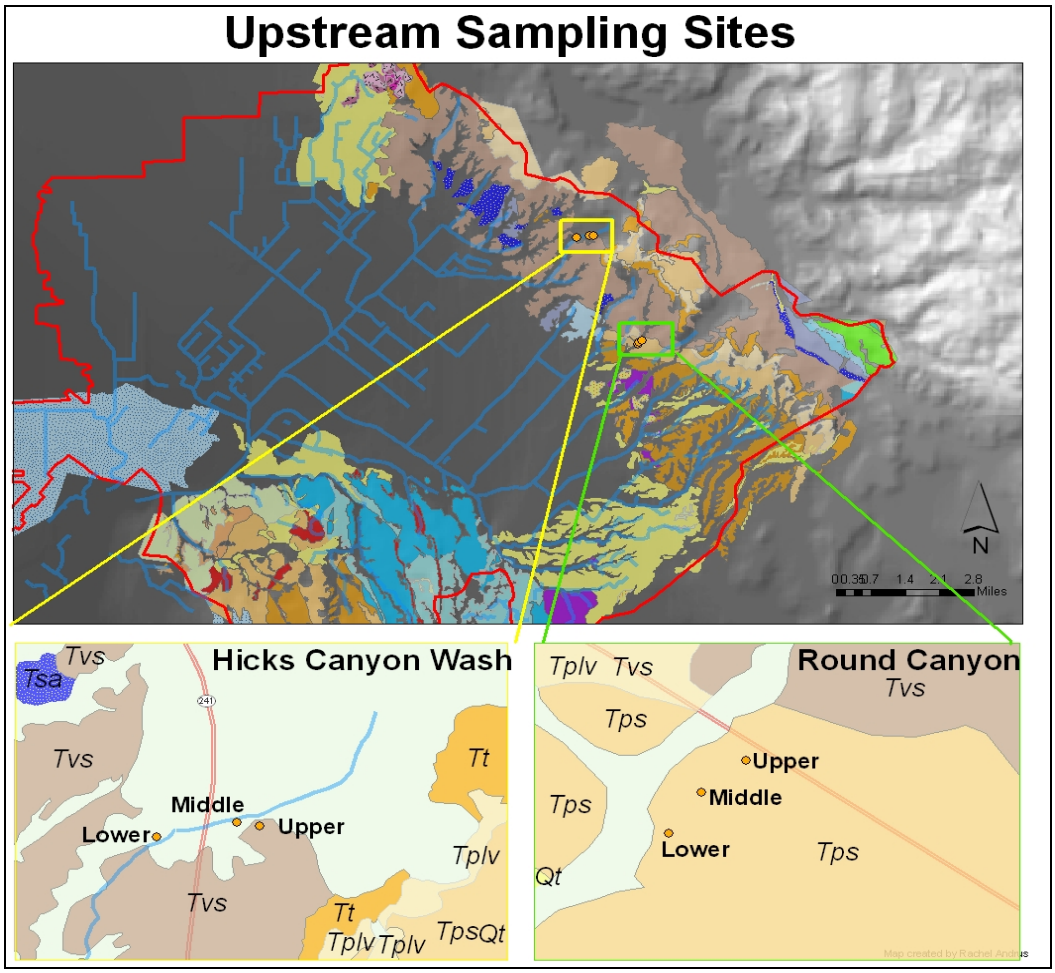

Figure 7.1. Digital Elevation Model (DEM) revealing topography of the study area with overlays of stream channels, geology, upstream sampling sites (orange points), and rain gauge stations (blue points). Insets show position of sampling sites relative to local outcrops (Tplv: La Vida Member of the Puente Formation, Tps: Sespe Member of the Puente Formation, Tsa: Santiago Formation, Tt: Topanga Formation, Tvs: Vaqueros and Sespe Formations.)

METHODS

Two upstream tributaries were selected for monitoring: Hicks Canyon Wash, which drains the northern part of the watershed and empties ultimately into Peters Canyon Wash and Round Canyon, which drains the eastern part of the watershed and empties ultimately into San Diego Creek. Field parameters were measured on site with portable pH/temperature/conductivity and dissolved oxygen meters. Surface runoff was collected every two hours at a downstream point along Hicks Canyon Wash on January 5, 2008, following intensive precipitation. Flow in Round Canyon was not observed on this date.

We were able to sample surface waters from both tributaries during the storm that occurred January 6-7, 2008 as well as collect a rainwater sample from the vicinity of Hicks Canyon. During this event, surface flows were collected every two hours from the downstream station at each tributary. These water samples were analyzed for anions and dissolved selenium. Additionally, surface flows were collected from upstream, middle and downstream stations along each tributary (Figure 7.1). These "synoptic" samples were analyzed for an expanded set of parameters, including selenium speciation. Geologic maps as well as rainfall intensity graphs aid in the interpretation of observed changes in the geochemical parameters of interest.

Additionally soil samples were collected from each streambed in December prior to wet-weather flows, but after fires had exfoliated the surrounding terrain. These soils were analyzed for total selenium and selenium speciation as well as subjected to leaching tests (modified from Black et al., 1965) in order to quantify the amount of leachable nitrate and selenium contained therein. Prior to leaching, the soils were permitted to air dry for two weeks in an area protected from dust and other air-borne particulate matter. Soils were subjected to leaching by two types of water: artificial rainwater, which was made to mimic the concentration of standard inorganic

parameters found in rainwater native to southern California; and a nitrate-rich water, which was mixed to approximate the average nitrate concentration found in the shallow aquifer. The anionic composition and initial pH of these waters is shown in Table 7.1 while Table 7.2 shows the composition of rainwater collected at Hicks Canyon for comparison. The composition of the artificial rainwater agrees reasonably well with that of actual rainwater. Two soil-water slurries were prepared for each soil by mixing 250 mL of one of the leaching agents with 125 g of dried soil in a 1000 mL HDPE bottle and shaking via wrist-action shaker for one hour. Leachate was immediately filtered after shaking and aliquots were set aside for dissolved selenium and anion analysis.

Table 7.1. Composition of Waters Used in Leaching Experiment.

Water type	Computed Composition (mg/L)						Actual anionic composition (mg/L) by IC			
	Na	Ca	K	Cl	SO_4	NO_3	pH	Cl	SO4	NO_3 as NO_3
Nitrate-rich water	0.018	ND	ND	ND	ND	50	8.62	0.061	0.0315	49.3
Artificial Rainwater	1.65	0.60	0.20	3.0	0.75	0.40	8.60	3.17	0.873	0.560

Table 7.2. Composition of Hicks Canyon Rainwater. (Collected January 6, 2008)

Time	pH	EC (µS)	Chloride (mg/L)	Sulfate (mg/L)	NO_3 as NO_3 (mg/L)	NO_3-N (mg/L)	HPO_4-P (mg/L)
11:25 PM	8.12	121.5	2.5525	0.7519	0.380	0.0859	ND

RESULTS

Results are presented in two sub-sections. The first summarizes data collected during runoff events in the upstream tributary basins over two monitoring events. Following this are the

results of soil sampling and leaching experiments from the upstream basins. The discussion section integrates these results into a holistic picture of selenium and nutrient sources in these ephemeral upland tributaries.

I. Runoff Events

Rain was minimal during the first monitoring event, which took place January 5, 2008. The hyetograph in Figure 7.2 shows that the most intense precipitation occurred just before monitoring began. It was not actively raining when sampling began at 6:30 AM. It began misting at approximately 7:00 AM, but even this light precipitation had ceased by 7:30 AM. Minor drizzling lasting no more than a few minutes occurred between 11:00 AM and 1:00 PM.

The discontinuous and insubstantial nature of precipitation resulted in continuously diminishing streamflow over the monitoring period. The greatest volume of run-off was observed along Hicks Canyon Wash. Run-off was greatest at the beginning of monitoring, diminishing continuously throughout the day. No active run-off was observed in Round Canyon. Nevertheless, numerous ponding features of depression storage were observed. Water was collected from one such pond during this monitoring event (Figure 7.3). These ponds were very shallow (< 3 inches deep) and appeared to be lined with layers of silt and clay. They appeared to form in the center of the main channel as remnants of the runoff event trapped in small depressions in the streambed. The water contained therein was very turbid possibly owing to high levels of organic matter or iron. Water quality data for this ponding feature are presented in Table 7.3.

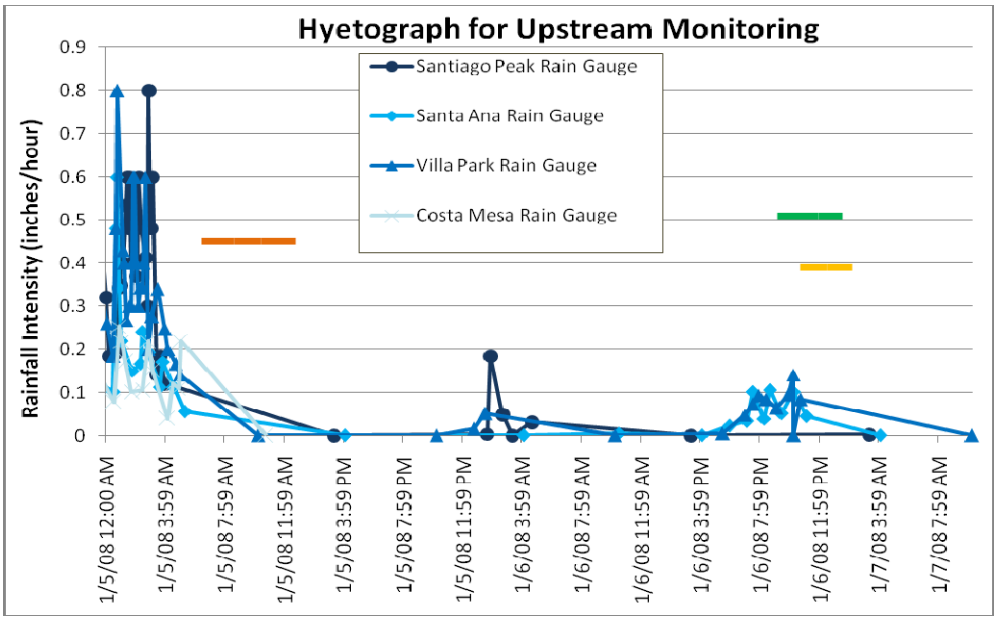

Figure 7.2. Hyetograph showing rainfall intensity between January 5, 2008 and January 7, 2008. Colored bars indicate the time frame during which monitoring took place (orange bar: January 5, Hicks Canyon; green bar January 6-7, Round Canyon; yellow bar: January 6-7, Hicks Canyon).

A.

B.

Figure 7.3. Chain of ponding features observed along Round Canyon during the January 5, 2008 monitoring event (A). Graduate student collecting water from one such pond using a syringe (B).

Table 7.3. Results from January 5, 2008 Monitoring From Round Canyon Pond.

Time	pH	D.O. (mg/L)	D.O. (%)	Temp (°C)	EC (µS)	Chloride (mg/L)	Sulfate (mg/L)	NO3-N (mg/L)	HPO4-P (mg/L)	Dissolved Se (µg/L)
12:10 PM	8.16	9.58	96.5	15.9	1273	41.754	350.191	29.974	1.108	7.339

Initially, it was possible to measure field parameters in situ at Hicks Canyon Lower, but as streamflows diminished over the course of the monitoring period, water had to be collected in a clean, triple-rinsed plastic container in order to measure field parameters. Stream discharge was not measured because attention was focused on collecting water quality data when the

opportunity to do so was available. Visual estimate of stream discharge in cubic feet per second (cfs) are shown in Table 7.4 along with water quality data. These are very rough estimates of stream discharge with a margin of error estimated at ± 30%. The value for the earliest estimate (6:30 AM) of stream discharge is the least accurate due to the difficulty of making visual estimates with negligible light.

At Hicks Canyon Lower, salinity and pH increase over the monitoring period while dissolved oxygen concentrations remain fairly constant (Table 7.4). The observed increase in salinity is reflected in increasing concentrations of chloride, nitrate and orthophosphate (Table 7.4). While nitrate and orthophosphate concentrations increased over the course of the monitoring, selenium exhibited an initial decline then increased gradually, closely mimicking the pattern exhibited by sulfate (Table 7.4).

Table 7.4. Results from January 5, 2008 Monitoring At Hicks Canyon Lower.

Time	Estimated Discharge (cfs)	pH	D.O. (mg/L)	D.O. (%)	Temp (°C)	EC (µS)	Chloride (mg/L)	Sulfate (mg/L)	NO3-N (mg/L)	HPO4-P (mg/L)	Dissolved Se (µg/L)
6:30 AM	(1.15)	7.95	10.19	97.3	13.4	462	28.627	106.641	1.675	0.619	6.975
8:40 AM	0.813	8.23	9.94	95.4	13.3	533	28.105	86.654	1.809	1.477	2.743
10:30 AM	0.542	8.25	9.79	94.6	14.1	775	41.615	125.025	2.098	2.246	4.007
12:50 PM	0.363	8.31	9.87	96.9	14.8	1076	64.497	178.429	2.355	2.960	4.704

The hyetograph in Figure 7.2 shows that rainfall intensity before and during the January 6-7 monitoring was 5 to 8 times less than the storm event that produced the January 5 runoff.

Nevertheless, rainfall was sufficient to induce active run-off in both sub-basins during the event. Precipitation was continuous during the first part of this monitoring event. It was actively drizzling when sampling began at 9:40 PM. Rainfall intensity increased at approximately 11:05 PM for about 20 minutes, after which it began to decline again. By 11:45 PM it was no longer raining. As precipitation tapered off over the course of the monitoring period, streamflows diminished. This decline in discharge was especially dramatic along Round Canyon, where, by the final sampling event at 1:35 AM flows had diminished to a trickle. Based on the time it took to collect enough sample to measure field parameters, flow can be estimated at approximately 200 mL/min. This equates to 0.00012 cubic feet per second. Water quality data are shown in Table 7.5 and 7.6 for Hicks Canyon Lower and Round Canyon Lower respectively. Estimates for stream discharge are not included due to the difficulty of making accurate visual estimates in the dark.

Collection of downstream samples in time series during the January 6-7 monitoring began during the period of greatest precipitation (Figure 7.2). Salinity at Hicks Canyon Lower exhibited initial values in the same range of initial values obtained during the January 5 monitoring and increased over the course of monitoring, but did not reach the values obtained toward the end of the January 5 monitoring (compare Tables 7.4 and 7.5). Similarly pH increased at Hicks Canyon Lower. Dissolved oxygen remained fairly constant for the first two hours after which no data is available due to excess silt and debris, which caused the instrument to malfunction (Table 7.5). Nutrient concentrations (nitrate and orthophosphate) showed very little variation whereas selenium decreased continuously at Hicks Canyon Lower from an initial value of 8 µg/L to 2 µg/L at the end of the monitoring period (Table 7.5). This is similar to the pattern exhibited by sulfate (Table 7.5).

Just as at Hicks Canyon Lower, salinity and pH at Round Canyon Lower increased over the course of the monitoring period (Table 7.6). Dissolved oxygen remained fairly constant for the first two hours after which no data is available due to excess silt and debris, which caused the instrument to malfunction (Table 7.6). Nutrients exhibited a dramatic increase at Round Canyon Lower, with NO_3-N and HPO_4-P rising from initial values of 0.7 mg/L and 0.5 mg/L respectively to 14 mg/L and 1.2 mg/L at the end of the monitoring. Selenium exhibited marginal variability (< 2 µg/L) over the January 6-7 monitoring at Round Canyon (Table 7.6).

Table 7.5. Results from January 6-7, 2008 Monitoring at Hicks Canyon Lower.

Time	pH	D.O. (mg/L)	D.O. (%)	Temp (°C)	EC (µS)	Chloride (mg/L)	Sulfate (mg/L)	NO3-N (mg/L)	HPO4-P (mg/L)	Dissolved Se (µg/L)
10:40PM	8.00	11.01	97.8	9.9	439	29.599	125.134	0.889	0.744	8.100
12:30 AM	8.06	10.5	96.6	11	503	29.495	94.656	1.042	0.927	2.754
2:15 AM	8.14	-	-	11.6	609	32.422	93.640	0.603	1.572	1.982

Table 7.6. Results from January 6-7, 2008 Monitoring at Round Canyon Lower.

Time	pH	D.O. (mg/L)	D.O. (%)	Temp (°C)	EC (µS)	Chloride (mg/L)	Sulfate (mg/L)	NO3-N (mg/L)	HPO4-P (mg/L)	Dissolved Se (µg/L)
9:10 PM	8.11	11.62	104.2	10.8	130.9	2.600	10.408	0.770	0.540	1.254
11:55 PM	8.16	11.14	98.8	9.9	732	52.963	112.853	8.534	1.038	2.914
1:35 AM	8.25	-	-	10.3	784	61.518	80.732	14.199	1.181	1.875

Because it was actively raining initially, discharge was much higher at both sites, which permitted the collection of Lower, Middle and Upper samples in that order from each stream reach (Figure 7.1). An expanded set of analyses was performed on these "synoptic" samples including selenium speciation. Synoptic samples were collected as near to the beginning of the storm as possible, first at Round Canyon then, roughly one hour later at Hicks Canyon. Results of the synoptic sampling reveal how water compositions evolve along the stream reach.

Along Round Canyon, electrical conductivity drops from an upstream value of ~350 µS to a downstream value of 131 µS. Chloride mimics this pattern most closely dropping from an upstream value of 23 mg/L to 2.6 mg/L at the most downstream station while sulfate drops continuously along the flowpath from 26 mg/L (Upper) to 10 mg/L (Lower). Nutrients (nitrate and orthophosphate) show an overall decline while dissolved selenium shows a marginal increase (< 1 µg/L) along the flowpath. These patterns can clearly be seen in Figures 7.4, 7.5 and 7.6. Data from synoptic sampling along Round Canyon are summarized in Table 7.7.

Table 7.7. Summary for Synoptic Sampling along Round Canyon

Location	Time	pH	D.O. (mg/L)	D.O. (%)	Temp (°C)	EC (µS)	Chloride (mg/L)	Sulfate (mg/L)	NO3-N (mg/L)	HPO4-P (mg/L)	Dissolved Se (µg/L)
Upper	9:55 PM	8.19	10.91	96.4	9.7	348.1	24.565	25.711	4.835	1.324	0.825
Middle	9:30 PM	8.15	10.92	97.5	9.9	345	22.374	19.614	4.413	1.452	0.643
Lower	9:10 PM	8.11	11.62	104.2	10.8	130.9	2.600	10.408	0.770	0.540	1.254

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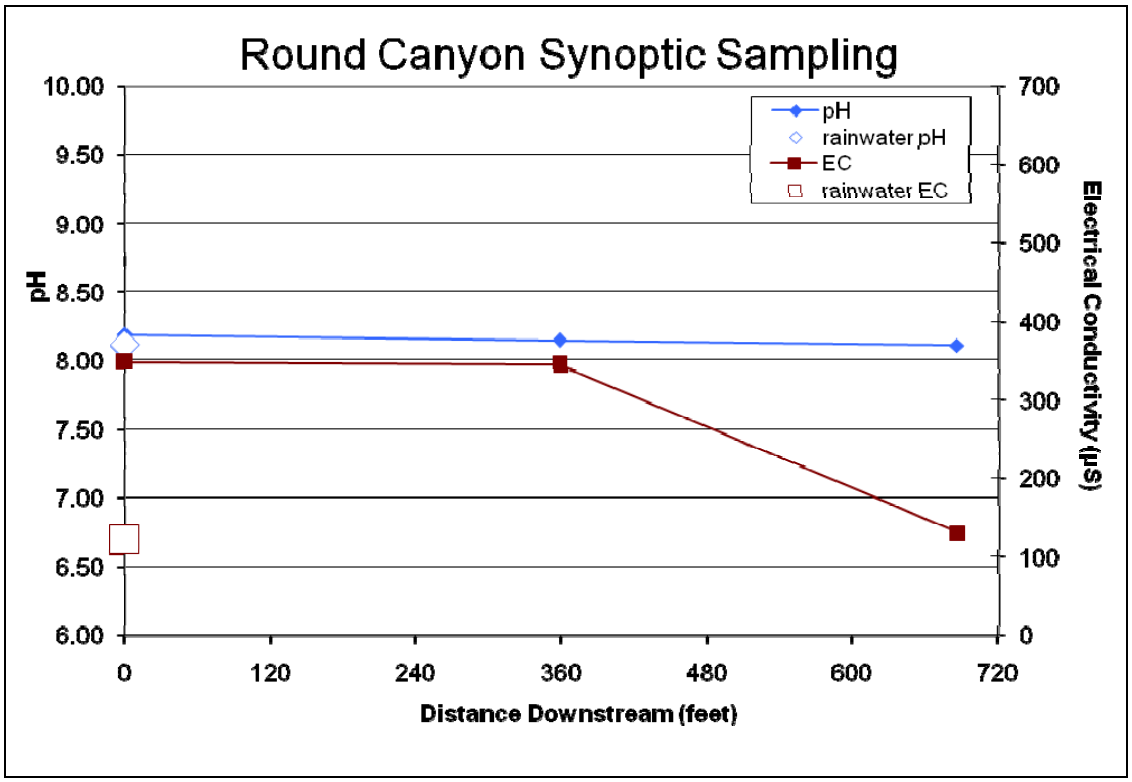

Figure 7.4. Changes in pH (blue line) and EC (red line) as waters flow from upstream to downstream along Round Canyon. Values of pH (open square) and EC (open diamond) for rainwater shown for comparison.

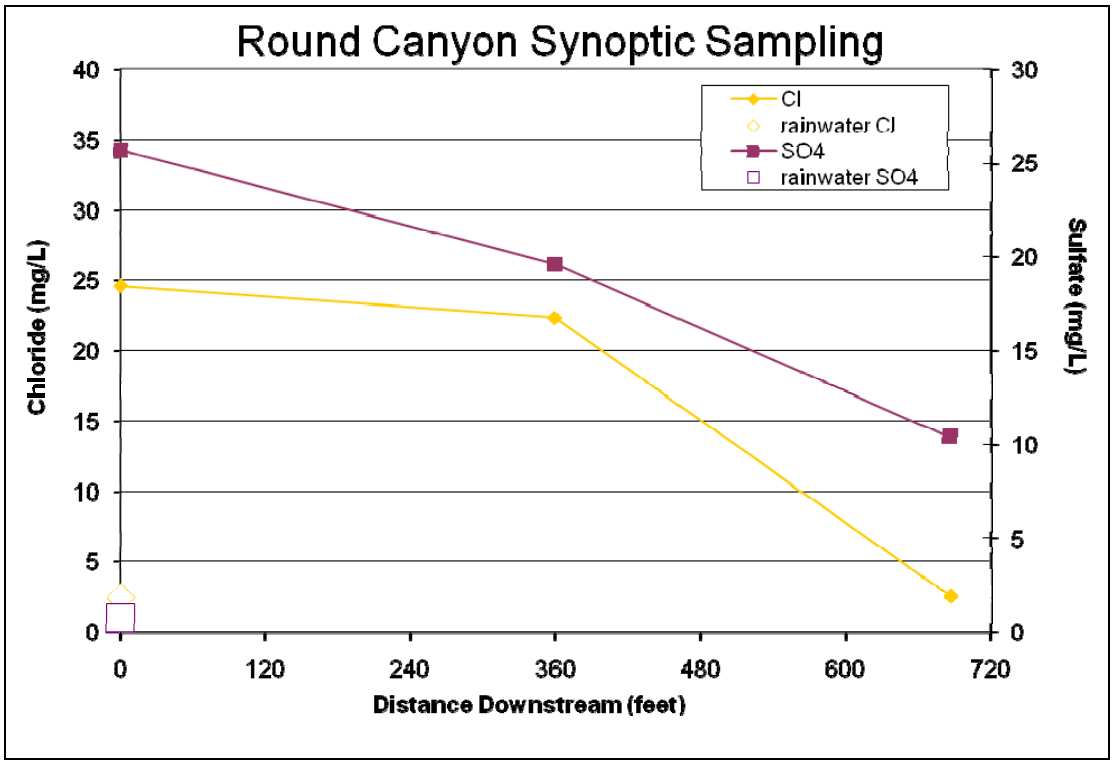

Figure 7.5. Changes in sulfate (purple line) and chloride (yellow line) as waters flow from upstream to downstream along Round Canyon. Values of sulfate (open square) and chloride (open diamond) for rainwater shown for comparison.

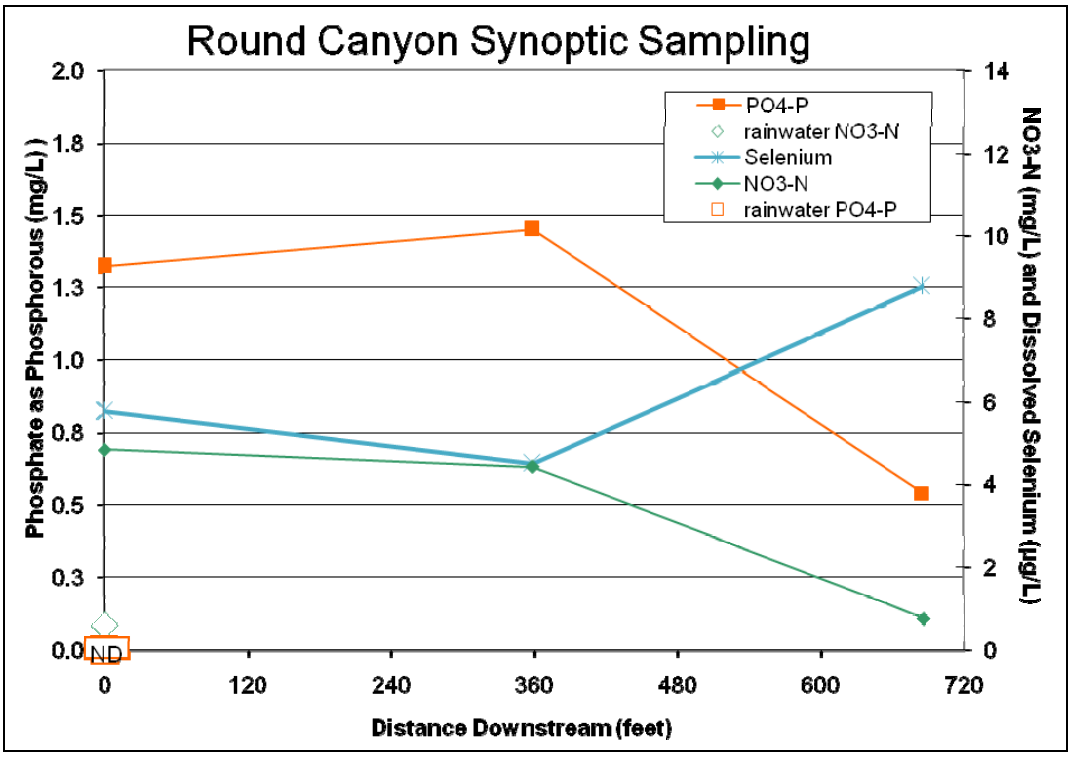

Figure 7.6. Changes in HPO_4-P (orange line), NO_3-N (green line) and dissolved selenium (blue line) as waters flow from upstream to downstream along Round Canyon. Values of HPO_4-P (open square) and NO_3-N (open diamond) for rainwater shown for comparison.

Along Hicks Canyon, electrical conductivity drops continuously from upstream (672 µS) to downstream (439 µS). Sulfate closely mimics this pattern dropping from 238 mg/L to 125 mg/L while chloride increases initially from upstream (16 mg/L) then remains steady at ~30 mg/L along the downstream reach. Nutrients (nitrate and orthophosphate) exhibit very little variability along the length of the flowpath (<0.4 mg/L). Dissolved selenium declines marginally but steadily from an upstream value of 13.3 µg/L to a downstream value of 8.1 µg/L. These patterns can clearly be seen in Figures 7.7, 7.8 and 7.9. Data from synoptic sampling along Hicks Canyon Wash are summarized in Table 7.8.

Table 7.8. Summary for Synoptic Sampling along Hicks Canyon

Location	Time	pH	D.O. (mg/L)	D.O. (%)	Temp (°C)	EC (µS)	Chloride (mg/L)	Sulfate (mg/L)	NO3-N (mg/L)	HPO4-P (mg/L)	Dissolved Se (µg/L)
Upper	11:15 PM	7.86	11.17	98.3	9.4	672	16.050	238.194	0.760	0.437	13.307
Middle	10:55 PM	8.20	11.19	97.9	9.3	627	30.463	161.507	0.819	0.780	10.296
Lower	10:40PM	8.00	11.01	97.8	9.9	439	29.599	125.134	0.889	0.744	8.100

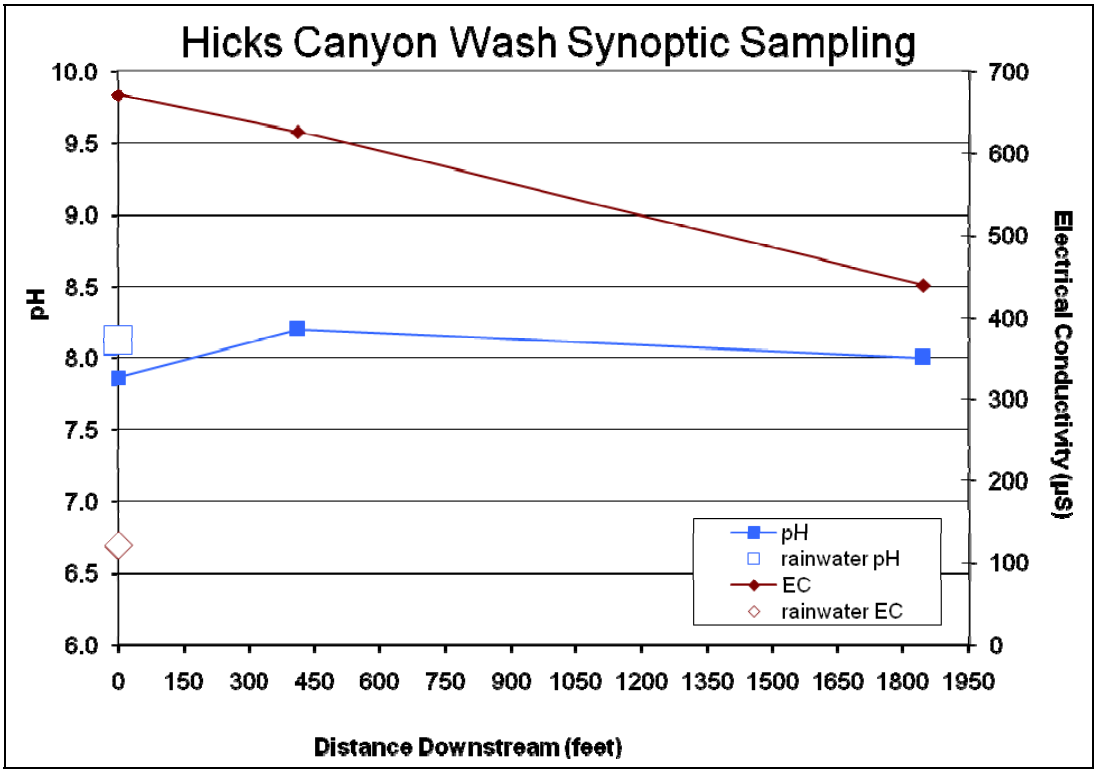

Figure 7.7. Changes in pH (blue line) and EC (red line) as waters flow from upstream to downstream along Hicks Canyon. Values of pH (open square) and EC (open diamond) for rainwater shown for comparison.

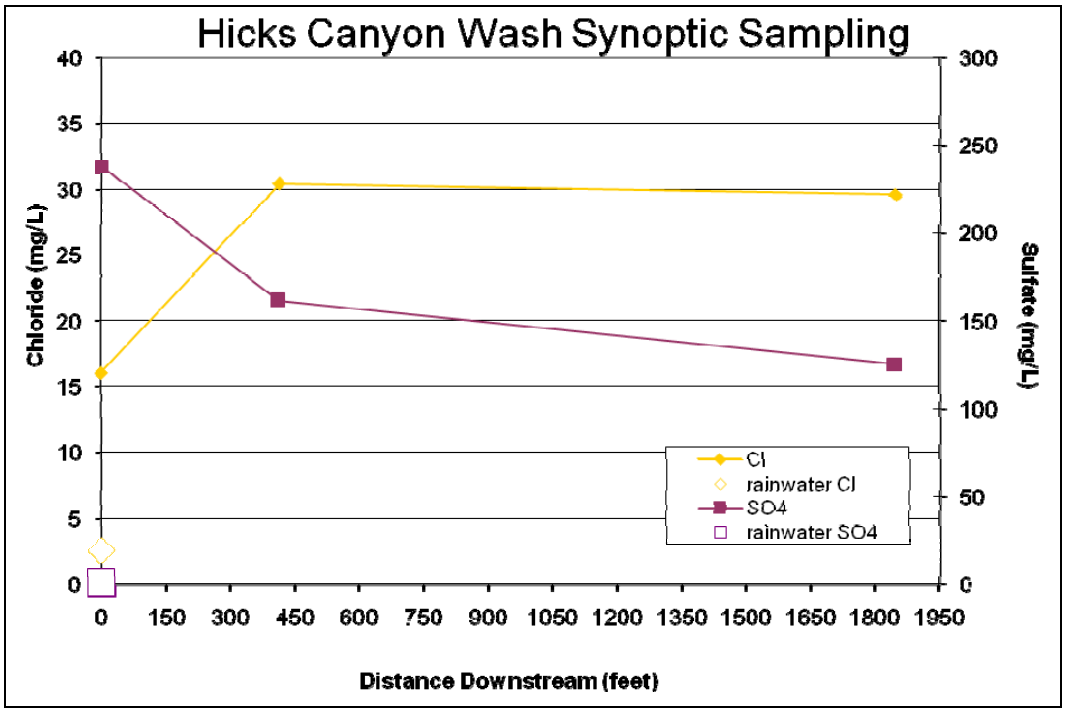

Figure 7.8. Changes in sulfate (purple line) and chloride (yellow line) as waters flow from upstream to downstream along Hicks Canyon. Values of sulfate (open square) and chloride (open diamond) for rainwater shown for comparison. *Note the y-axis for sulfate has been enlarged 10x from that showing changes in these constituents along Round Canyon in Figure 7.5.*

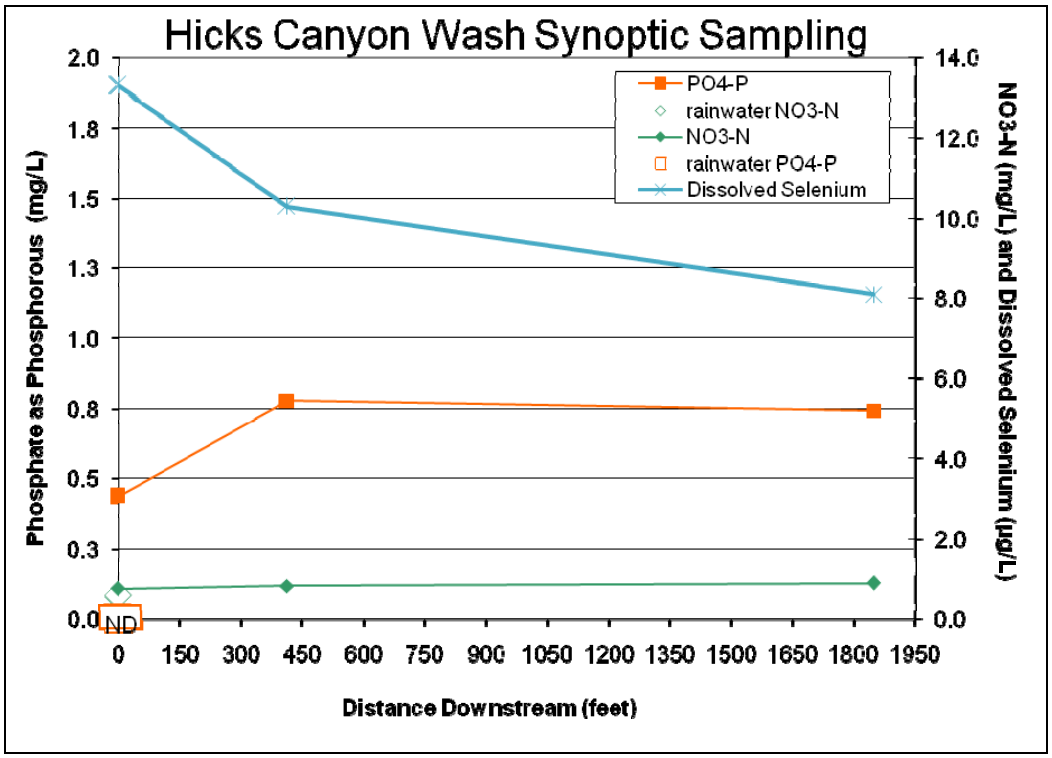

Figure 7.9. Changes in HPO_4-P (orange line), NO_3-N (green line) and dissolved selenium (blue line) as waters flow from upstream to downstream along Hicks Canyon. Values of HPO_4-P (open square) and NO_3-N (open diamond) for rainwater shown for comparison.

While selenium concentrations are higher along Hicks Canyon Wash, selenate is the dominant form of selenium in both tributaries, comprising 85% to 89% of dissolved selenium along Hicks Canyon and 60% to effectively 100% of dissolved selenium along Round Canyon (Table 7.9). Organic forms of selenium average 0.5 µg/L in runoff from both tributaries. Overall, organic forms of selenium comprise a greater fraction (33%) of the dissolved selenium in surface runoff at Round Canyon Lower than at any station along Hicks Canyon Wash (4%).

Table 7.9. Selenium Speciation Data for Synoptic Sampling

Site	Time	Dissolved Se (µg/L)	Se (IV) (µg/L)	Se (VI) (µg/L)	Org-Se (µg/L)	% Selenate
Round Canyon Upper	9:55 PM	0.825	< 0.4	0.825	< 0.4	100
Round Canyon Mid	9:30 PM	0.643	< 0.4	0.643	< 0.4	100
Round Canyon Lower	9:10 PM	1.254	< 0.4	0.833	0.421	66
Hicks Canyon Upper	11:15 PM	13.307	1.29	11.342	0.675	85
Hicks Canyon Mid	10:55 PM	10.296	0.853	8.874	0.569	86
Hicks Canyon Lower	10:40PM	8.100	0.569	7.228	0.303	89

II. Soil Sampling and Leaching Experiments

Background concentrations of *total* selenium in typical soils (i.e. those that are not impacted by selenium) are on the order of 0.4 mg/kg, while soils derived from Cretaceous rocks have higher *total* selenium content on the order of 5 mg/kg (Thomas et al., 1998). Data show that these soils, unlike those collected from within the boundary of the historic "Swamp of the Frogs" marsh (discussed in Chapter 1), contain total selenium below "normal" background concentrations. Negligible selenium oxyanions (Se IV or Se VI) are present in these upland soils, however leaching experiments reveal that there are leachable quantities present (Table 7.10). Interestingly, although there is about 30% more *total* selenium in soils collected from Round Canyon, soils collected from Hicks Canyon contain about 60% as much *leachable* selenium. The streambed soils from the upland reaches of the catchment also contain elevated levels of leachable nitrate as well as leachable orthophosphate. Soils from the streambed of Round Canyon contain twice as much leachable orthophosphate and roughly 60% more leachable nitrate (Table 7.10).

Table 7.10. Data from Upstream Soils Analysis.

	Se-speciation (mg/kg)		Total Se (mg/kg)	Leachable selenium (avg, mg/kg)	Leachable NO3-N (avg, mg/kg)	Leachable Ortho-P (avg, mg/kg)
	Se (IV)	Se(VI)				
Round Canyon streambed	ND (< 0.02)	ND (< 0.046)	0.360	0.003	0.006	0.002
Hicks Canyon Streambed	ND (< 0.02)	ND (< 0.046)	0.198	0.009	0.004	0.001

DISCUSSION

During the first monitoring period (January 5, 2008) at Hicks Canyon Lower, salinity and pH increase over the monitoring period while dissolved oxygen concentrations remain fairly constant (Table 7.4). The observed increase in salinity is reflected in increasing concentrations of sulfate, chloride, nitrate and orthophosphate (Table 7.4) and can be explained by two factors (1) the absence of substantial precipitation diminishes its diluting effect on surface waters and (2) streamflow changing in composition (i.e. increasing in salinity) due to greater travel time and longer contact with geologic materials. Waters that have traveled a greater distance over land surface pick up salts along the way before arriving at the downstream sampling site. While nitrate and orthophosphate concentrations increased over the course of monitoring, selenium exhibited an initial decline then increased gradually, closely mimicking the pattern exhibited by sulfate (Table 7.4).

Comparing water quality parameters for the pond-water (Table 7.3) with the average values observed in runoff along Round Canyon (Table 7.6) reveals much higher salinity in the pond water than in active runoff. Electrical conductivity is four times higher for the Round Canyon pond-water than the average value observed in runoff along Round Canyon on January 6-7, 2008. Chloride concentrations in the pond-water are double the average chloride concentration in runoff while sulfate concentrations are more than an order of magnitude higher

in pond-water than in the average sulfate concentration in runoff. Likewise, nitrate exhibits an eight-fold increase in the pond water compared with the average value observed in runoff. The high salinity observed in the pond-water is most likely the result of interflow and residual (ponded) stormflows leaching salts out of the soils.

Recall that collection of downstream samples in time series during the January 6-7 monitoring began during the period of greatest precipitation whereas collection of downstream samples during the January 5 monitoring took place after the heaviest precipitation had ceased. In short, monitoring of this stream took place during different points on the stream hydrograph during the two different monitoring events (Figure 7.10). Because these are ephemeral streams that flow exclusively in response to precipitation, the hydrograph will not have a baseflow component in the traditional sense. Instead, baseflow is essentially equivalent to interflow, which, like baseflow, will have higher salinity due to greater opportunity to interact with and leach salts from geologic materials. At Hicks Canyon Lower, initial salinity values were roughly equivalent during both monitoring events, increased over the course of monitoring and were closely linked with sulfate concentrations (Tables 7.4 and 7.5). Increasing contribution of baseflow (i.e. interflow) in proportion to other components of flow may account for increasing salinity observed during both monitoring events.

It is also interesting to note that salinity increases in time series at Round Canyon Lower over the course of monitoring (Table 7.6). As flow diminished along Round Canyon electrical conductivity, the conservative ions chloride and nitrate as well as orthophosphate all tend to increase. However, neither sulfate nor selenium exhibits this pattern. Initial flows are composed of primarily runoff (overland flow) and interflow whereas later flows are made up interflow alone (Figure 7.10). The fact that chloride, nitrate and orthophosphate increase over the

monitoring period suggest that there are readily leachable levels of these constituents in streambed and near-surface soils through which the interflow component flows. Sulfate and selenium peak following the period of most intense precipitation (Figure 7.2 and Table 7.6). This suggests that they are most likely derived from more distal upland materials and are brought to the stream via overland flow. Later in the monitoring period when interflow is the dominant component of streamflow, sulfate and selenium concentrations decrease, which suggests that there are relatively low levels of these constituents in readily leachable form in the streambed and near-surface soils. The fact that both sulfate and selenium are initially higher when stream discharge is higher supports this interpretation.

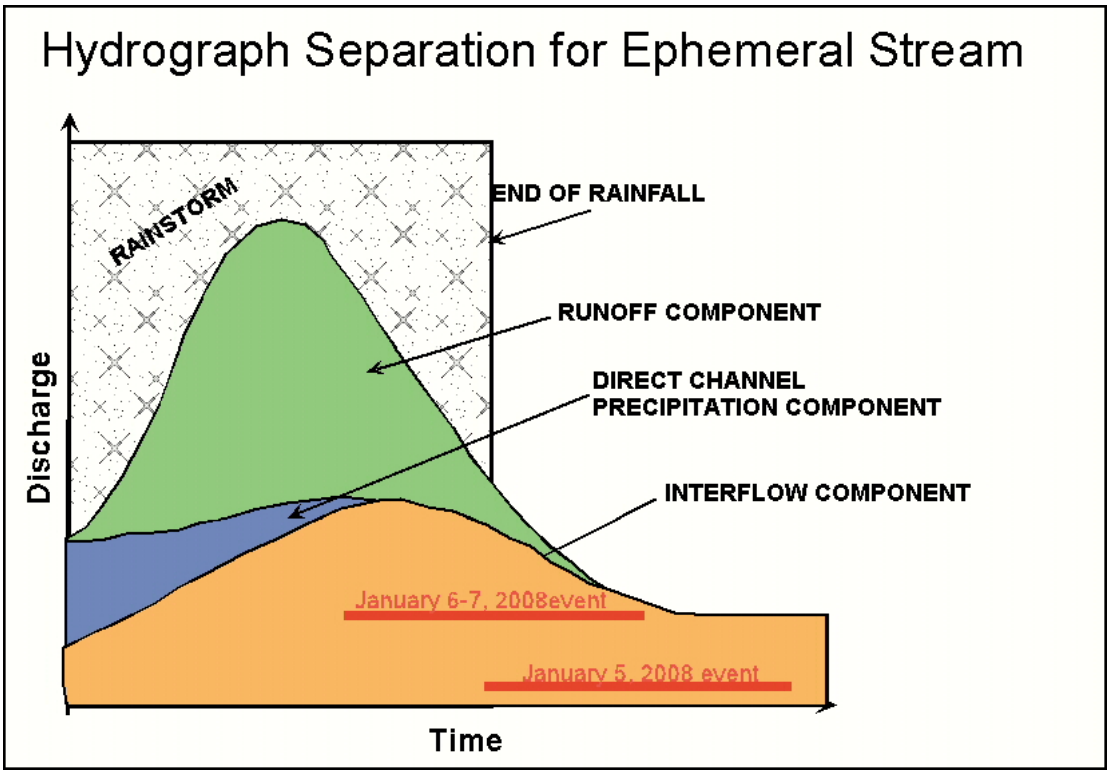

Figure 7.10. Conceptual hydrograph depicting the various components of streamflow in an ephemeral stream such as those found in the uplands of the San Diego Creek Watershed. Red bars show the hypothetical position of the two monitoring events relative to the end of the precipitation event.

Results from time series as well as "synoptic" sampling reveal that salinity appears to be linked to chloride concentrations along Round Canyon whereas salinity is strongly coupled to sulfate along Hicks Canyon. It is interesting that selenium concentrations are lowest where salinity is closely coupled to chloride (Round Canyon) and highest where salinity is closely coupled to sulfate (Hicks Canyon). This association suggests pyrite in marine shales may ultimately be the source of selenium in the watershed.

Selenium tends to concentrate in marine shales, especially those of Cretaceous and Miocene age (Thomas et al., 1998; Wright, 1999; Tracy, 1990). The geologic map (Figure 7.1) shows a greater abundance of the Miocene Puente formation in the vicinity of Round Canyon than there is near Hicks Canyon Wash. However, the map also shows that the Soquel Member of the Puente Formation dominates in the vicinity of Round Canyon. This member is predominantly comprised of sandstones (Morton and Miller, 1981). In the Hicks Canyon area the La Vida Member is present along the drainage area. This is a shaley member of the Puente Formation (Morton and Miller, 1981) and may be one explanation for why more selenium is observed in runoff emanating from Hicks Canyon than that coming from Round Canyon. Topography is another possible control. Round Canyon has steeper topography than Hicks Canyon. Therefore surface runoff would reach the major drainage channel faster and have less of an opportunity to interact with and leach selenium from geologic materials. Regardless, these data clearly show that substantial amount of selenium is being transported from the uplands in aqueous form.

Overall runoff from Round Canyon had higher nitrate levels than Hicks Canyon (Table 7.4, 7.5, 7.6). Likewise, soils collected from Round Canyon streambed had twice as much leachable nitrate and orthophosphate as soils collected from the Hicks Canyon streambed (Table

7.10). This is consistent with the interpretation that these constituents are being leached from streambed soils. It is likely that elevated nitrate is associated with aerial deposition following the wildfires. Wildfires burned much of the landscape in eastern Orange County between late October and early November 2007, approximately one month before soil samples were collected from the upstream sites. Wildfires have been shown to convert nitrogen and phosphorous to readily leachable forms (Neary et al., 2005). Higher levels of leachable nutrients in the vicinity of Round Canyon may be the result of greater vegetative cover in the area before the fires. Wildfire activity would have converted organic forms of nitrogen to forms that are more readily nitrified and leached from the soils (Neary et al., 2005). However, without pre-fire data, it is difficult to speculate if organic selenium is the result of the wildfires or if it rather reflects "normal" background concentrations in upland surface waters.

The land surrounding these tributaries may have been used historically as rangeland for grazing livestock. This is another possible source for elevated levels of nitrate in these undeveloped upland tributaries.

CONCLUSION

This study shows selenium-enriched waters flow from upstream tributaries in response to precipitation. This supports the model put forth by Hibbs and Lee (2000) that high levels of selenium that were sequestered in the historic "Swamp of the Frogs" marsh originated from the uplands. The data suggest that a greater amount of selenium originates in the northern part of the watershed, although there are numerous upstream canyons that were not sampled (such as Bee Canyon, Agua Chinon Canyon, Rattlesnake Canyon, and others). It is likely that these additional Canyons contribute variable quantities of selenium to the downstream drainage network. The

association of sulfate and selenium suggest that these two constituents originate from a common source, most likely pyrite in upland marine shales. Results of this investigation reveal that leachable quantities of selenium are present in upland soils, which shows that the mobility of selenium is not limited to transport in the solid phase.

Variable nitrate concentrations were observed in upland surface flows and were especially high in surface runoff from Round Canyon, exceeding the EPA MCL of 10 mg/L nitrate as nitrogen at the downstream station. High levels of nitrate are most likely related to recent wildfire activity, but may also be due to the historic land use for ranching. Expanded and continued monitoring of wet-weather flows in these upstream tributaries is advisable in order to conclusively determine the source of nitrate in these waters.

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