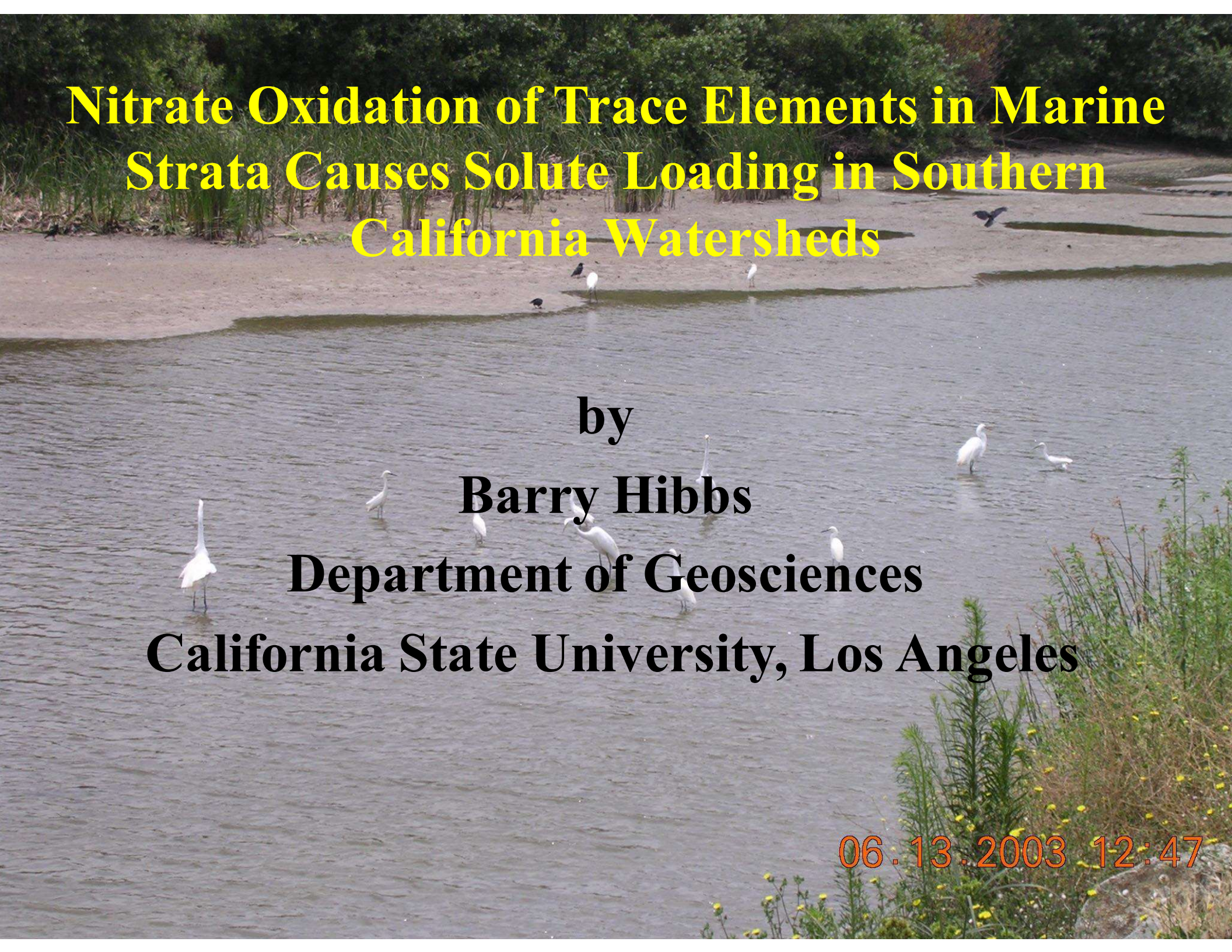
Nitrate Oxidation of Trace Elements in Marine Strata Causes Solute Loading in Southern California Watersheds



by

Barry Hibbs

Department of Geosciences

California State University, Los Angeles

Study Region

Figure I

WATERSHED FEATURES

North Santa Monica Bay Regional Watershed Implementation Plan

CALLEGUAS MUNICIPAL WATER DISTRICT

Las Virgenes Creek

HIDDEN VALLEY MUNICIPAL WATER DISTRICT

MALIBU CREEK WATERSHED

TOPANGA CREEK WATERSHED

CITY OF LA WATER DISTRICT

LAS VIRGENES MUNICIPAL WATER DISTRICT

COASTAL WATERSHEDS

WEST BASIN MUNICIPAL WATER DISTRICT

VENTURA COUNTY

LOS ANGELES COUNTY

Lindero Canyon

Russell Valley

Triunfo Canyon

Sherwood

Arroyo Sesnit

La Virgenes Canyon

Monte Nido

Topanga Canyon

Las Alisos Canyon

Nicholas Canyon

Encinal Canyon

Zuma Canyon

Trancas Canyon

Ramera Canyon

Escondida Canyon

Latigo Canyon

Solstice Canyon

Corral Canyon

Carbon Canyon

Las Flores Canyon

Tuna Canyon

Piedra Gorda Canyon

Pena Canyon

Pacific Ocean

LEGEND

Interstates and Highways

- Interstate
- Highway

Hydrologic Features

- Streams
- 303d Listed Streams
- Lake, reservoir, or pond
- NSMB Watershed Boundary
- Hydrologic Area Boundary
- Hydrologic Sub-Area Boundary
- Water District Boundary

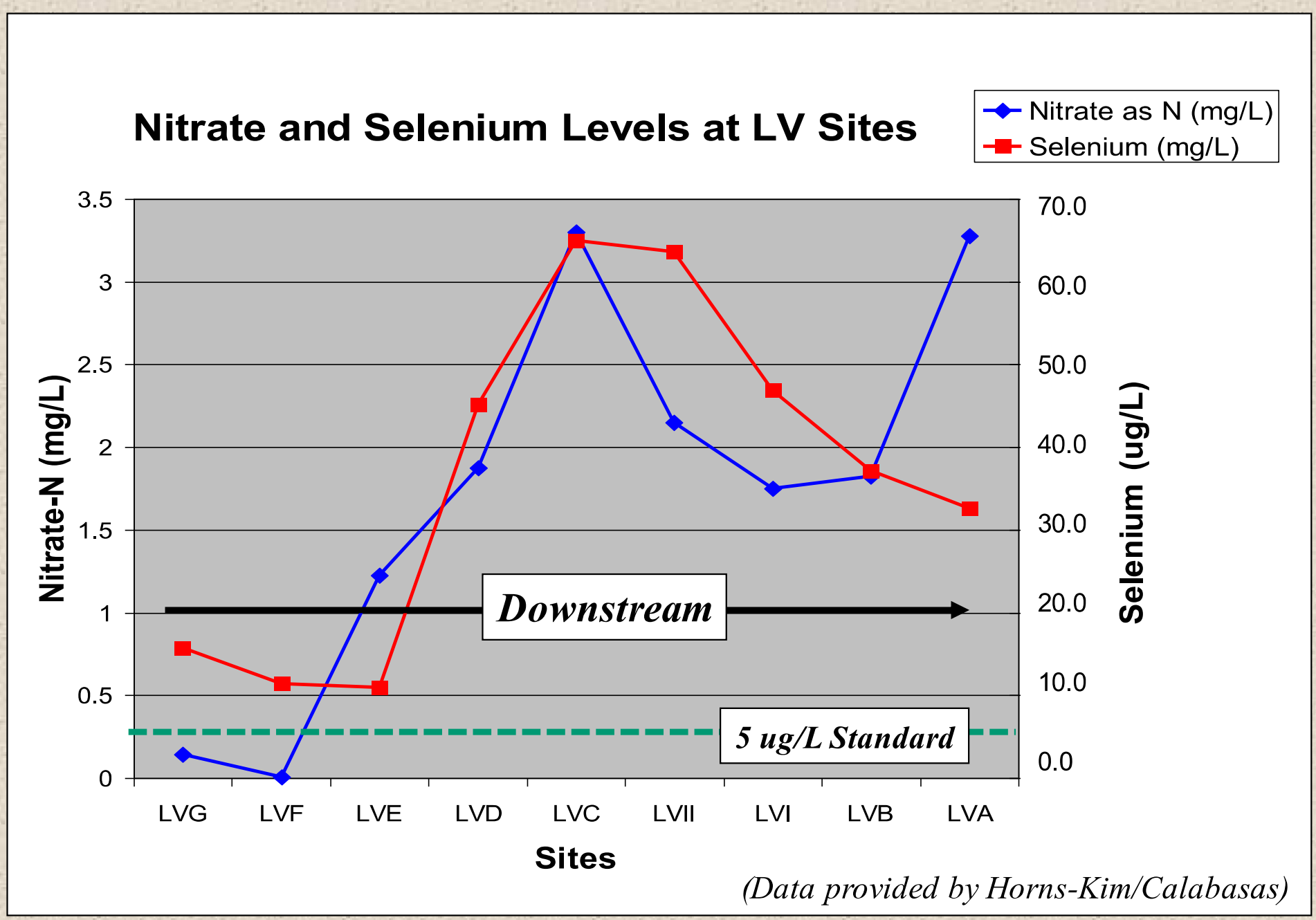
0 1 2

Miles

Map prepared by:

IWR INTEGRATED WATER RESOURCES, INC.

January 2006

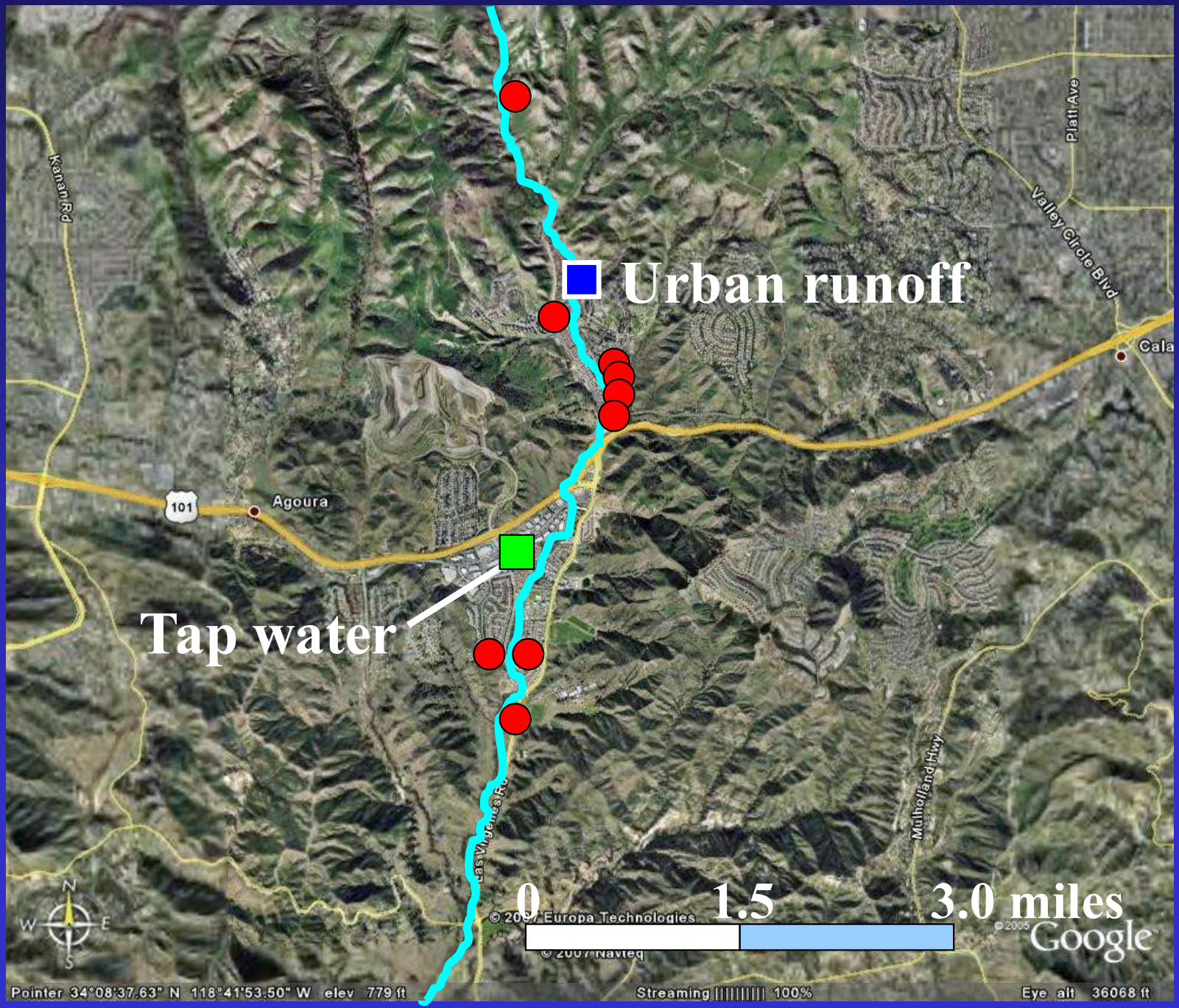


(Data provided by Horns-Kim/Calabasas)

Does Las Virgenes Creek contain urban runoff primarily?

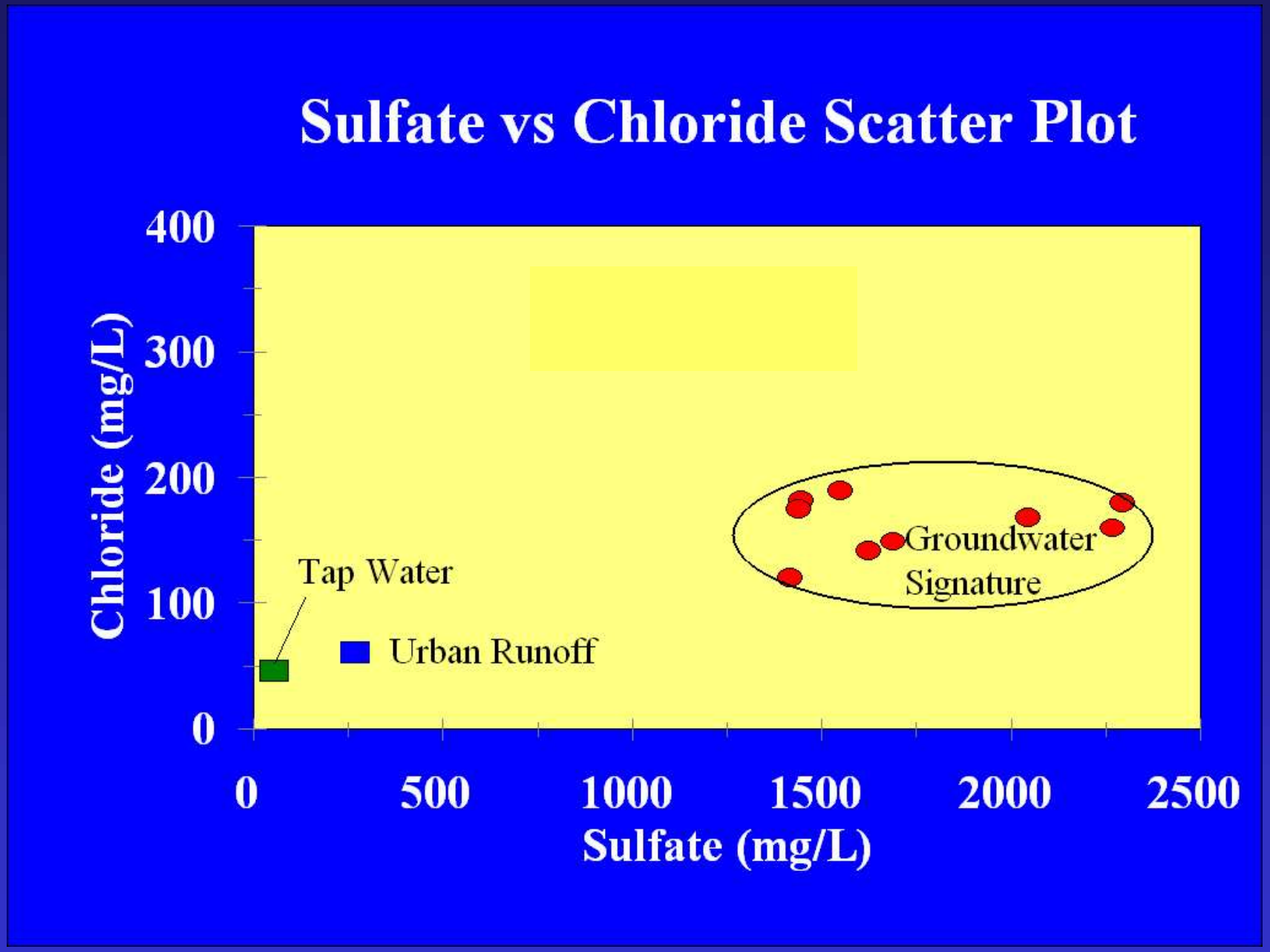
…..or are creek flows sourced from groundwater baseflow?

Sample Identification Map

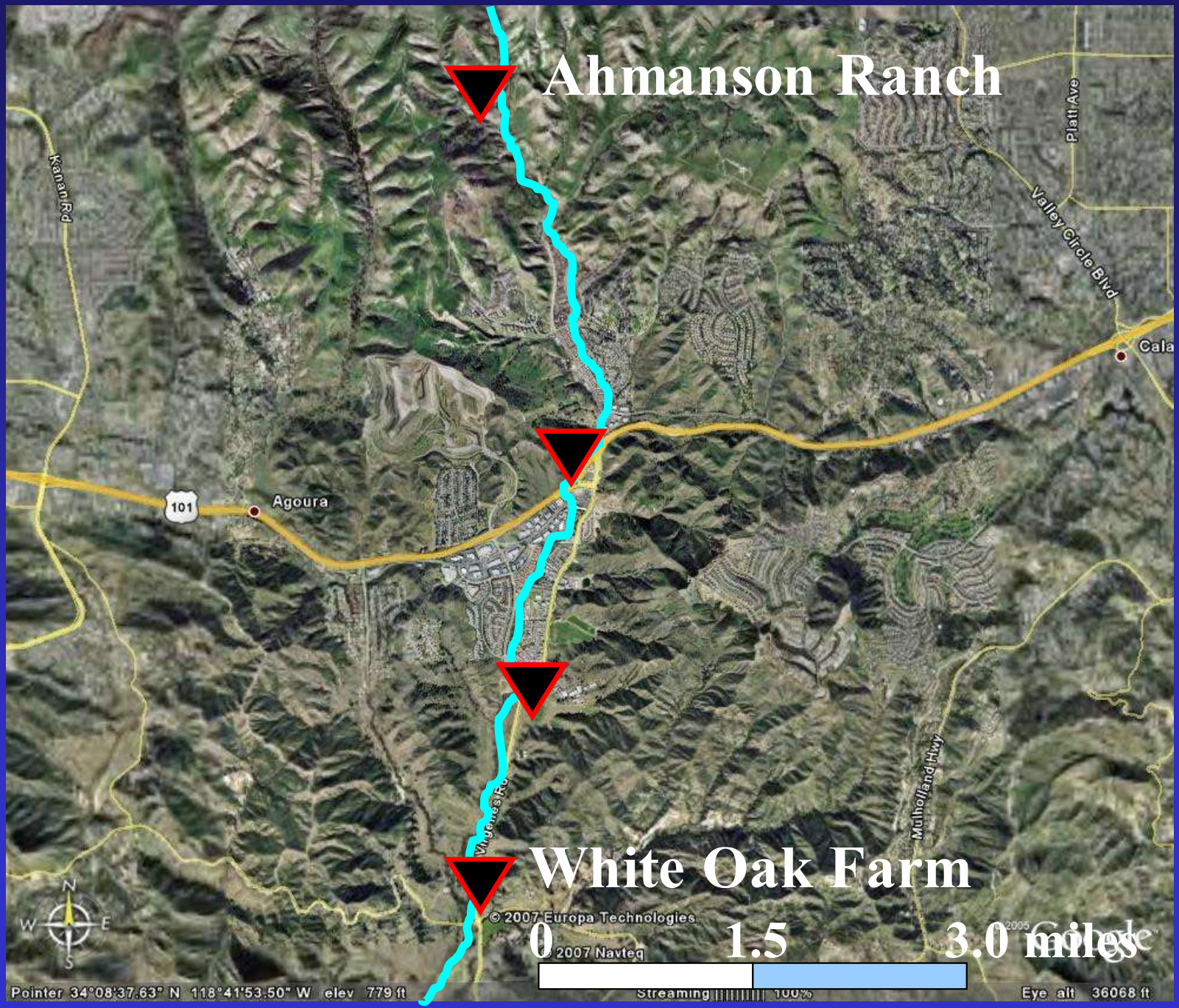


Explanation

- Groundwater Sample
- Tap water Sample
- Urban runoff Sample

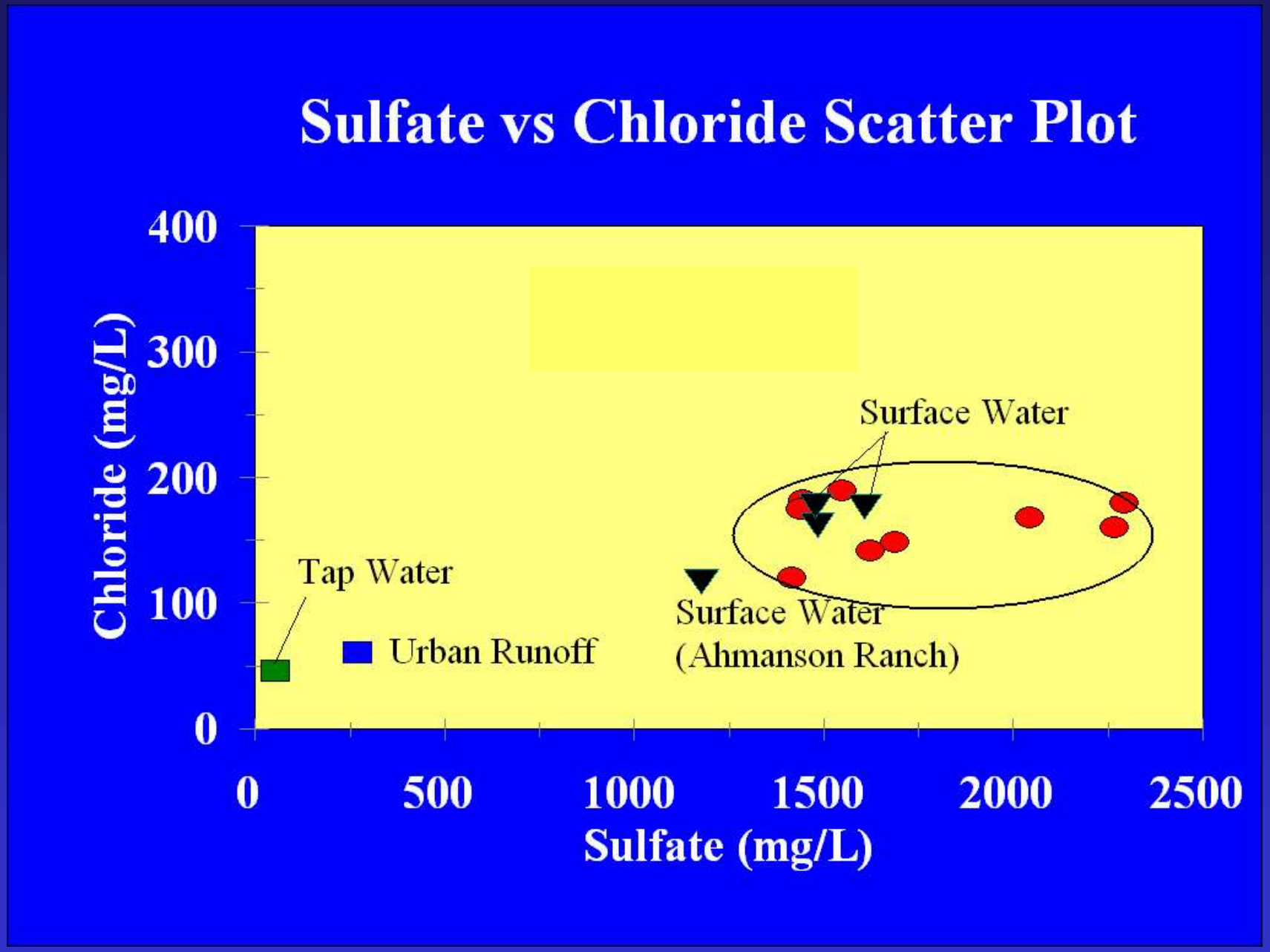

Sulfate vs Chloride Scatter Plot
Chloride (mg/L)
400
300
200
100
0
0
500
1000
1500
2000
2500
Sulfate (mg/L)
Tap Water
Urban Runoff
Groundwater
Signature

Surface Water Sampling Stations

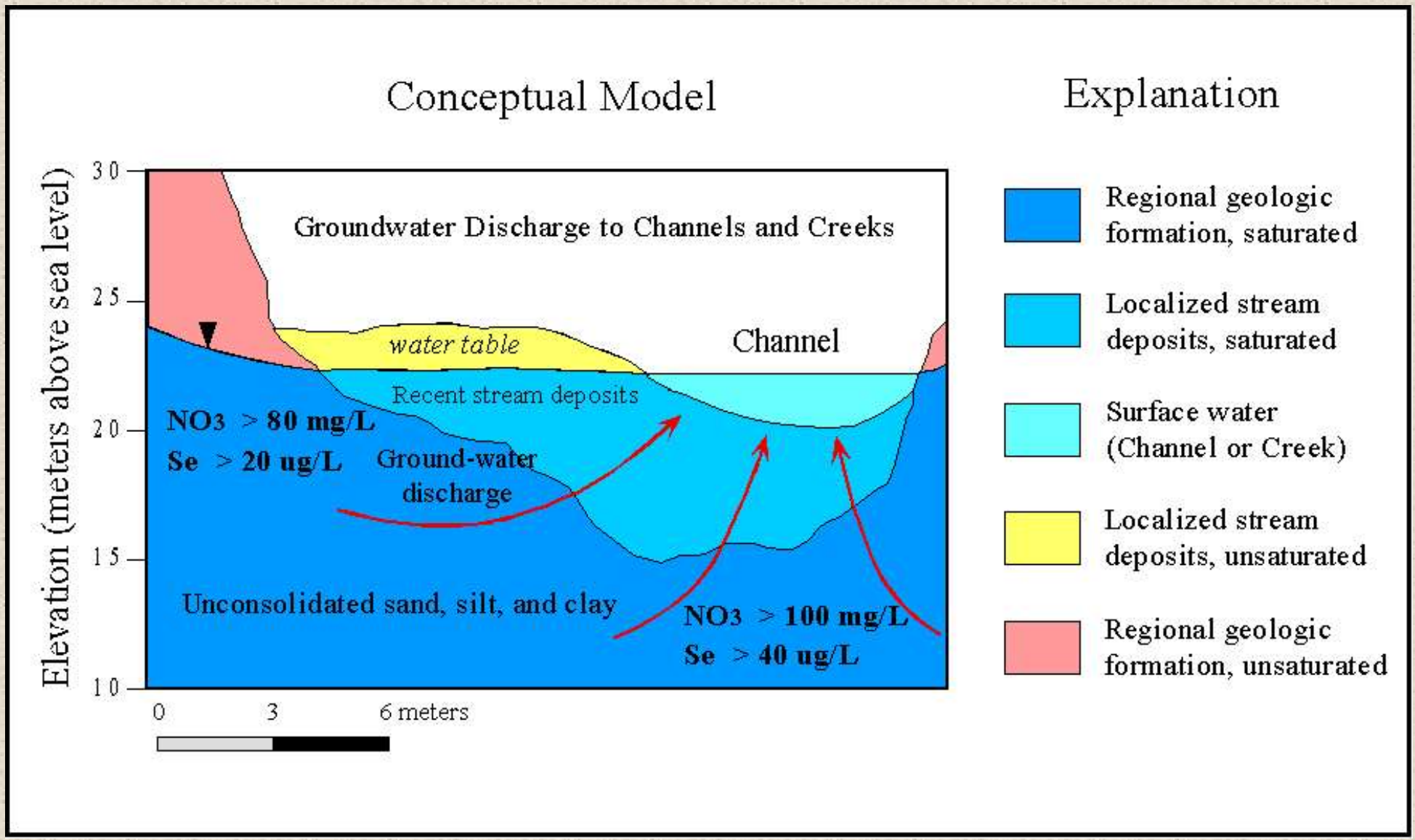


Explanation

Surfacewater Sample


Sulfate vs Chloride Scatter Plot
Chloride (mg/L)
400
300
200
100
0
0
500
1000
1500
2000
2500
Sulfate (mg/L)
Surface Water
Tap Water
Urban Runoff
Surface Water
(Ahmanson Ranch)

Las Virgenes Creek Flow Is Dominantly Groundwater Derived During Dry Weather Flows



Objectives

- Perform and compare streamflow water quality and groundwater quality in the Las Virgenes stream/aquifer system with other stream/ aquifer systems in Malibu Creek and adjacent watersheds, focusing on selenium and nitrate concentration (and Cr, Ni, Zn, Al, Cd in the future).

- Evaluate distribution and sources of selenium (and nitrate) in surface water and groundwater in these watersheds.

Methods

- Identify springs, drains, and surface water stations for dry weather sampling

- Measure index parameters, standard inorganic constituents, selenium species, other redox sensitive parameters, and stable isotopes of oxygen, hydrogen, and sulfur

Selenium: Why It Matters

Toxic Trace Element:

- Bioaccumulates in higher trophic levels.
- High levels induce teratogenesis in fish and waterfowl.

Selenium Levels of Concern for Water and Sediment

Indicator medium	Normal background	Level of concern	Toxicological and reproductive effects certain
Water	< 0.5 to 1.5 ug/L	2 to 5 ug/L	> 5 ug/L
Sediment	< 2 ug/g	2 to 4 ug/g	> 4 ug/g

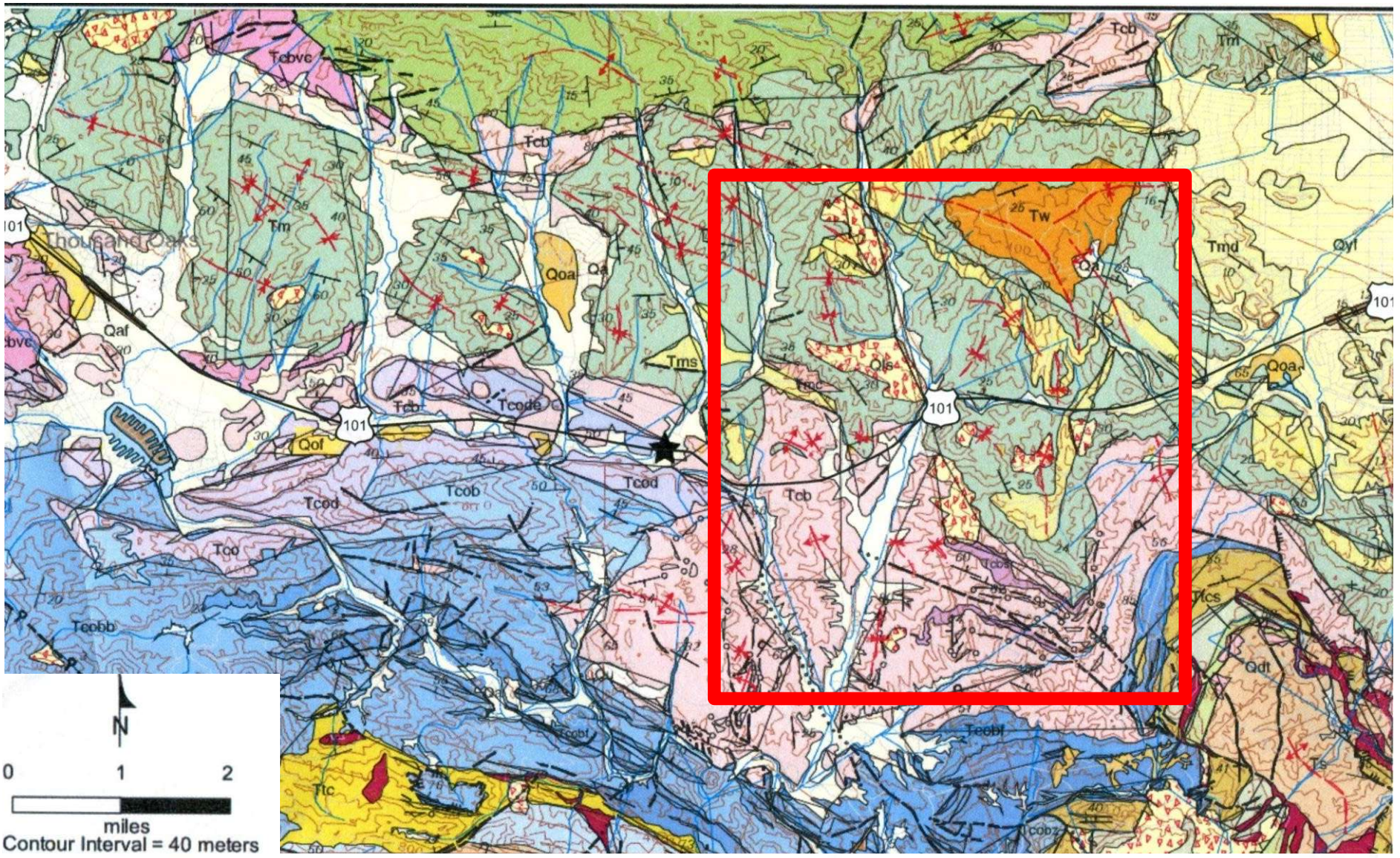


Figure modified from Kleinfelder West, Inc., 2011

SYMBOLS

- Surface Fault
- Concealed Fault

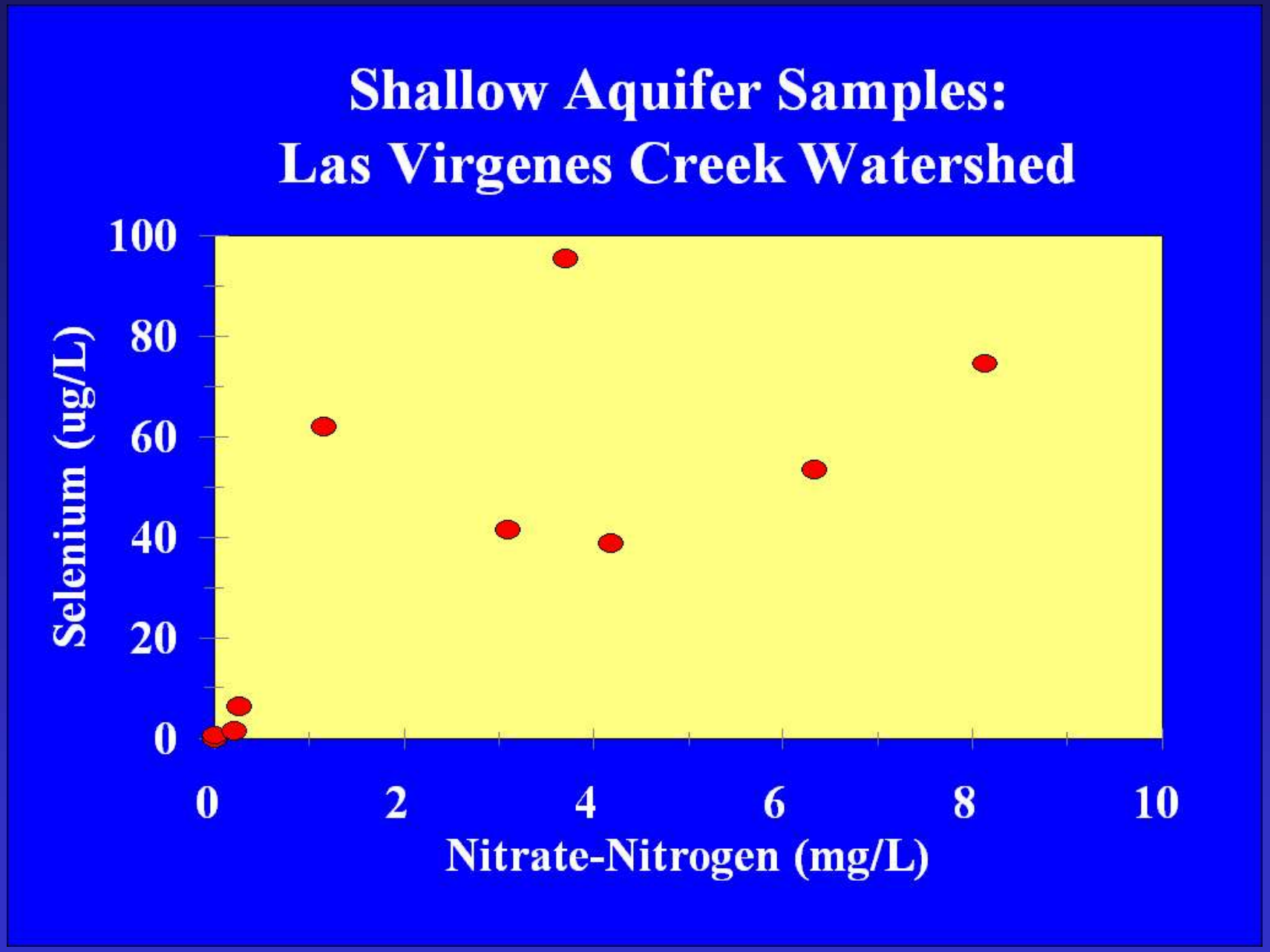
MAP UNITS

- Qls - landslide deposits
- Qa - alluvium
- Tm - Modelo Formation (undivided)
- Tms - Modelo Formation (sandstone)
- Tcb - Calabasas Formation (undivided)
- Tcod - Conejo Volcanics (dacite)
- Tcode - Conejo Volcanics (dacite w/ epiclastic lens
- Tcoob - Conejo Volcanics (basalt)

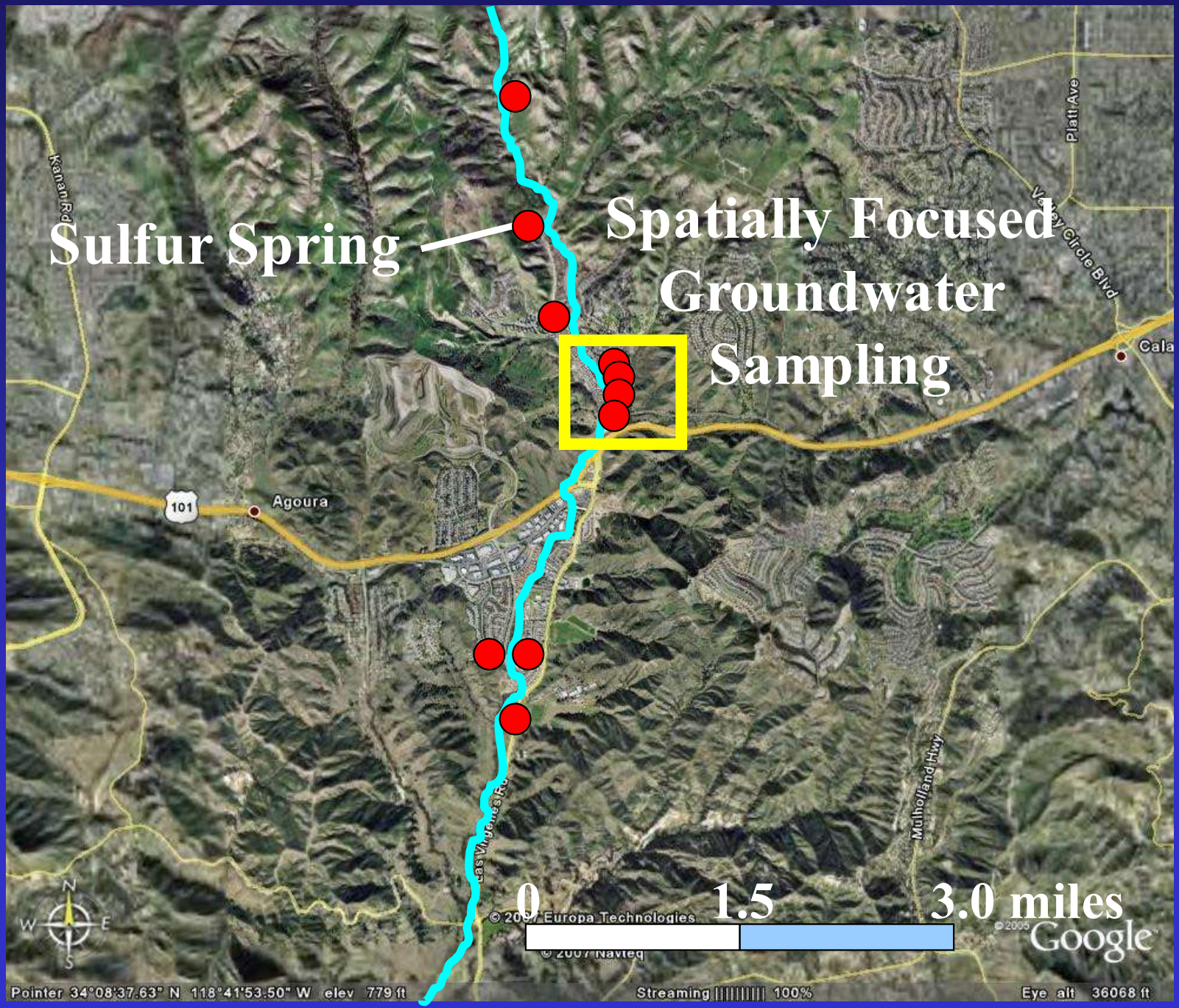
*Refer to Yerkes and Campbell (2005) for a complete explanation and list of units and symbols

Question:

What is the concentration of nitrate and selenium in groundwater and is there a direct cause-effect relationship between selenium and nitrate?

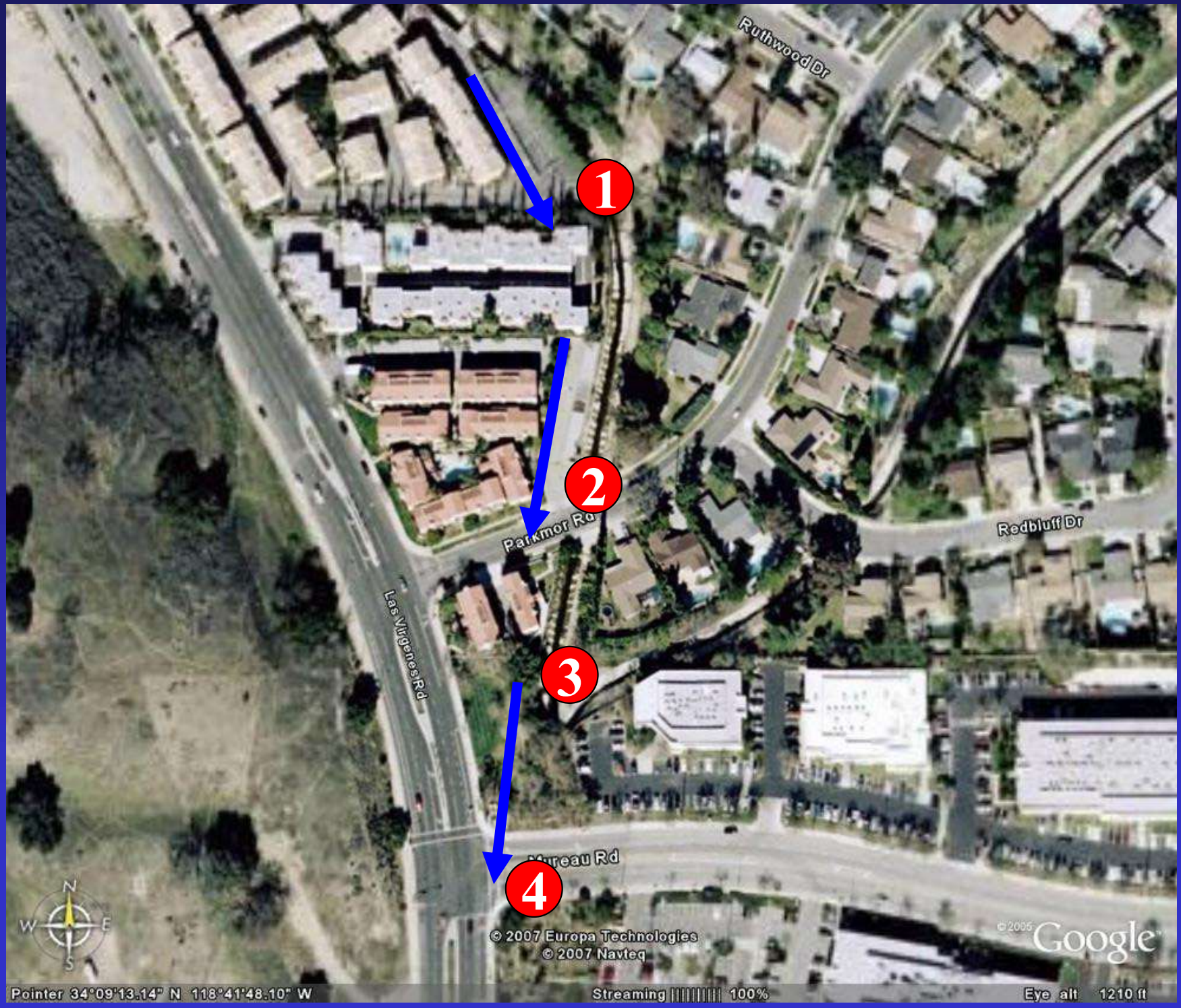

Shallow Aquifer Samples:
Las Virgenes Creek Watershed
Selenium (ug/L)
100
80
60
40
20
0
0
2
4
6
8
10
Nitrate-Nitrogen (mg/L)

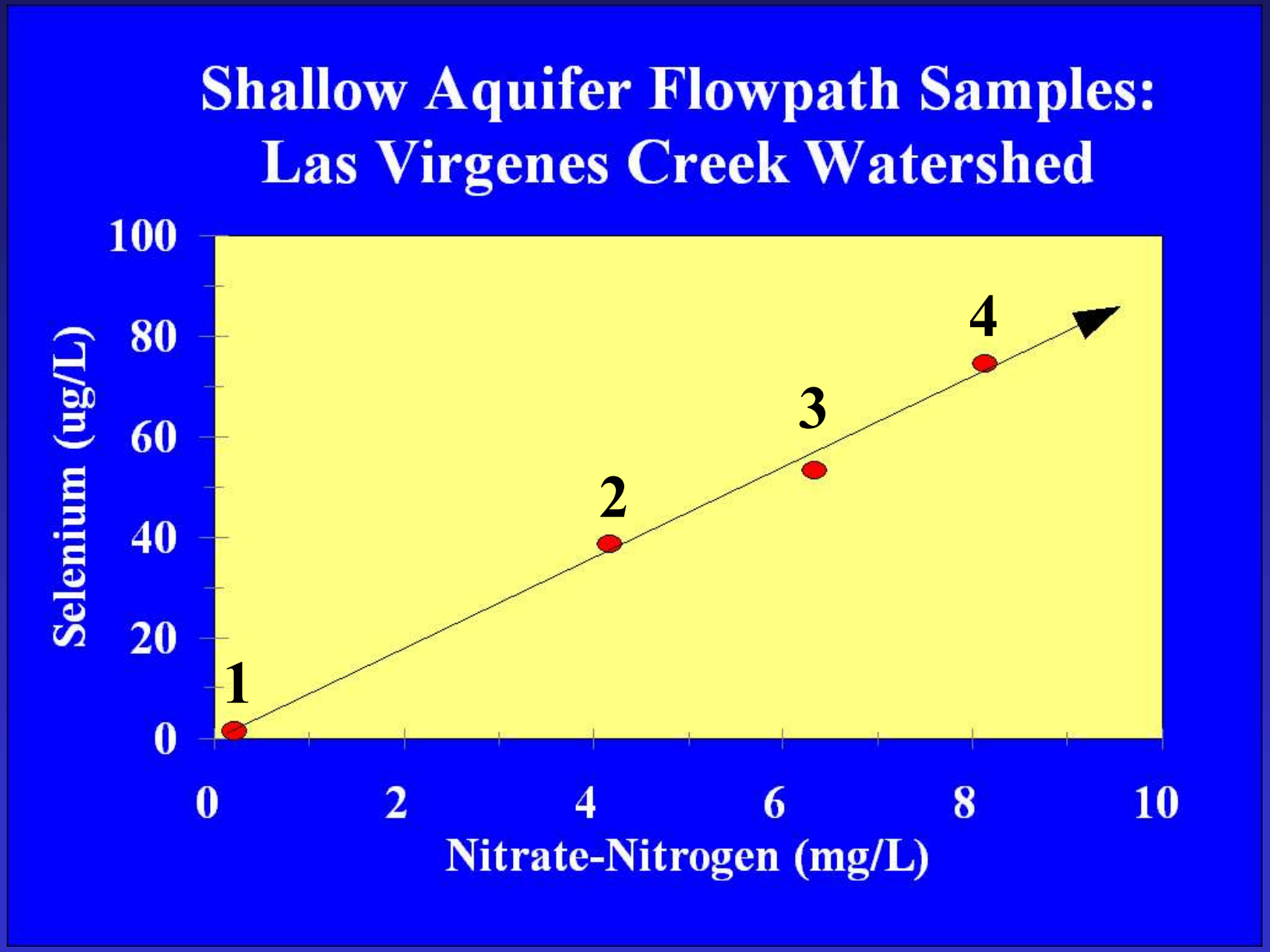
Study Area Location Map



Explanation

Groundwater Sample


Ruthwood Dr
1
2
Parkmor Rd
Redbluff Dr
Las Virgenes Rd
3
Mureau Rd
4
© 2007 Europa Technologies
© 2007 Navteq
© 2006 Google
Pointer 34°09'13.14" N 118°41'48.10" W
Streaming 100%
Eye alt 1210 ft

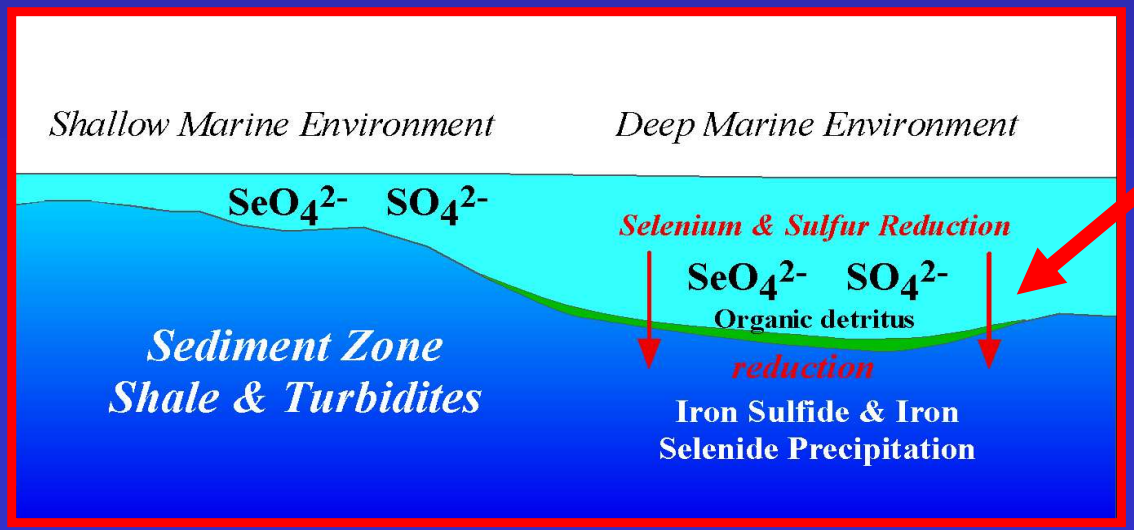

Shallow Aquifer Flowpath Samples:
Las Virgenes Creek Watershed
Selenium (ug/L)
100
80
60
40
20
0
1
2
3
4
0
2
4
6
8
10
Nitrate-Nitrogen (mg/L)

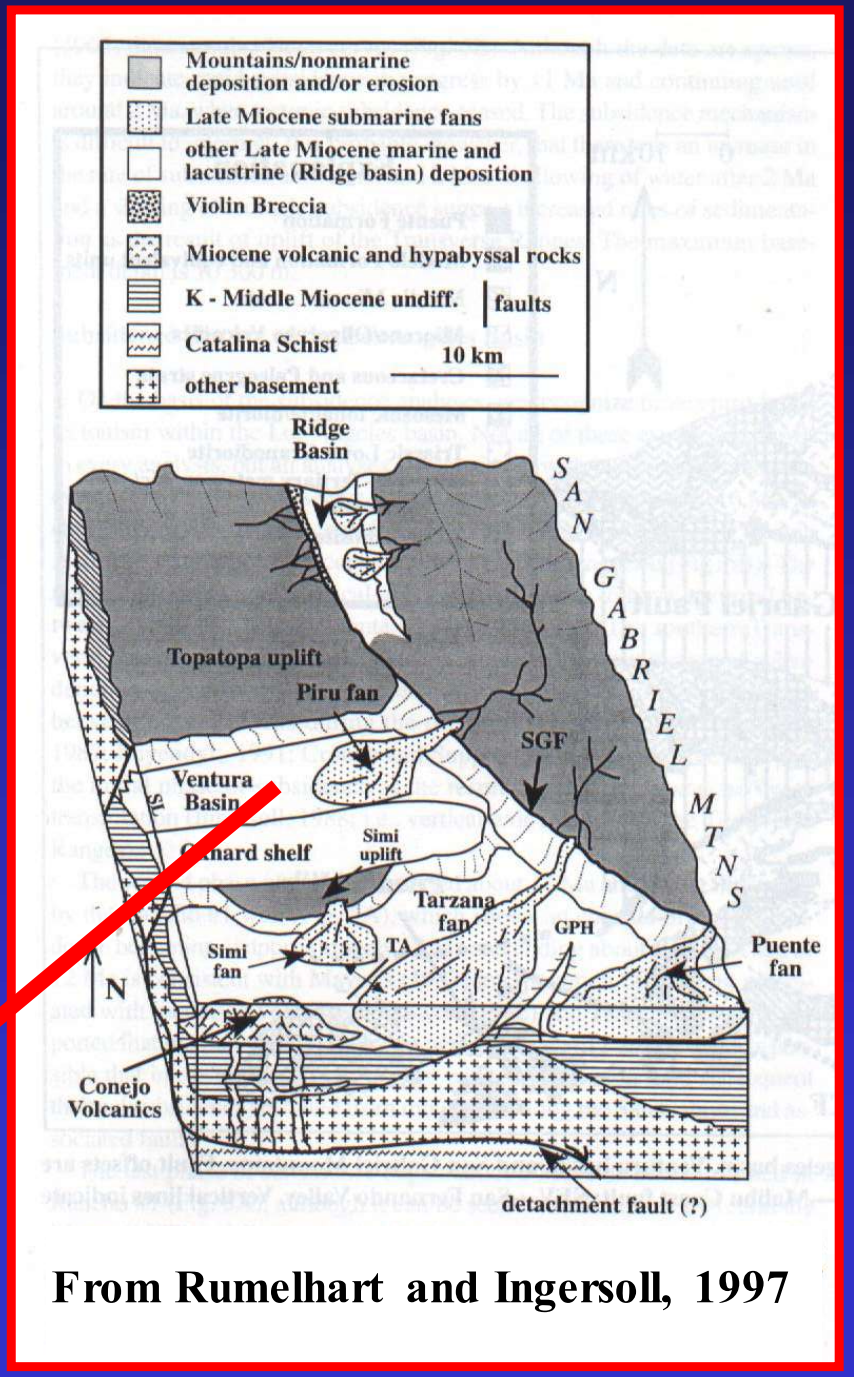
Selenium Redox Systematics & Possible Hydrochemical Links to Nitrate

Forms of Sulfur and Selenium in Oxidizing and Reducing Environments

Redox State	*Solubility Constraint*	*Selenium Ion*	*Selenium Oxidation State*	*Sulfur Ion*	*Sulfur Oxidation State*
Oxidizing					
	Highly soluble	SeO_4^{2-}	+VI	SO_4^{2-}	+VI
	Slightly soluble	SeO_3^{2-}	+IV		
	Insoluble	Elemental Se	0		
	Insoluble	Se^{2-}	-II	H_2S, HS^-, S^{2-}	-II
Reducing					

Origin of Metal Selenides in Miocene Marine Rocks and Sediments in Los Angeles Basin





From Rumelhart and Ingersoll, 1997


NEVADA
CALIFORNIA
SAN FRANCISCO
MONTEREY SHALE
BAKERSFIELD
LOS ANGELES
Yuba City
Carson City
Roseville
Sacramento
Santa Rosa
Fairfield
Concord
Stockton
Oakland
Modesto
Yosemite National Park
Hanford
Lancaster
Palmdale
Santa Barbara
Riverside
Indio

Relationship Between Nitrate, Selenium, and Groundwater

- Selenium can be oxidized by nitrate from nitrate sources coming in contact with certain marine rocks and marine eroded sediments

- Theoretical calculations for the oxidation of selenium by nitrate show favorable Gibbs free energies for the oxidation of selenium by nitrate (relative to dissolved oxygen; W. Wright, USGS, Journal of Environmental Quality, 1999)

Oxidation Reactions

dissolved oxygen and nitrate as oxidants of iron selenide

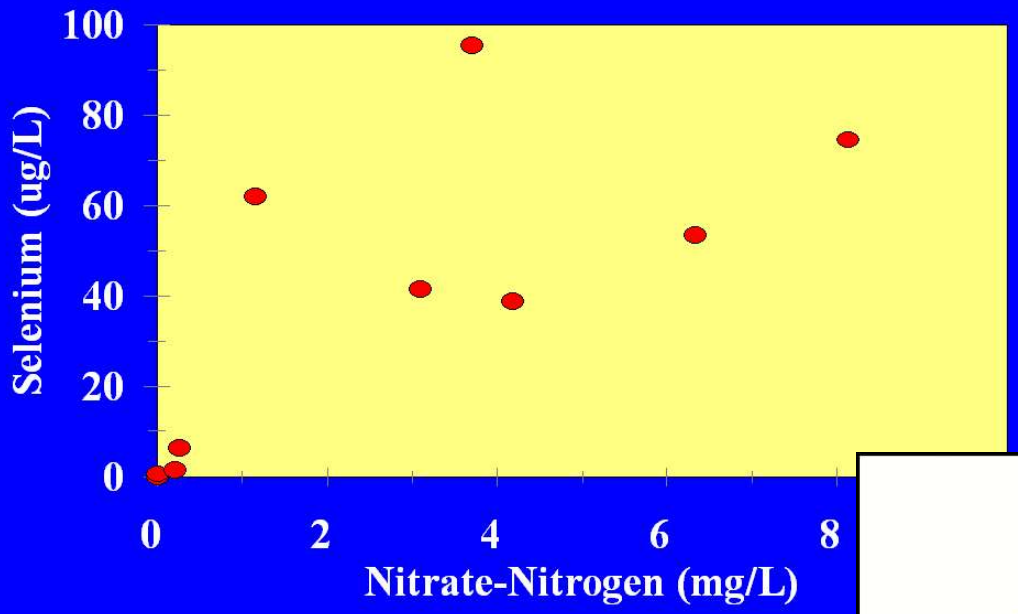
$$5FeSe_2 + 3.5\,O_2 + H_20 \rightarrow Fe^{2+} + 2SeO_4^{2-} + 2H^+$$

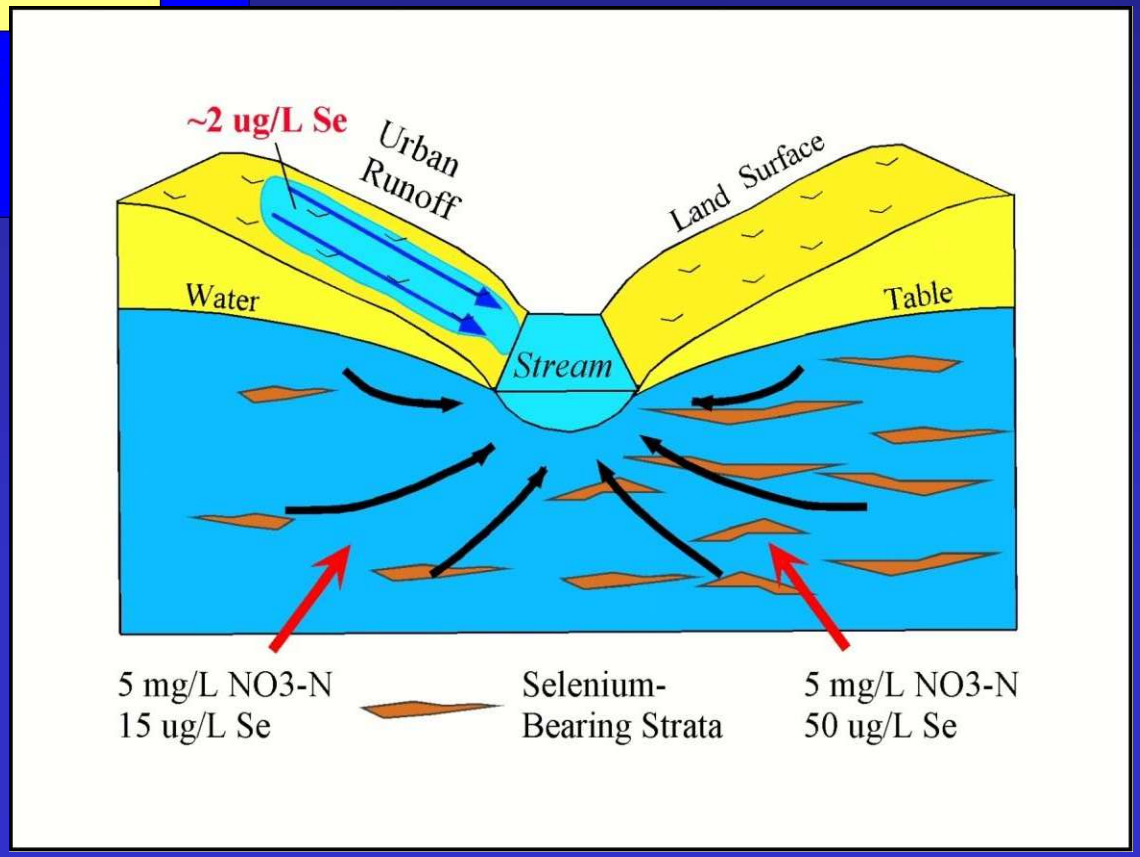
$$5FeSe_2 + 14NO_3^- + 4H^+ \rightarrow 7N_2 + 10SeO_4^{2-} + 5Fe^{2+} + 2H_2O$$

Hypothesis

Where present in moderate to high concentrations in ground water, nitrate acts as an oxidant of selenium where content of reduced forms of selenium (metal selenides, elemental selenium, and selenite) in geologic deposits is high; even where dissolved oxygen is depleted.

Shallow Aquifer Samples: Las Virgenes Creek Watershed





Surface Water Sampling Stations

Explanation

Surface water Sample

Nitrate-Nitrogen Versus Selenium Species and Uranium in Las Virgenes Creek

Sample Name	NO3-N (mg/L)	Se(VI) (ug/L)	Se(IV) (ug/L)	Uranium (ug/L)
Ahmanson Ranch	0.3	2.3	5.0	8.2
101 Freeway	2.0	54	5.0	36
De Anza Park	1.8	20	4.6	59
White Oak Farm	4.4	23	7.3	62

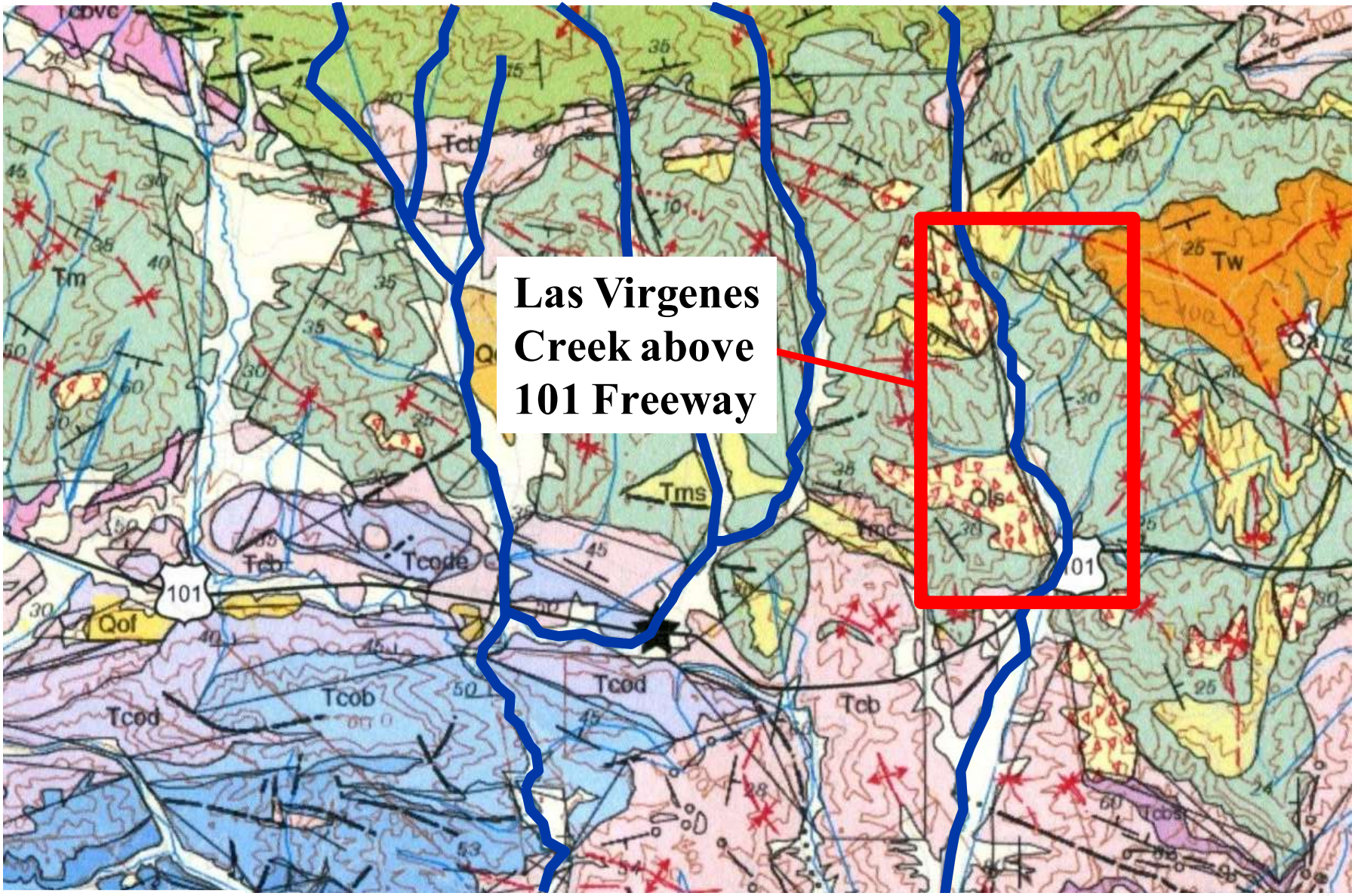


Figure modified from Kleinfelder West, Inc., 2011

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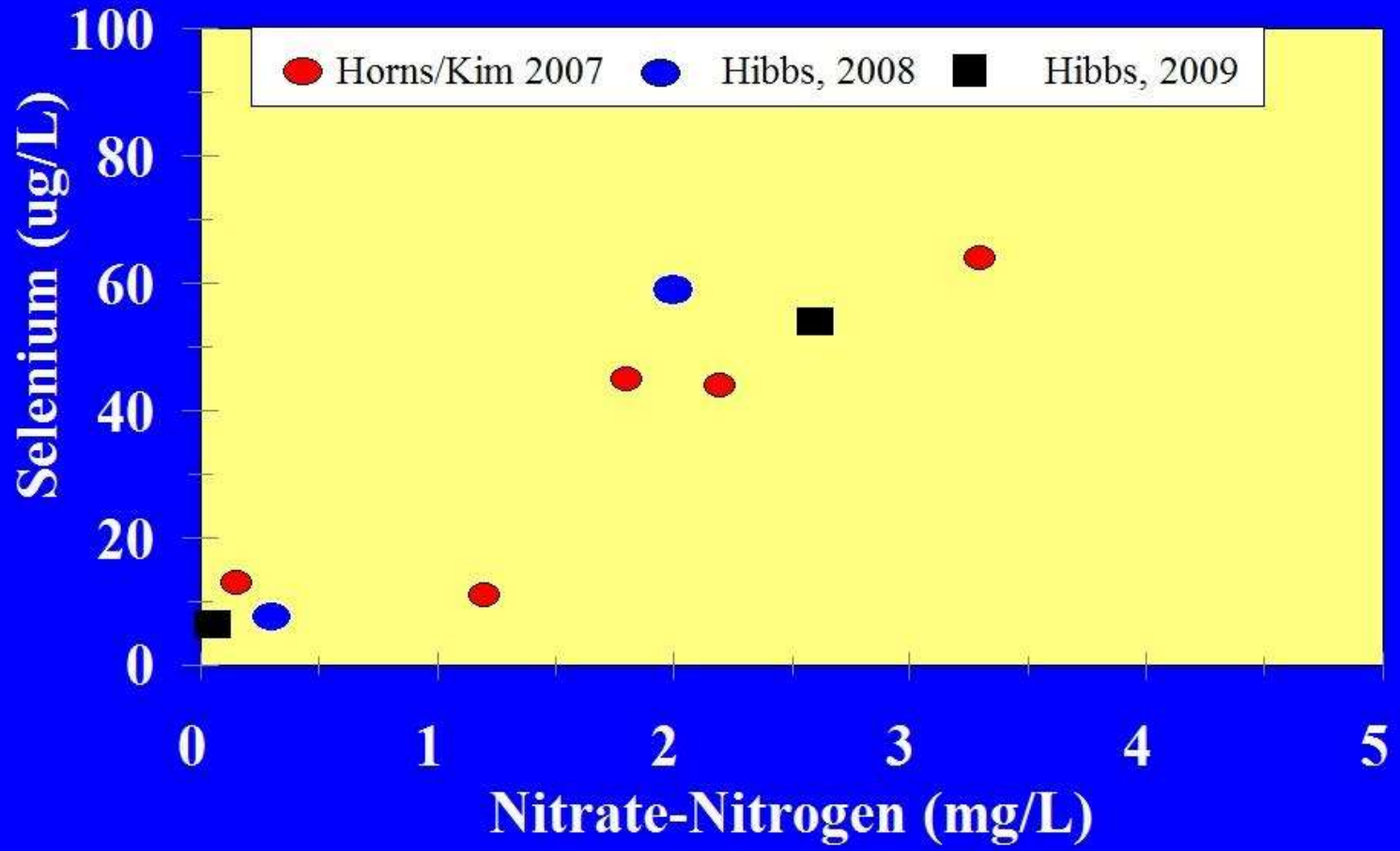
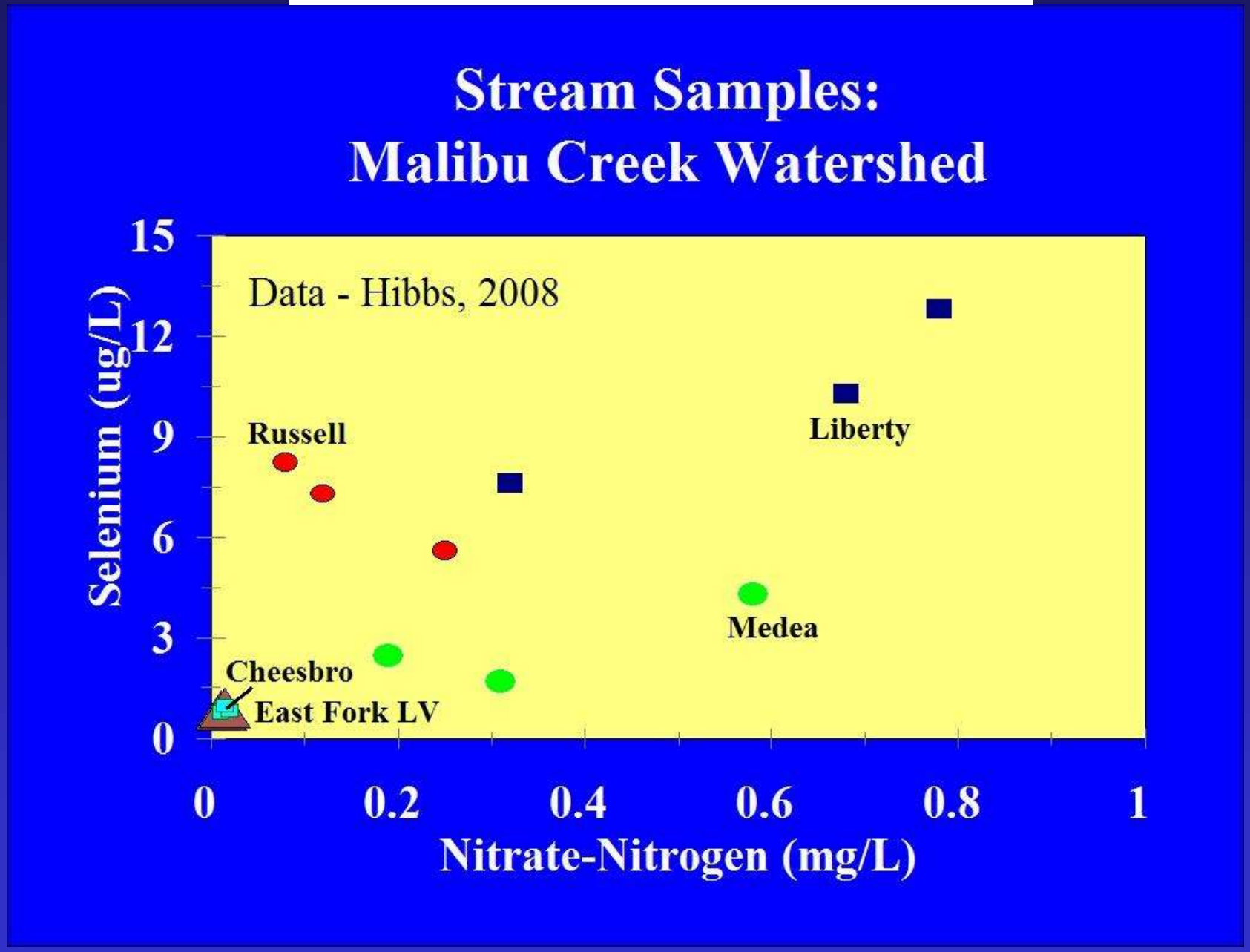
*Refer to Yerkes and Campbell (2005) for a complete explanation and list of units and symbols

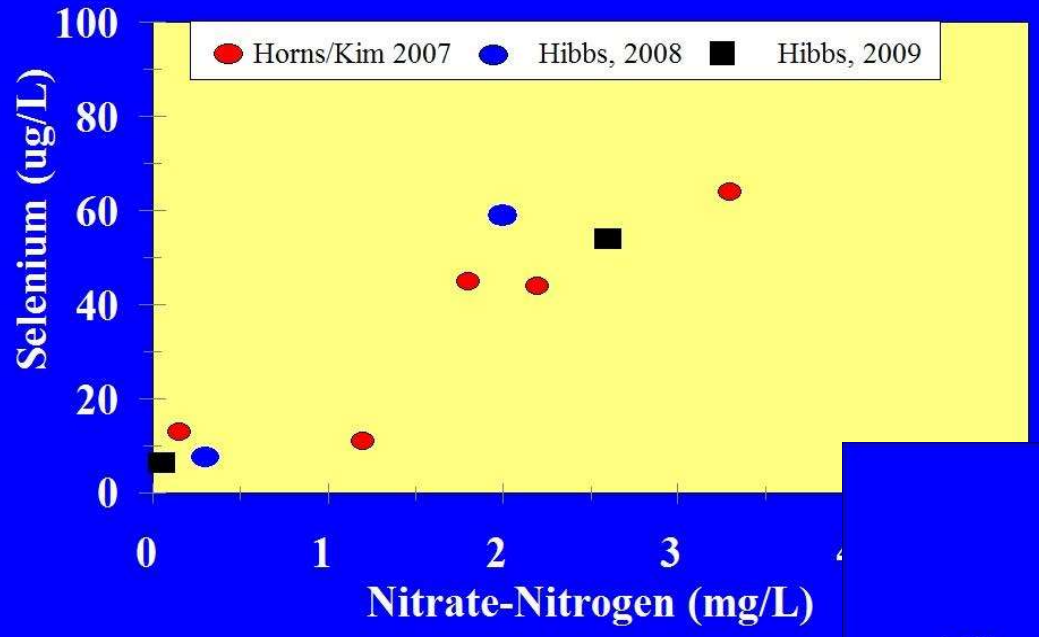
Stream Samples:
Las Virgenes Creek above 101 Freeway



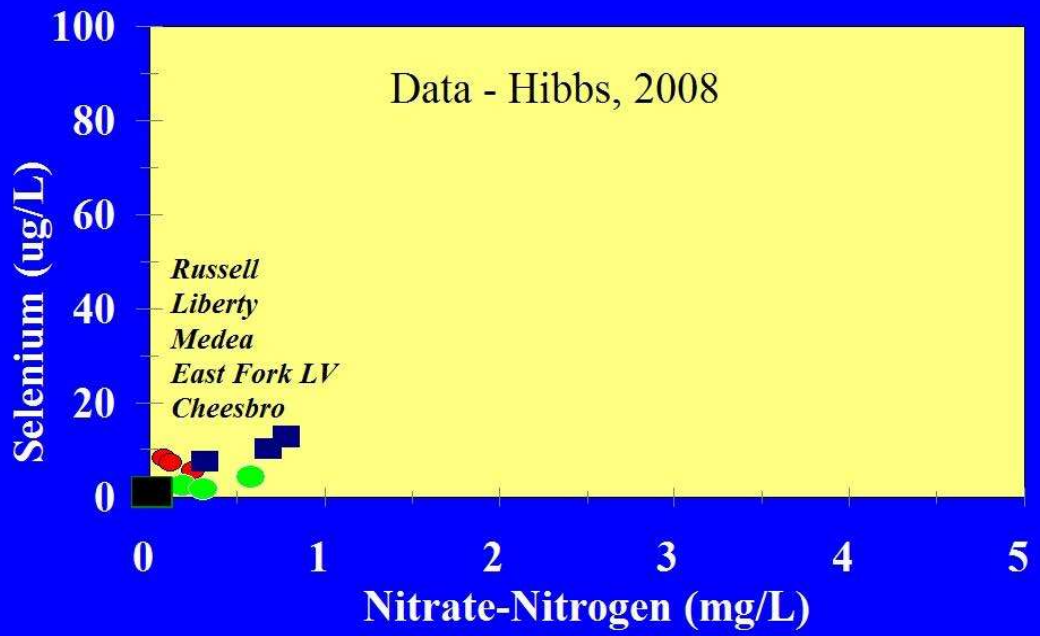
*all but Liberty Creek collected along stream reaches traversing Monterey/Modelo outcrops

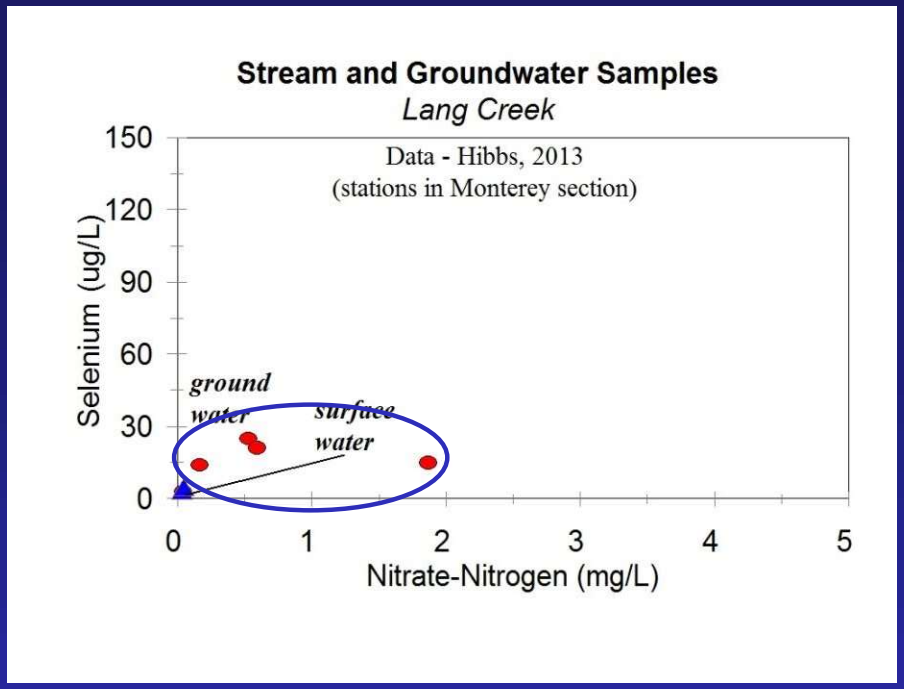


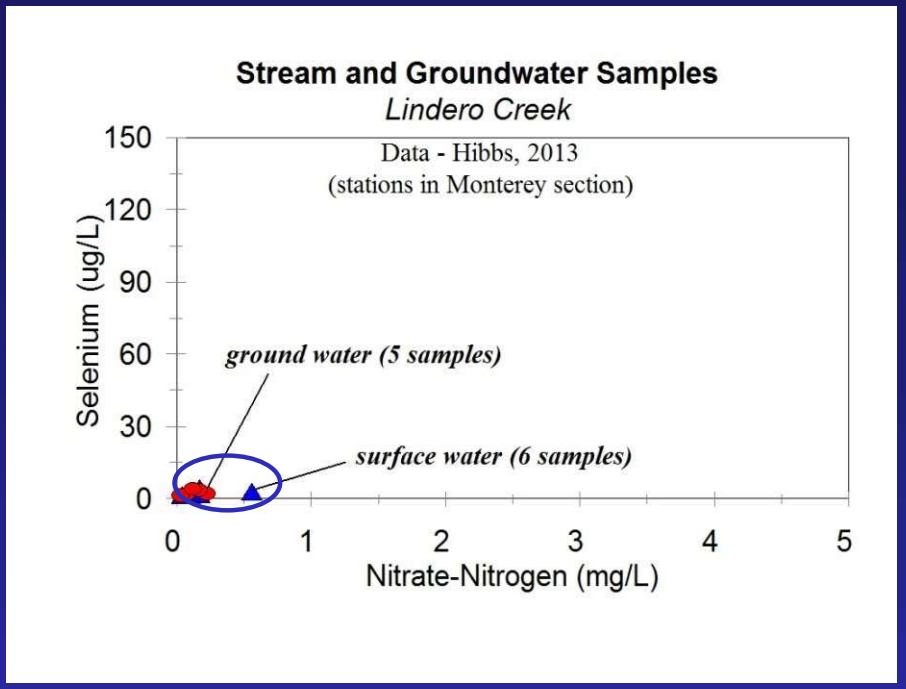
Stream Samples:
Las Virgenes Creek above 101 Freeway

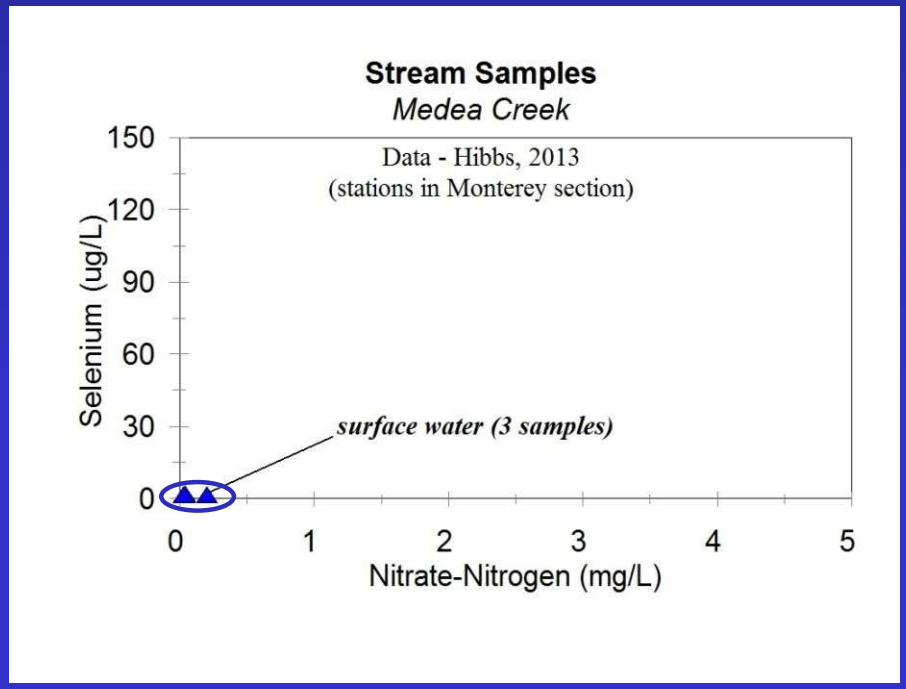


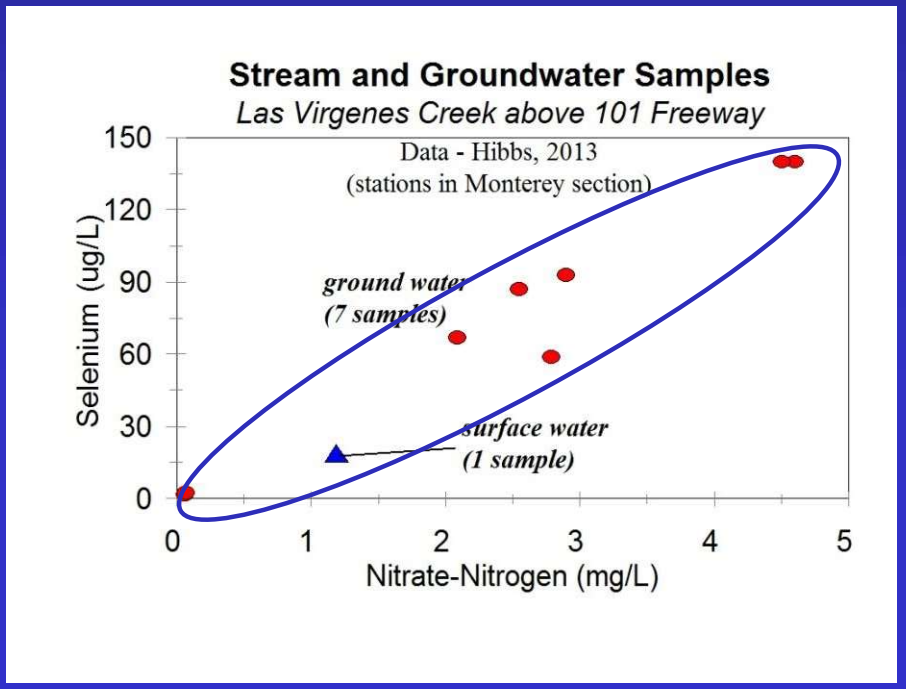
Stream Samples:
Malibu Creek Watershed




Stream and Groundwater Samples
Lang Creek
Data - Hibbs, 2013
(stations in Monterey section)
Selenium (ug/L)
Nitrate-Nitrogen (mg/L)
ground water
surface water
0
30
60
90
120
150
0
1
2
3
4
5

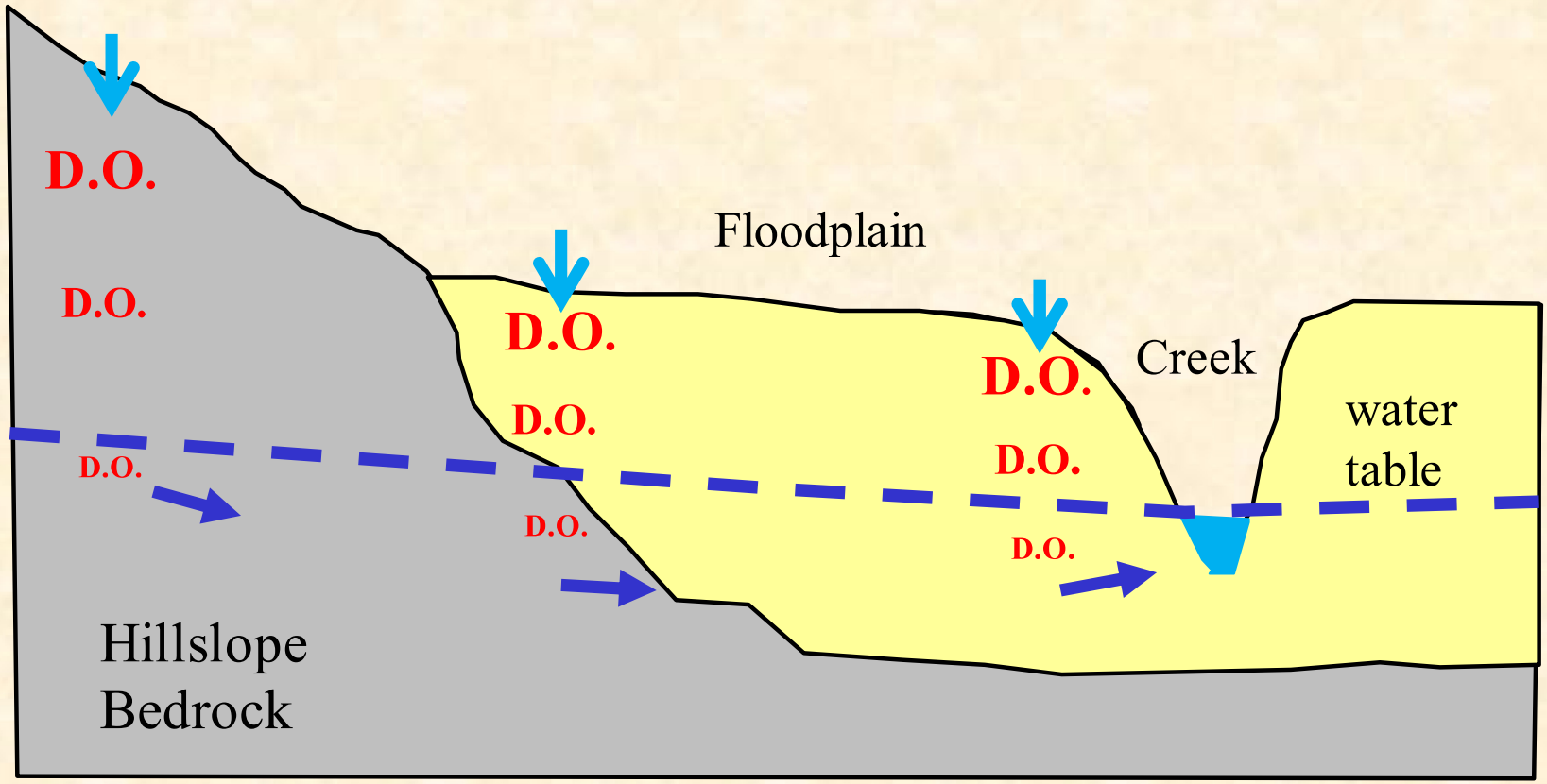

Stream and Groundwater Samples
Lindero Creek
Data - Hibbs, 2013
(stations in Monterey section)
Selenium (ug/L)
Nitrate-Nitrogen (mg/L)
ground water (5 samples)
surface water (6 samples)
0
30
60
90
120
150
0
1
2
3
4
5


Stream Samples
Medea Creek
Data - Hibbs, 2013
(stations in Monterey section)
Selenium (ug/L)
Nitrate-Nitrogen (mg/L)
surface water (3 samples)
0
30
60
90
120
150
0
1
2
3
4
5


Stream and Groundwater Samples
Las Virgenes Creek above 101 Freeway
Data - Hibbs, 2013
(stations in Monterey section)
Selenium (ug/L)
Nitrate-Nitrogen (mg/L)
ground water
(7 samples)
surface water
(1 sample)
0
30
60
90
120
150
0
1
2
3
4
5

Without Anthropogenic Nitrate

Limited Ground Recharge – Sluggish Groundwater Flow
D.O. Consumed by Soil Organic Carbon and Red./Ox.



Precipitation Recharge

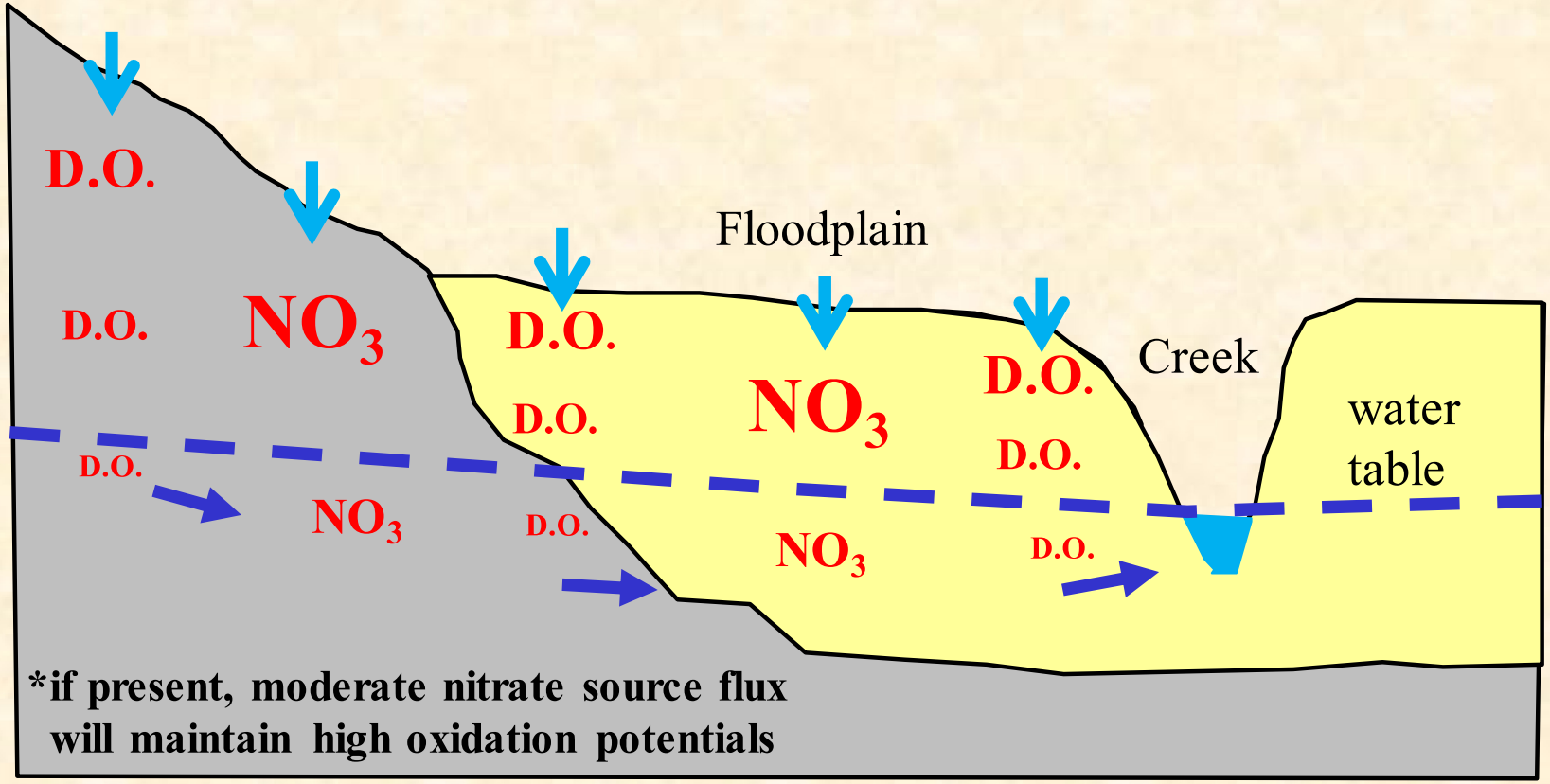
Groundwater Flow

NO_3 **Nitrate**

D.O. Dissolved Oxygen

With Anthropogenic Nitrate

The Addition of Anthropogenic (or any form of) Nitrate will Maintain Higher Oxidation Potentials in Groundwater



Precipitation Recharge

Groundwater Flow

NO_3 **Nitrate**

D.O. **Dissolved Oxygen**

Relationship Between NO3, Se, D.O., and Groundwater

- Selenium bearing strata (Monterey/Modelo) in the shallow aquifers connected to Santa Monica Mountain Creeks show a nitrate-selenium correlation probably due to selenium oxidization by anthropogenic nitrate

- Nitrate may be a relic from historic agriculture, septic tanks, ranch animals, and sludge injection; furthermore, nitrate may be loaded today from wastewater application

- Nitrate sources were not covered here, but we have collected a lot of groundwater data, nitrate isotopes and other data and we are looking at this issue now

Broader Technical Recommendations in LA Basin

What is the nature of the geology? Where are selenium bearing rocks and sediments located and where have their erosion products been deposited? Also, how do other trace elements in Miocene marine strata behave hydrochemically?

If streams gain baseflow from groundwater, and if the geology favors nitrate-facilitated oxidation of selenium from strata, it may be wise to restrict application of treated waste-water at green-belts and other vegetated areas