New Models on Sources of Selenium in Las Virgenes Creek

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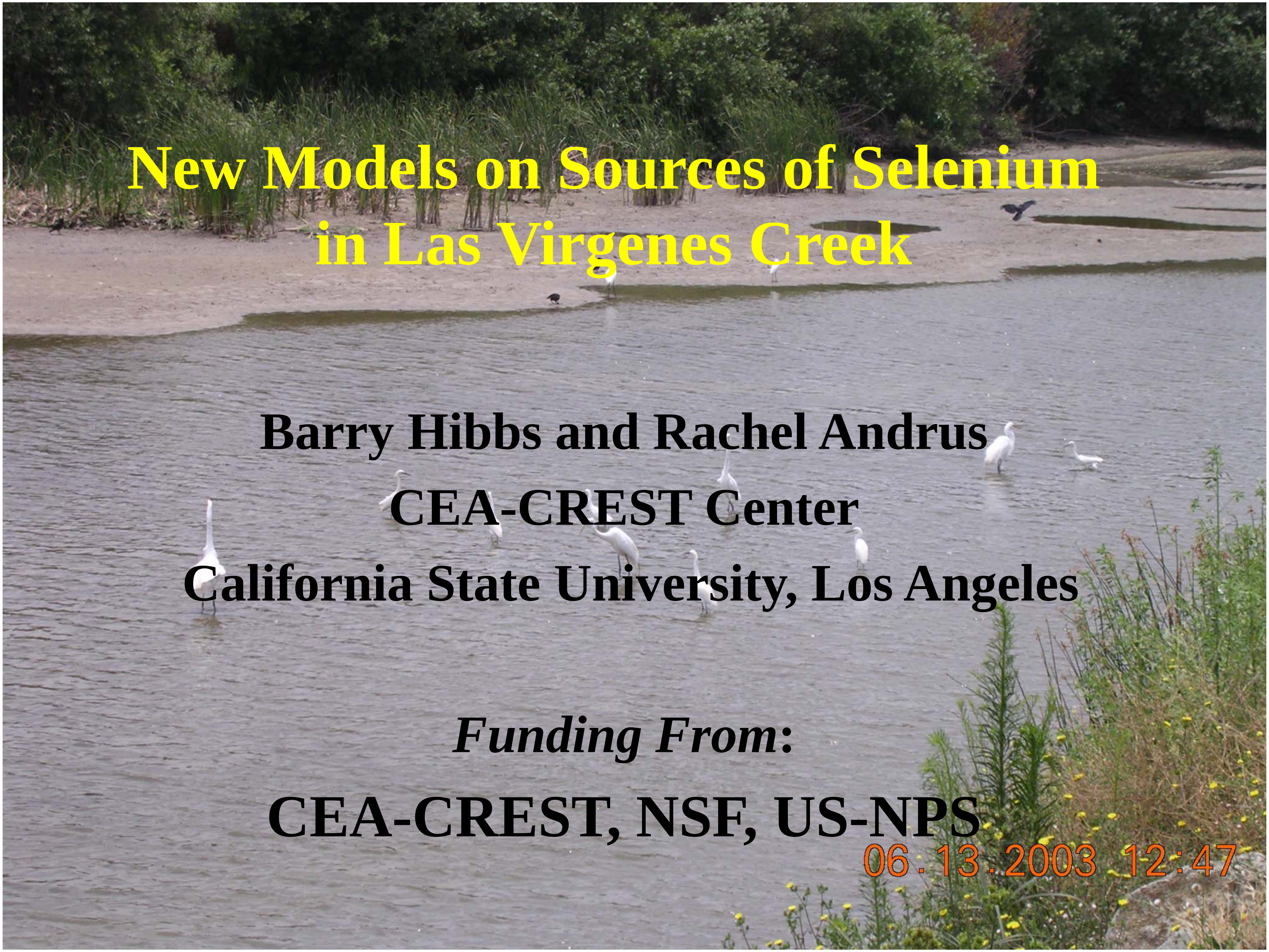
CEA-CREST Center

California State University, Los Angeles

***Funding From*:**

CEA-CREST, NSF, US-NPS

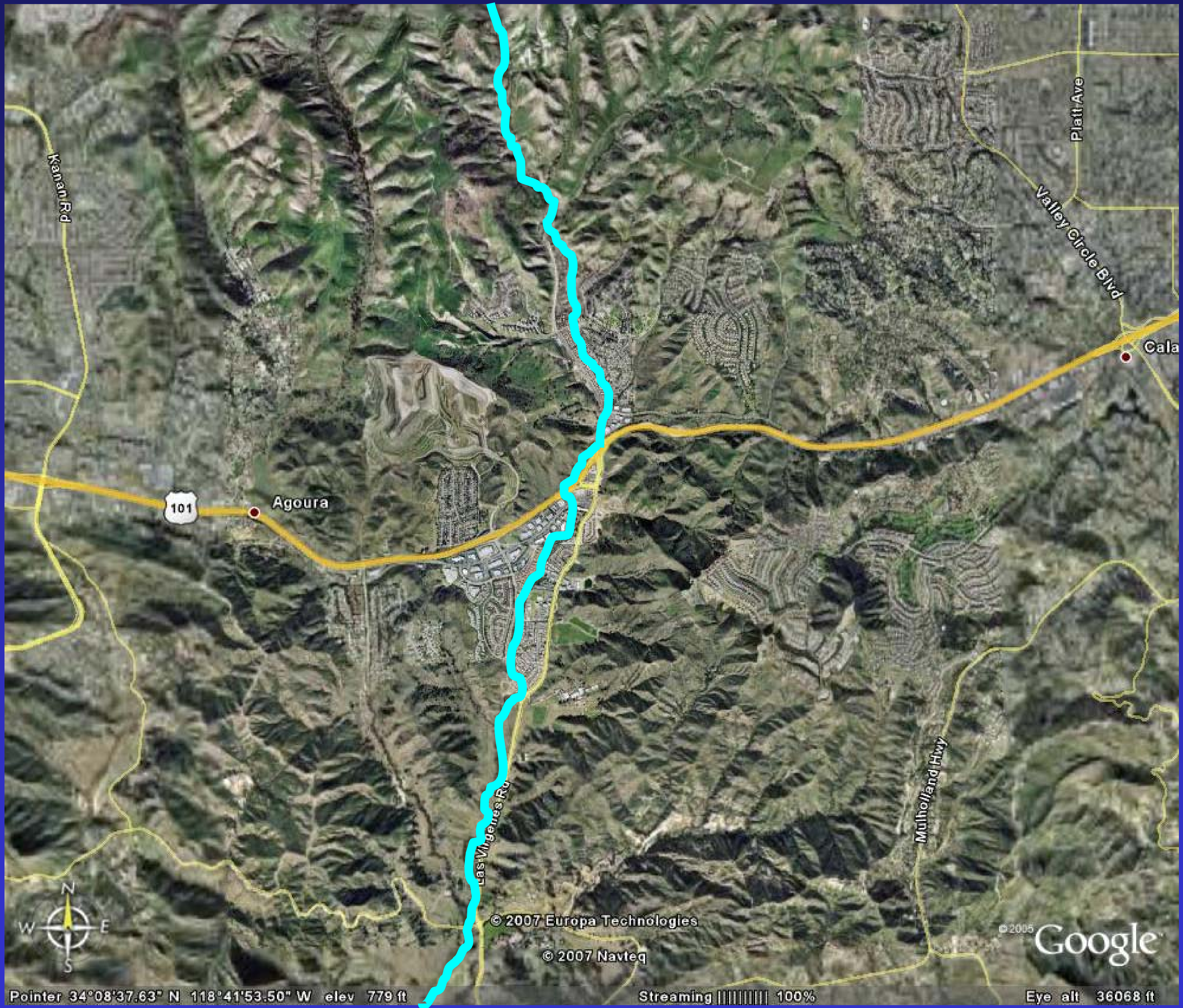


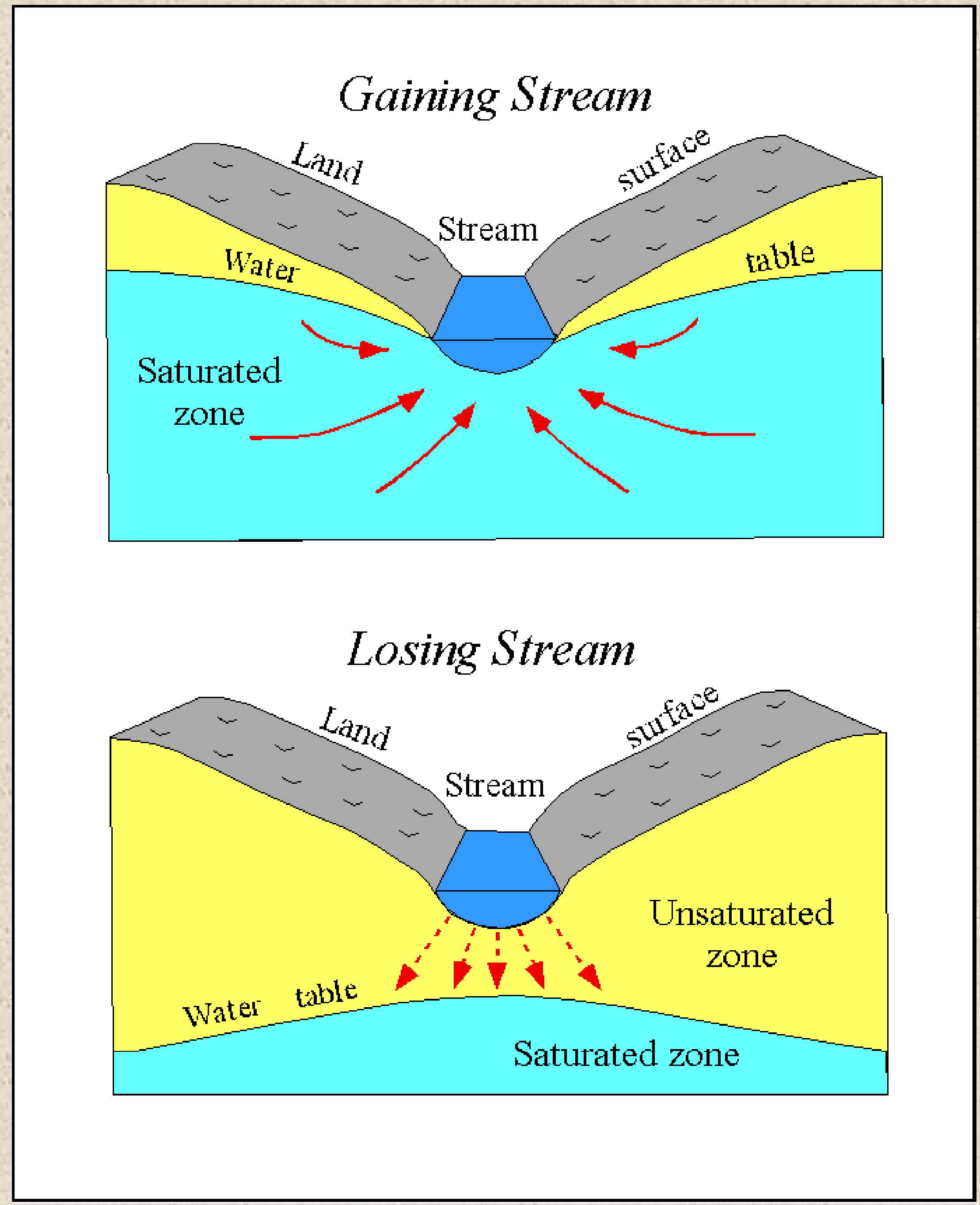
Objectives

- Perform a reconnaisance analysis of streamflow water quality and groundwater quality in the Las Virgenes stream/aquifer system - as followup to discussions with Horns/Kim – Calabasas monitoring group.
- Provide initial characterization on the interrelationships between surface water and shallow groundwater in the stream/aquifer system.
- Evaluate distribution of selenium and nitrate in surface water and groundwater in the watershed.
- Discuss a model that may point to an anthropogenic oxidizing agent for releasing selenium into groundwater from proposed redox processes in aquifer and vadose zone soils.


Las Virgenes Creek
Los Angeles Basin
N
W
E
S
Image © 2007 TerraMetrics
Image © 2007 DigitalGlobe
© 2007 Navteq
© 2005 Google
Pointer 33°47'03.64" N 117°55'55.31" W elev 120 ft
Streaming |||||||||| 100%
Eye alt 28.81 mi

Study Area Location Map





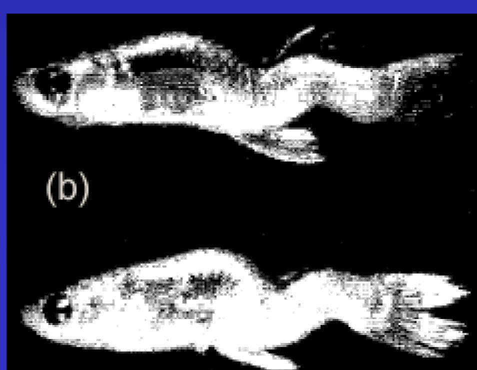
- Gaining stream condition when stream stage elevation is lower than water table elevation

- Losing stream condition when stream stage elevation is higher than water table elevation

Selenium: Why It Matters

<u>Toxic Trace Element:</u>

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



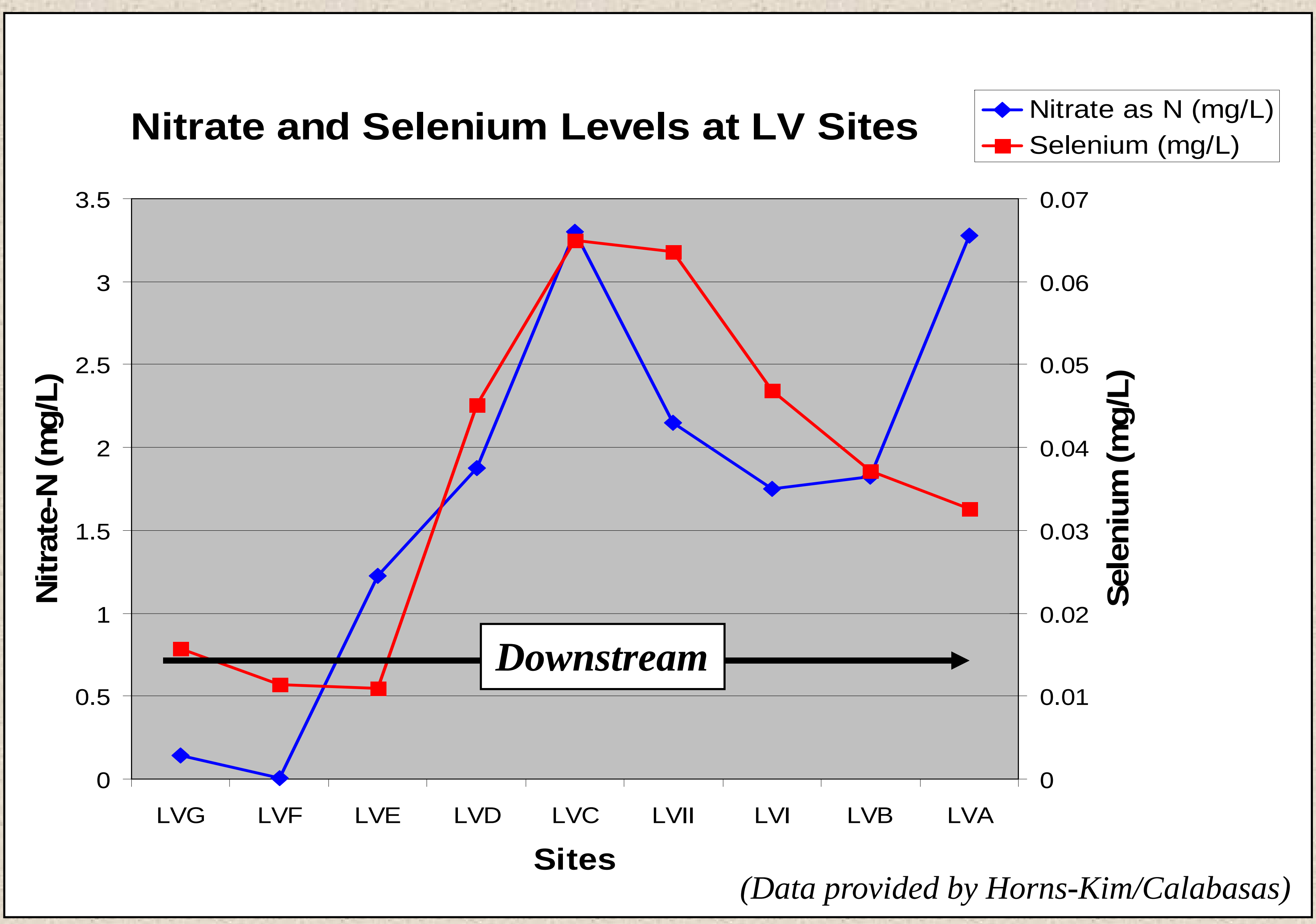
Selenium Levels of Concern

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

American White Pelicans

Great Blue Heron


Nitrate and Selenium Levels at LV Sites
Nitrate as N (mg/L)
Selenium (mg/L)
Nitrate-N (mg/L)
Selenium (mg/L)
3.5
3
2.5
2
1.5
1
0.5
0
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Downstream
LVG
LVF
LVE
LVD
LVC
LVII
LVI
LVB
LVA
Sites
(Data provided by Horns-Kim/Calabasas)

Los Angeles Basin: Areas Found with High Selenium And Nitrate in Streams

Problem – Many Foothills in LA Basin Consist of Marine Shales and Siltstones, Containing Selenium

Puente Formation – selenium bearing shale

Selenium bearing deposits eroded from foothills

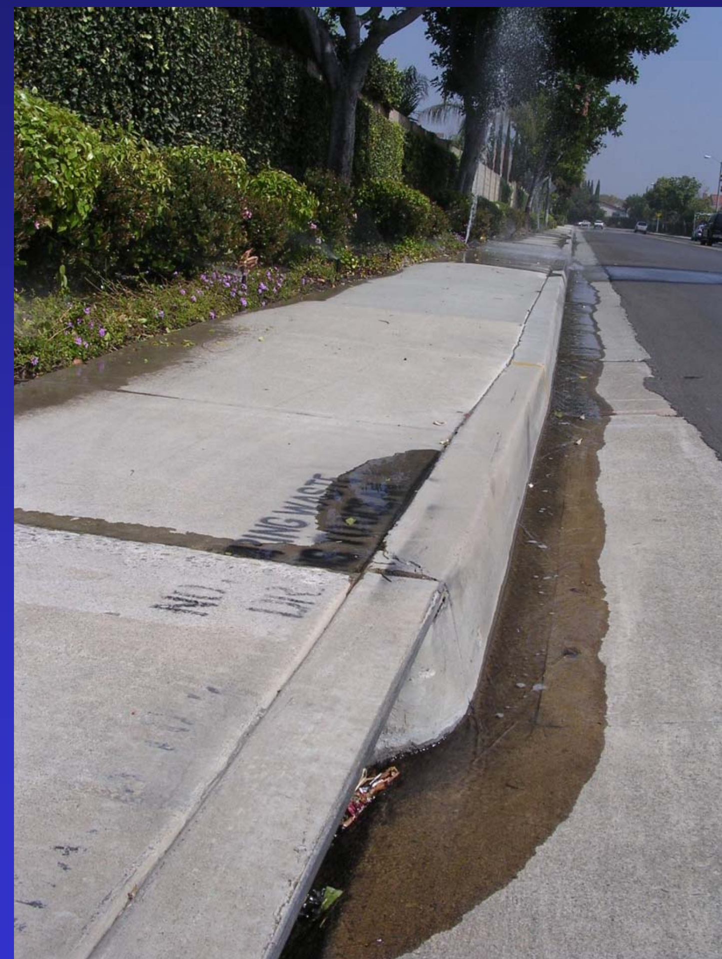
Methods

- Identification of springs, drains, and surface water stations for dry weather sampling between Ahmanson Ranch and White Oak Farm.
- Measurement of index parameters on-site (pH, specific conductance, temperature, dissolved oxygen).
- Sampling for standard inorganic constituents, selenium, selenium species, and stable isotopes of oxygen, hydrogen, and sulfur.
- Interpretation of results with geochemical plotting procedures.


LV Iron Spring

Urban runoff flows onto city streets….

…..and leaks into storm-drains

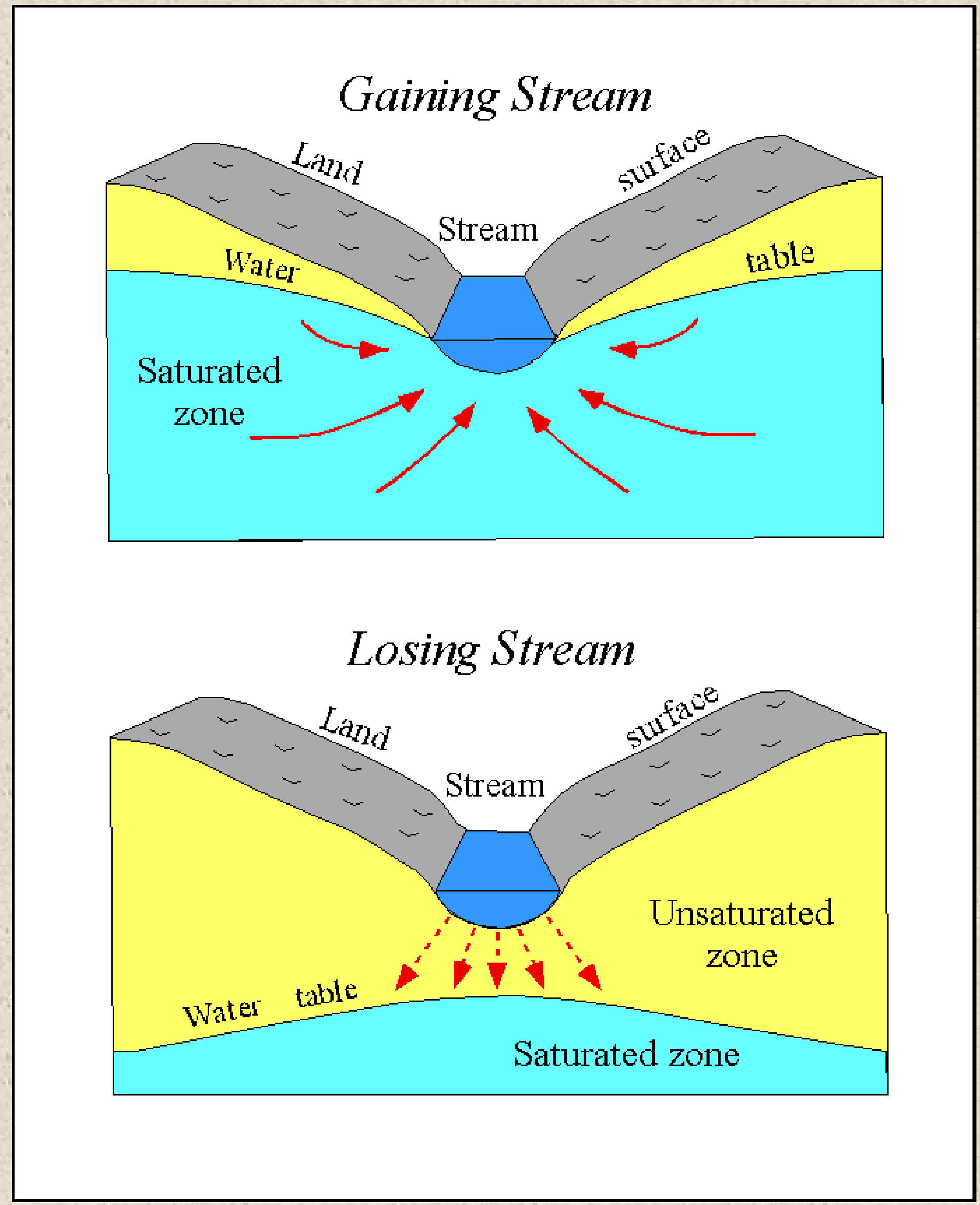


Do subdrain flows contain urban runoff primarily?

…..or are they sourced from groundwater?

Objective:

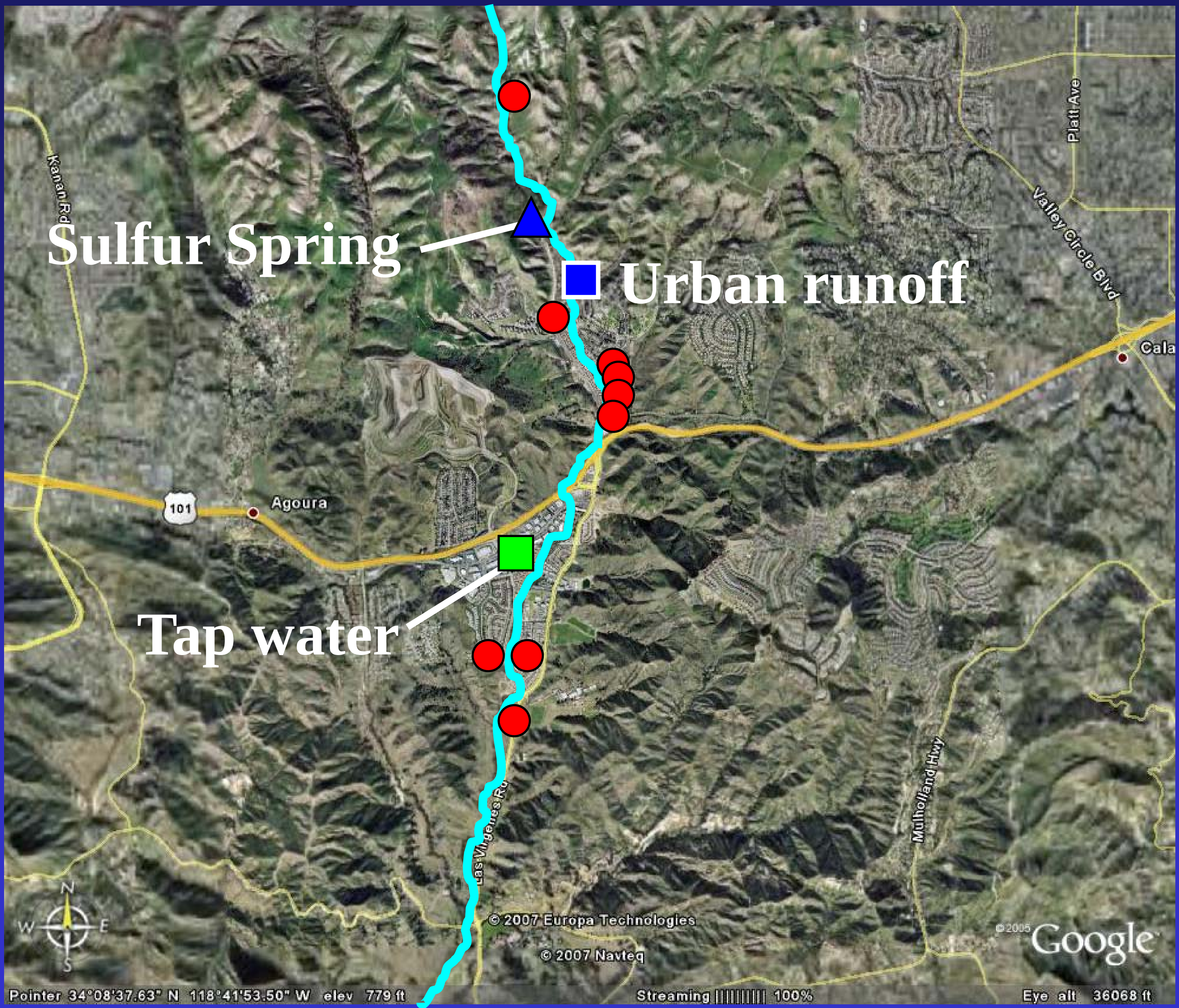
What is the Hydraulic Relationships Between Las Virgenes Creek and Associated Shallow Aquifers?



- Gaining stream condition when stream stage elevation is lower than water table elevation

- Losing stream condition when stream stage elevation is higher than water table elevation

Sample Identification Map



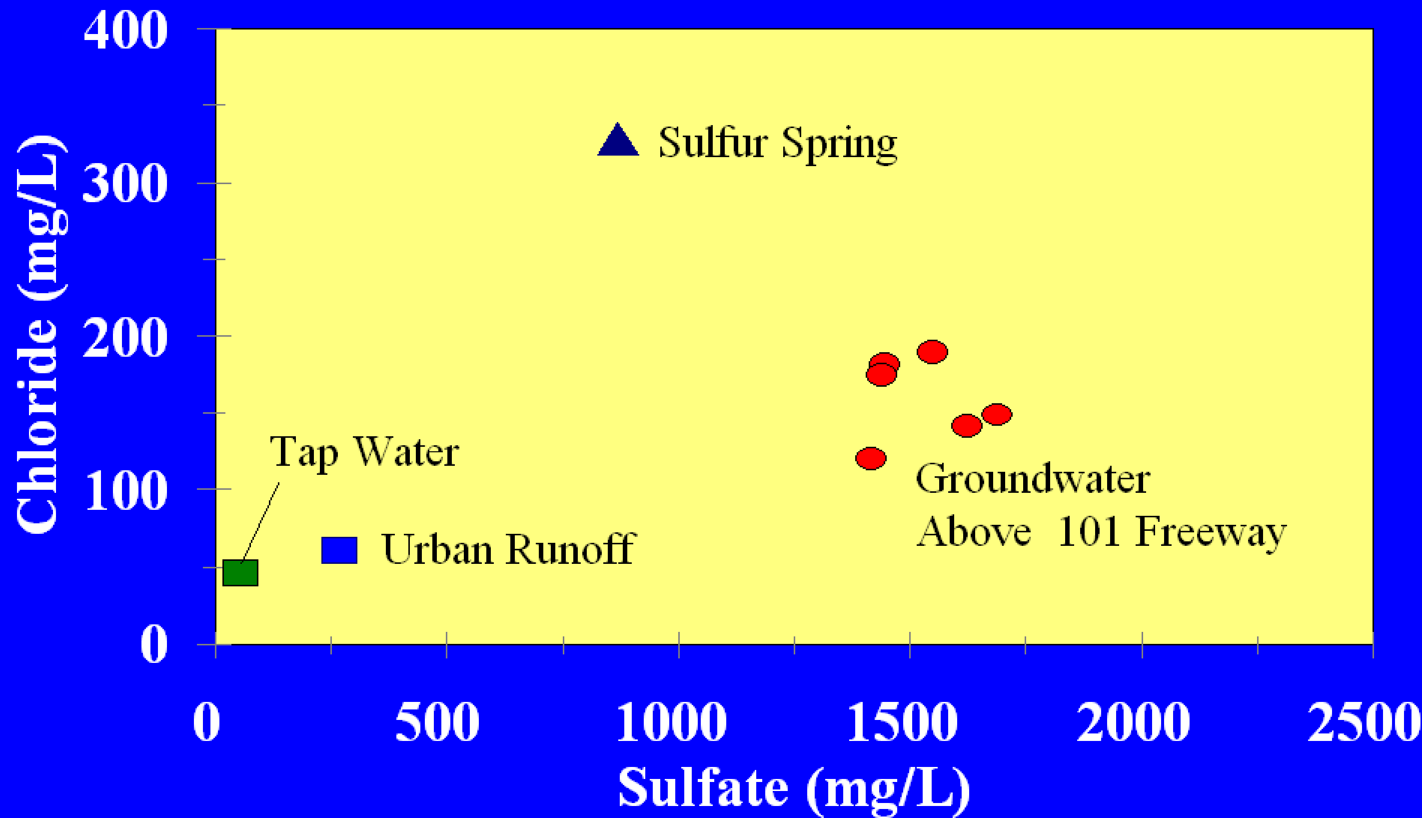
Explanation

Groundwater Sample

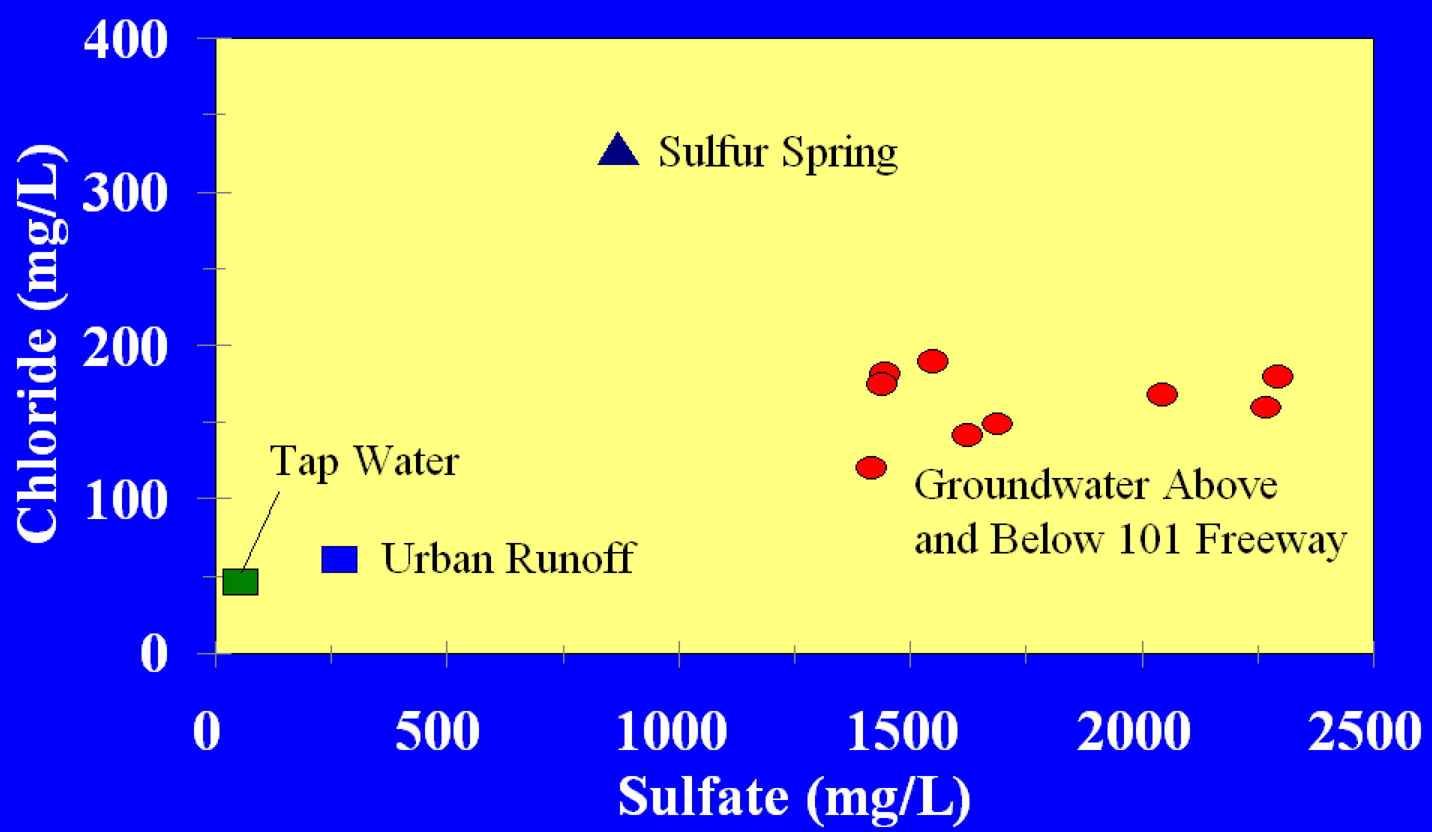
Tap water Sample

Urban runoff Sample

Sulfate vs Chloride Scatter Plot



Sulfate vs Chloride Scatter Plot



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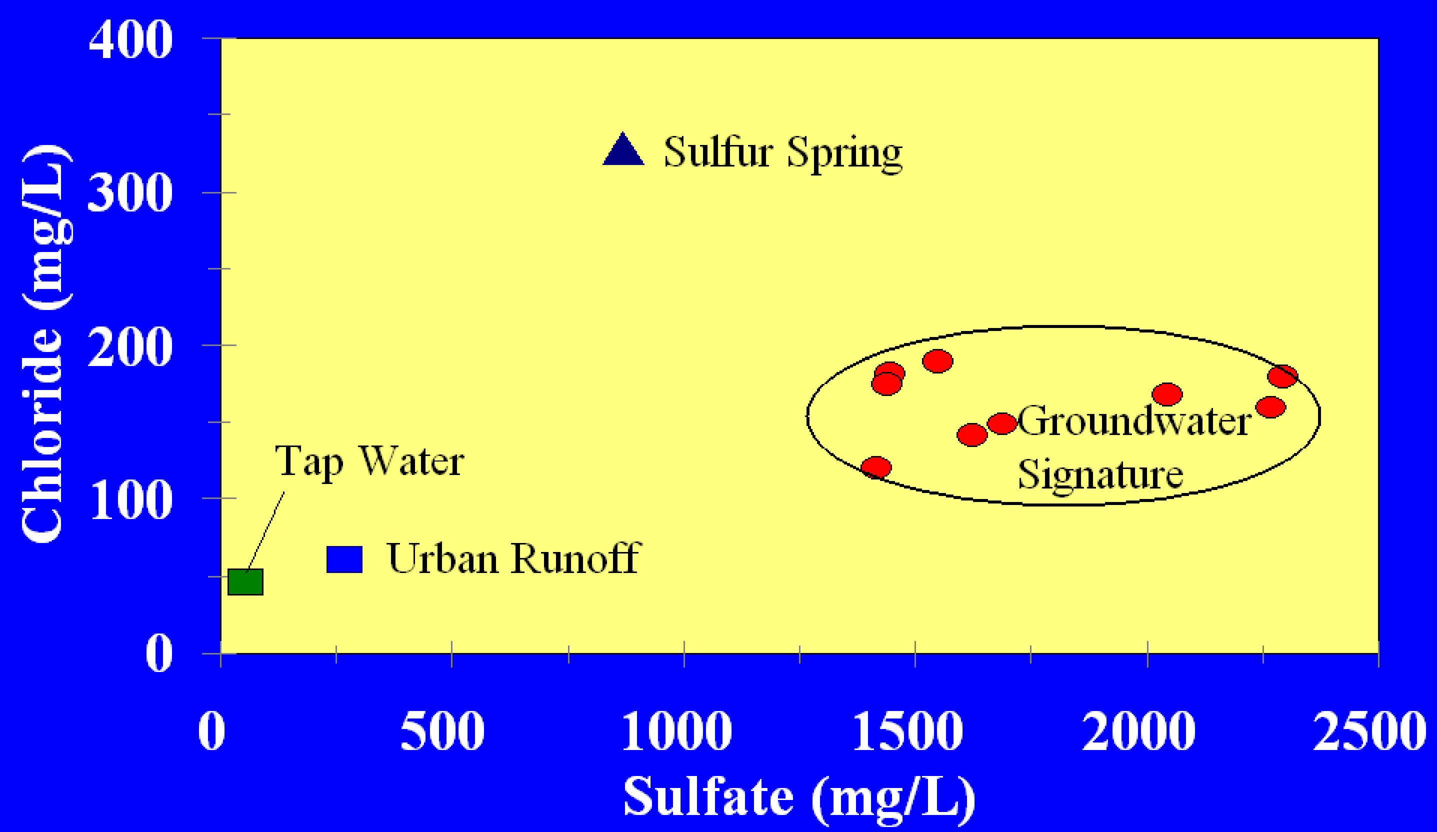
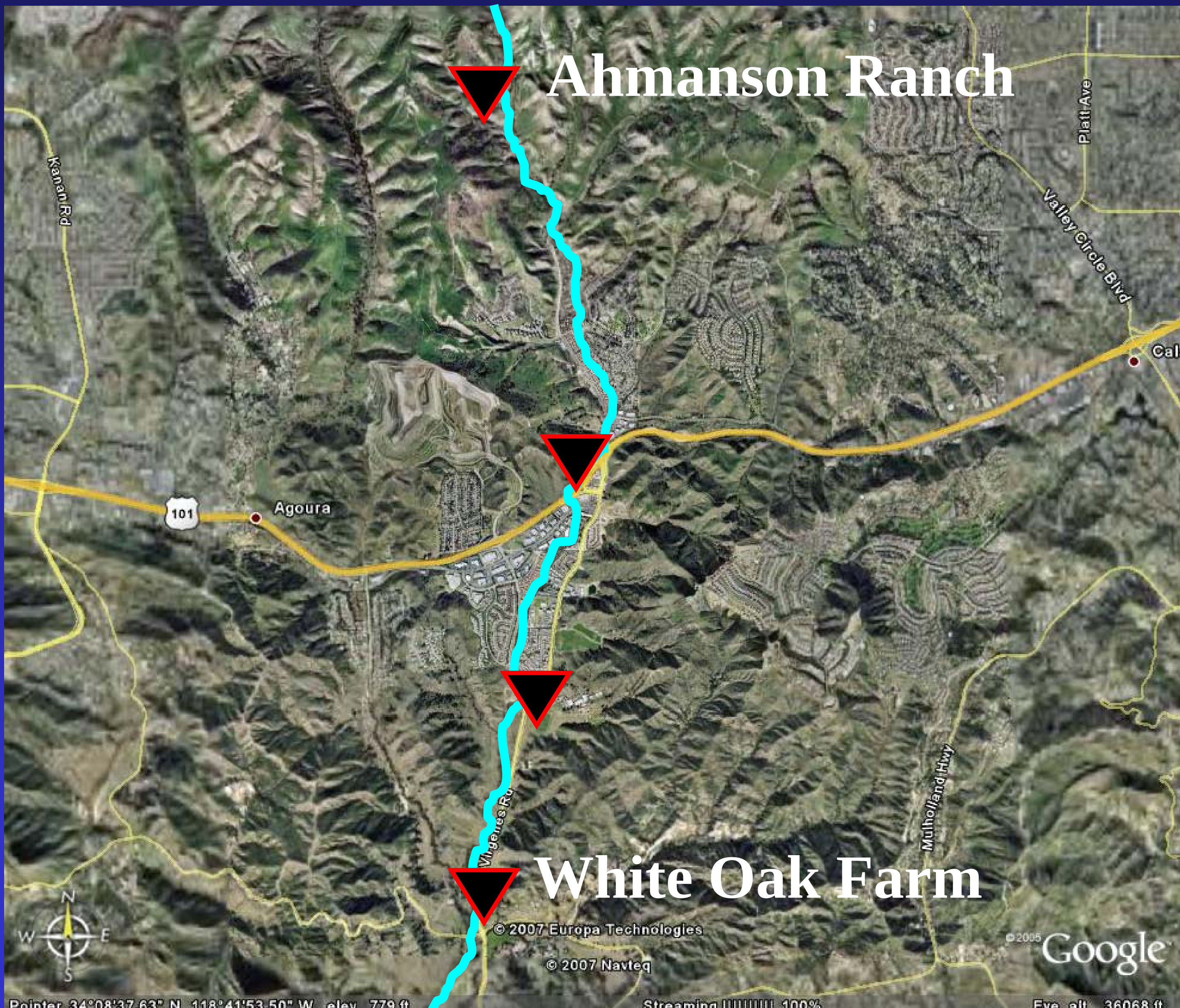


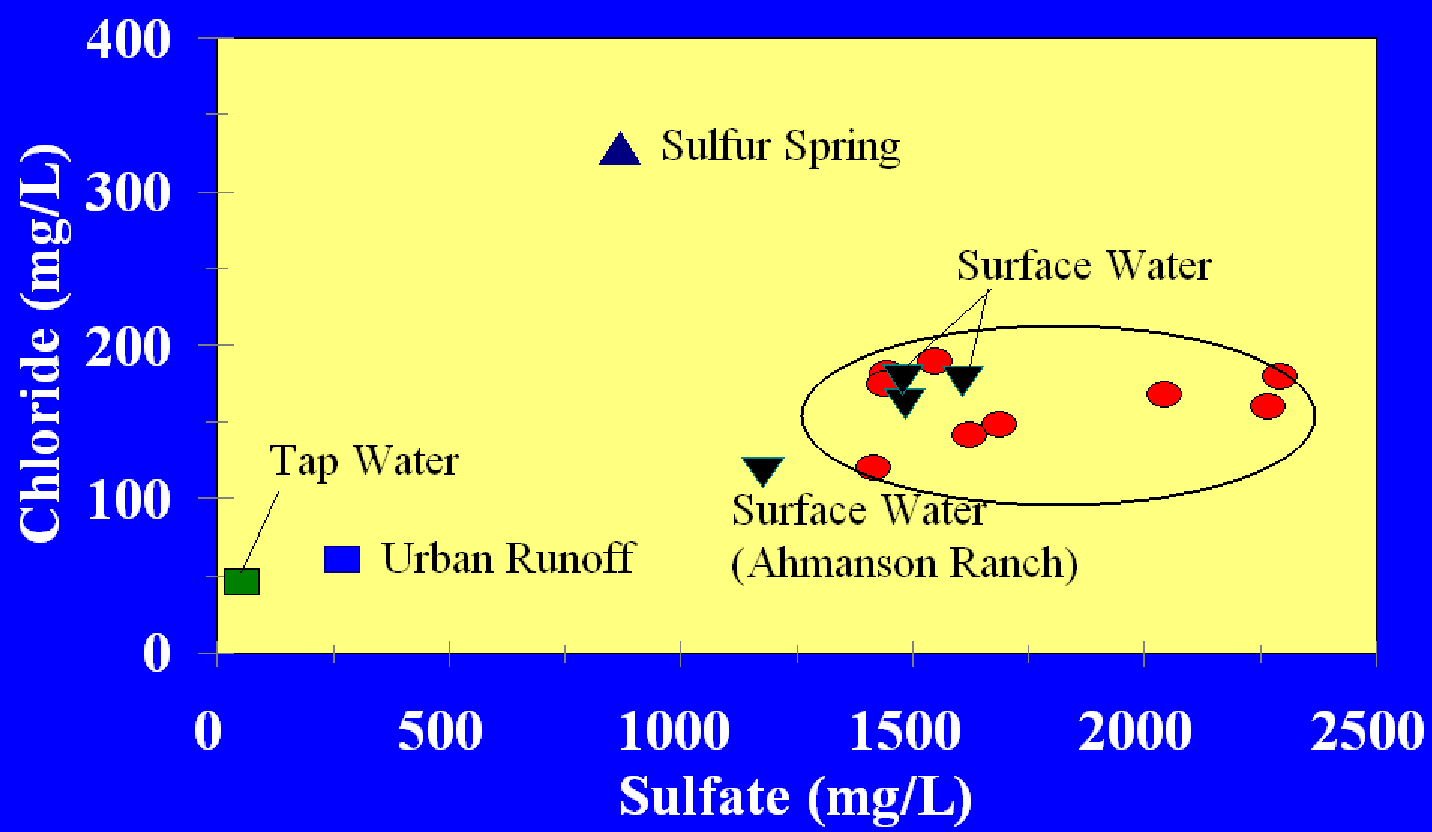
Surface Water Sampling Stations



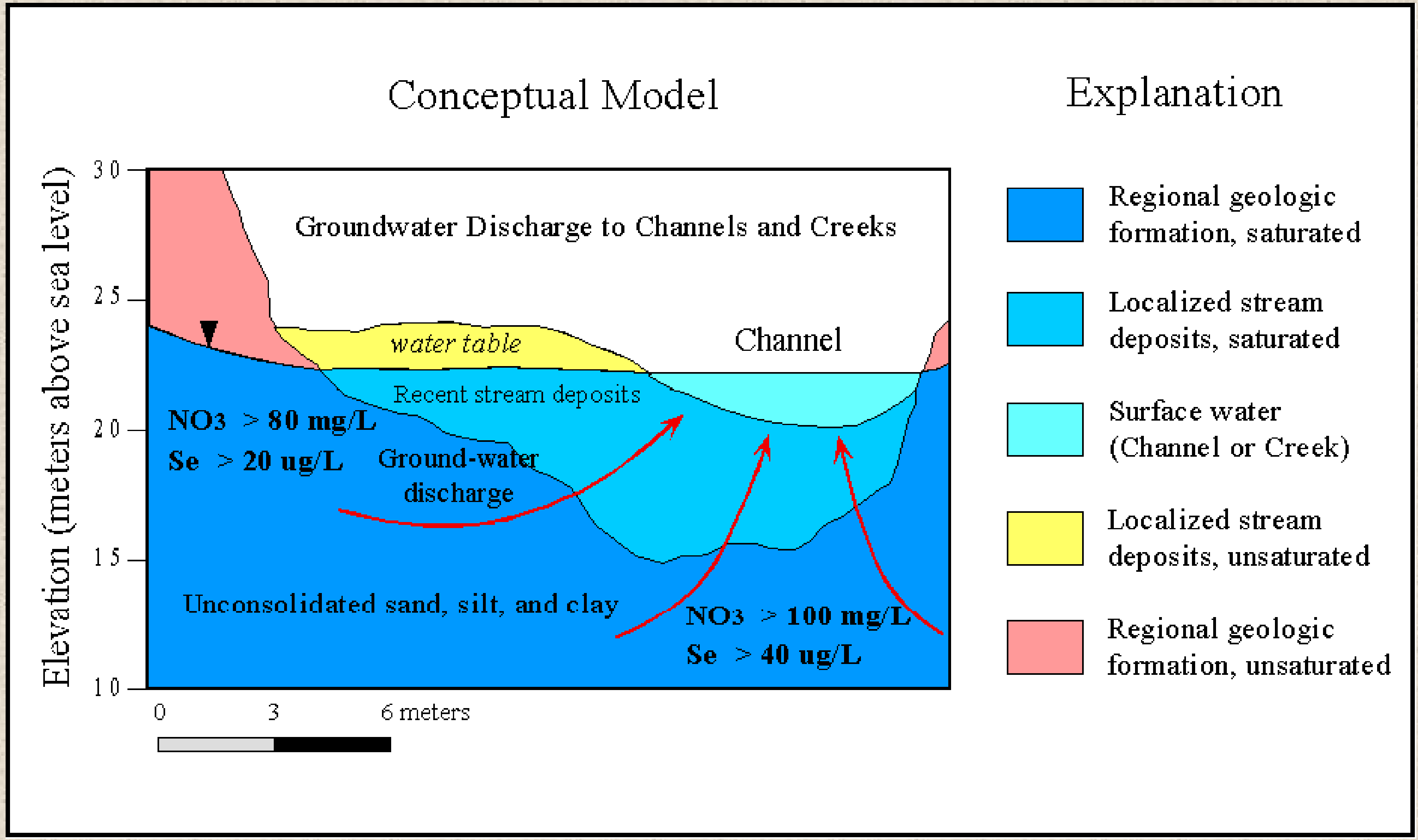
Explanation

Surfacewater Sample

Sulfate vs Chloride Scatter Plot



Las Virgenes Creek Flow Appears to be Dominantly Groundwater Derived During Dry Weather Flows

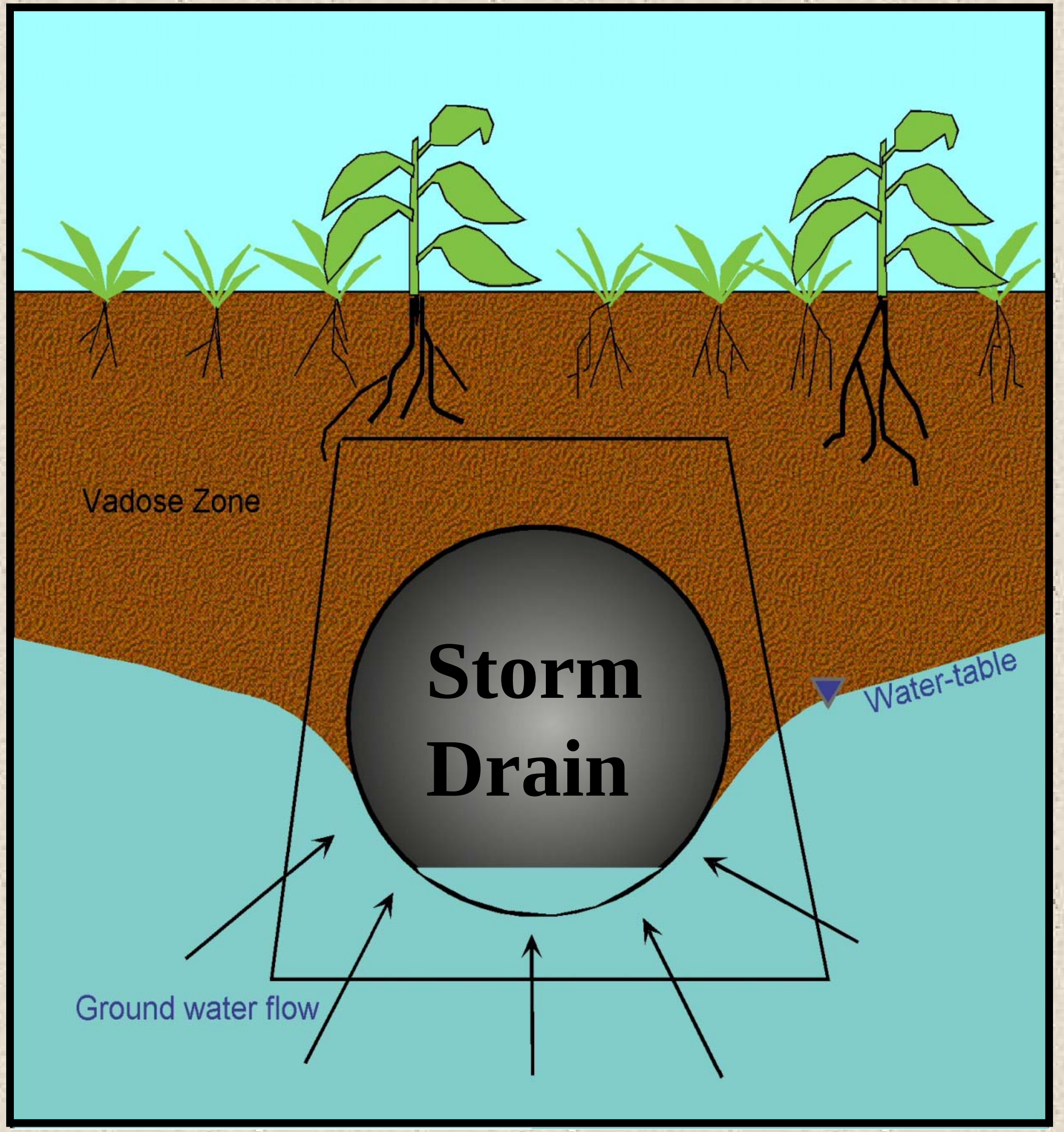


Question:

What is the Source Flows
In the Urban Subdrains During
Dry Weather Conditions?

New storm drains in San Diego Creek leaks from seepage from shallow groundwater

Seepage faces where groundwater percolates through joints in storm drain pipe



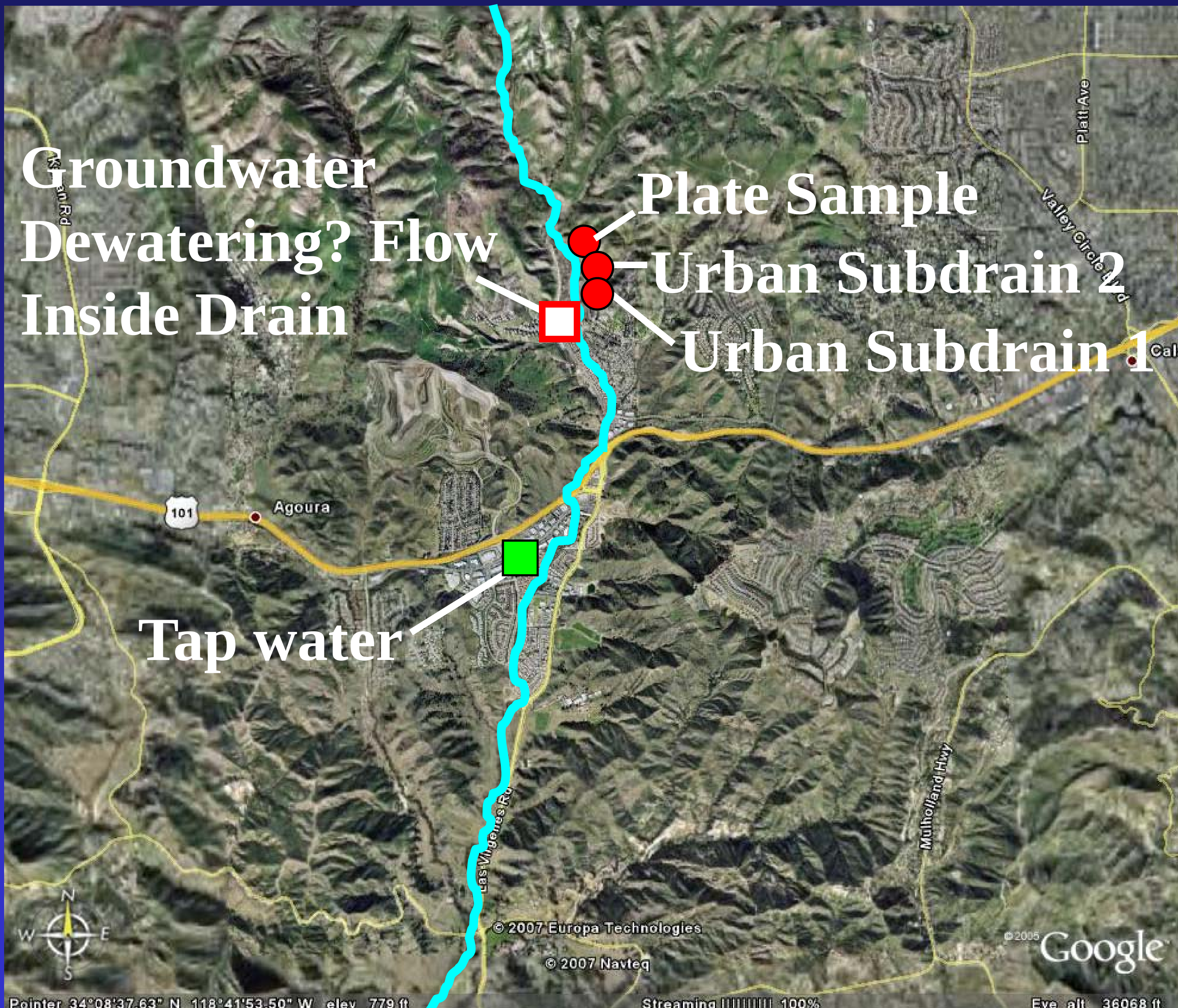
Conceptual model for leakage of ground-water into storm drains. In San Diego Creek and in many other LA Basin creeks, shallow ground-water contains high concentrations of nutrients and in some cases, high concentrations of selenium and arsenic. These pollutants flow from storm drains into creeks and often account for large percentages of pollutant loading

Urban runoff flows onto city streets….

…..and leaks into storm-drains

Intentional groundwater dewatering system inside storm drain in Las Virgenes Creek?

Sample Identification Map

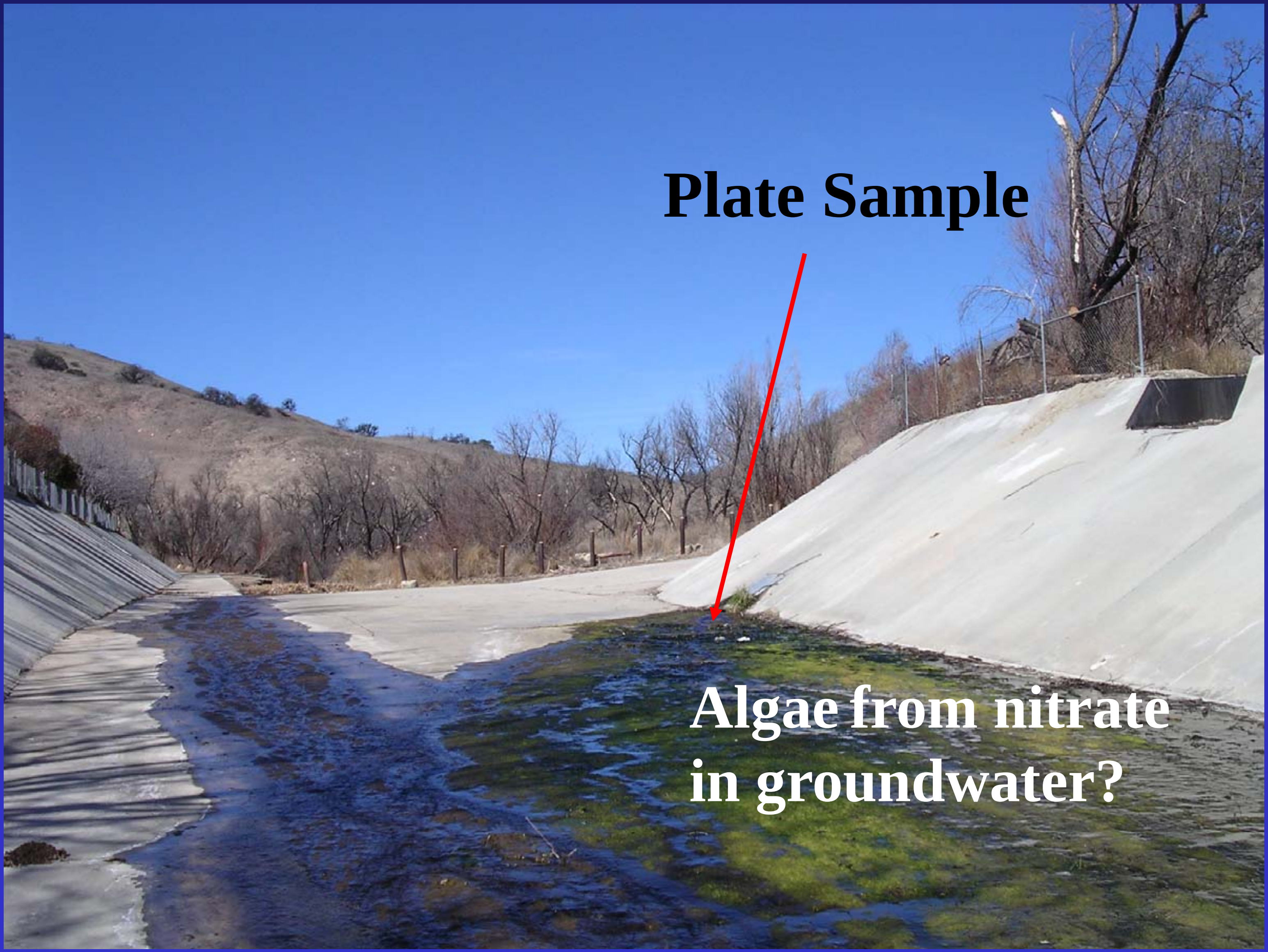


Explanation

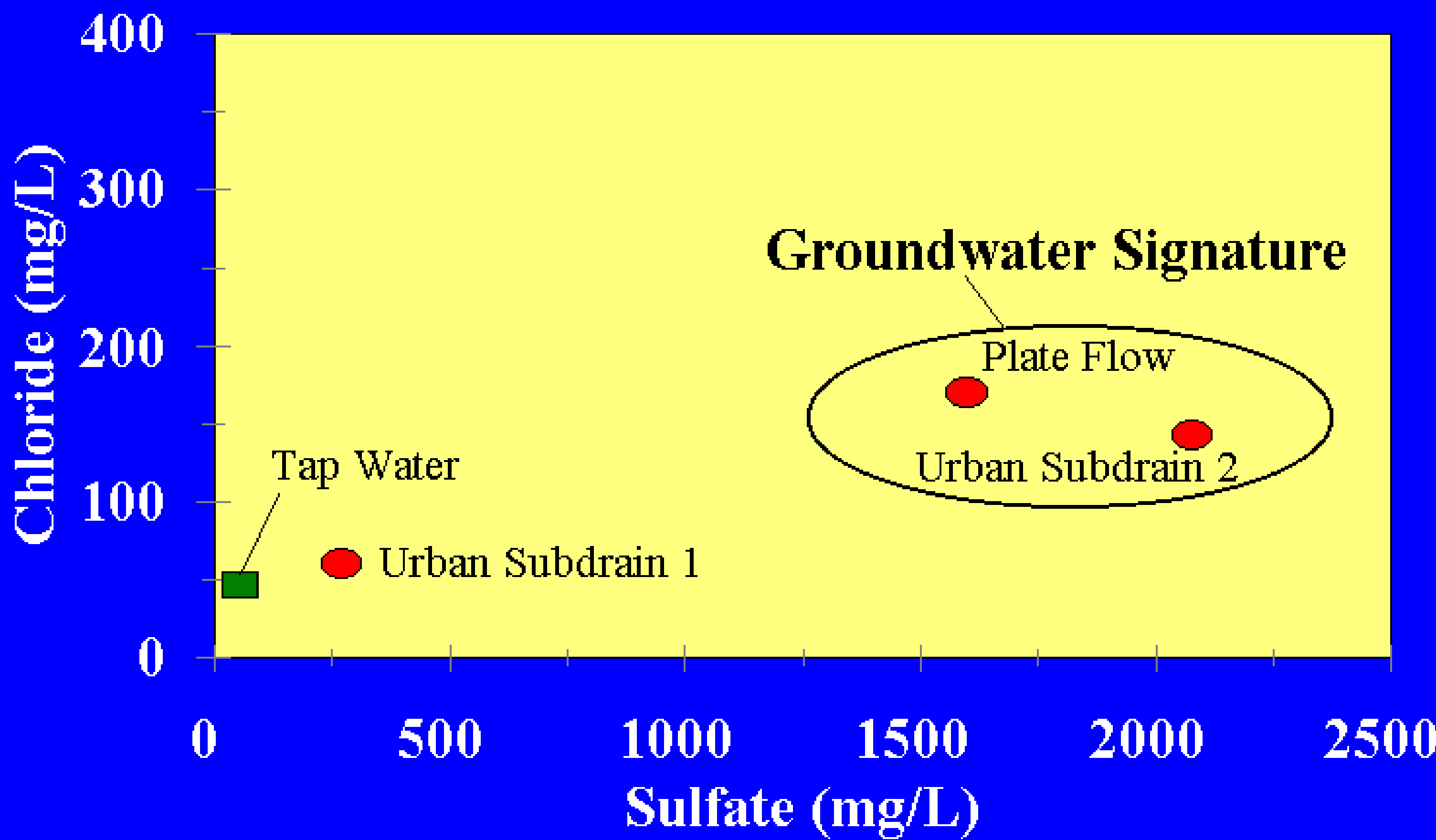
Subdrain Sample

Tap water Sample

Groundwater Loading? – Las Virgenes Creek



Sulfate vs Chloride Scatter Plot



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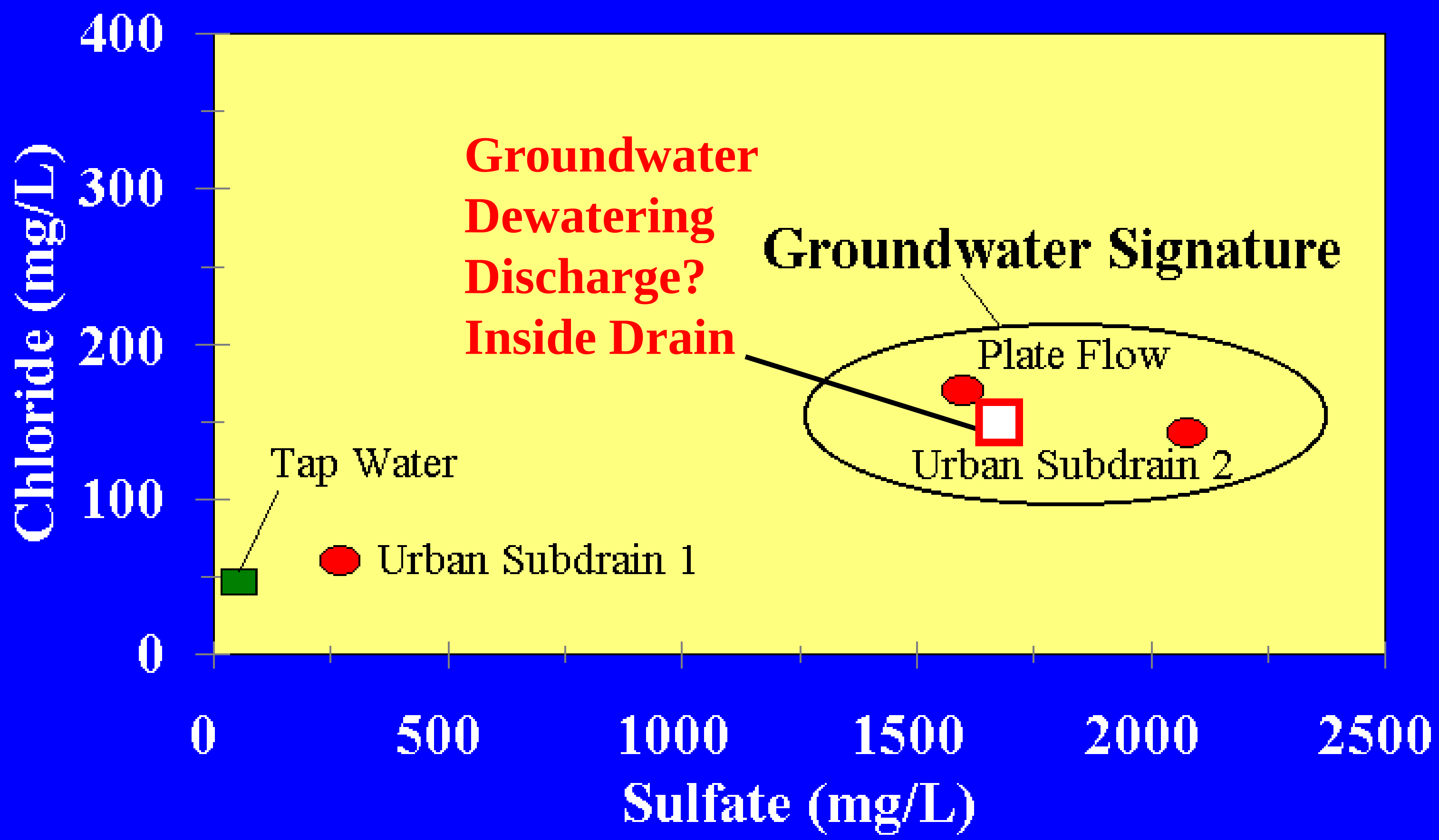
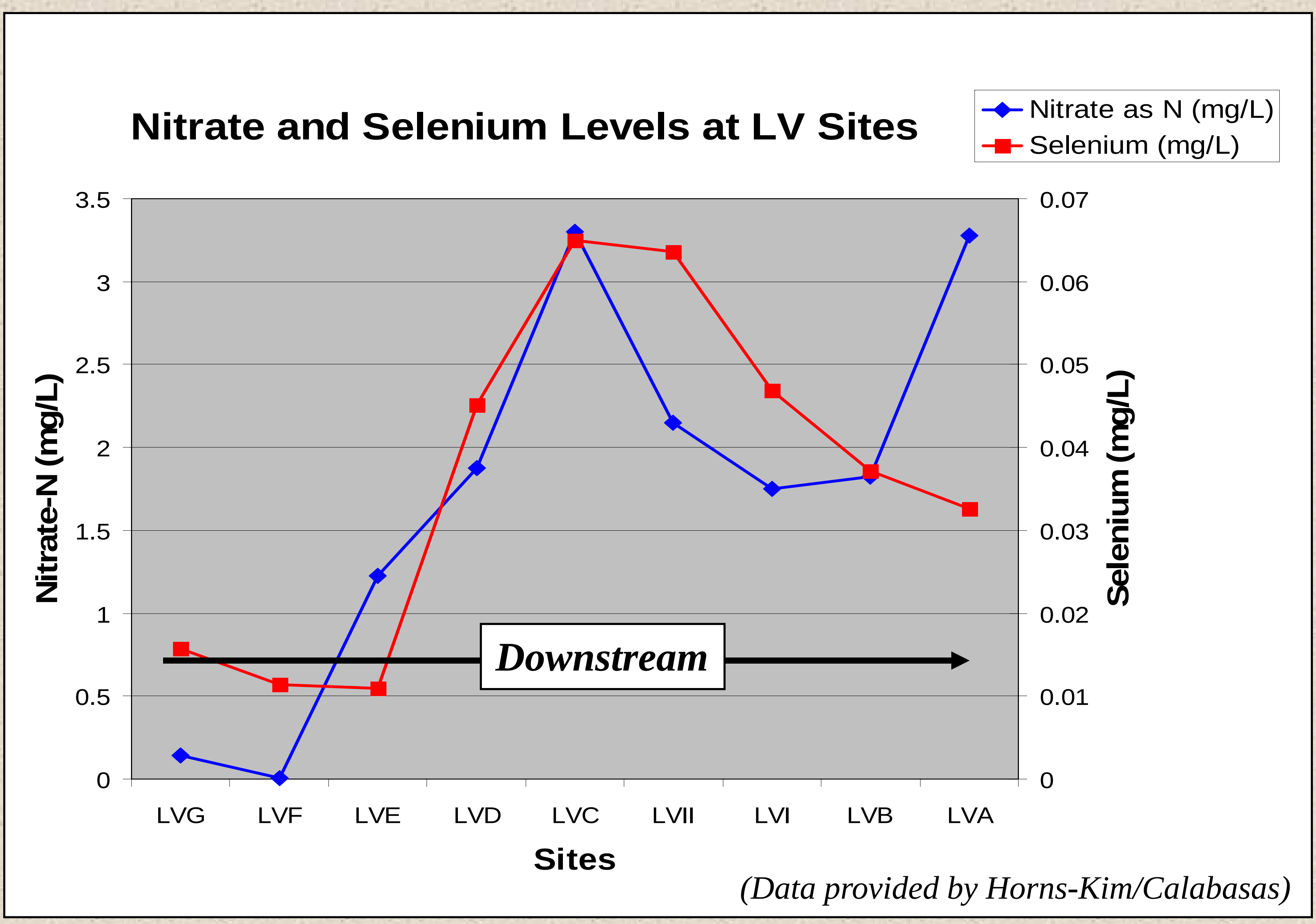


Select Water Quality Parameters in Subdrains and Dewatering Units

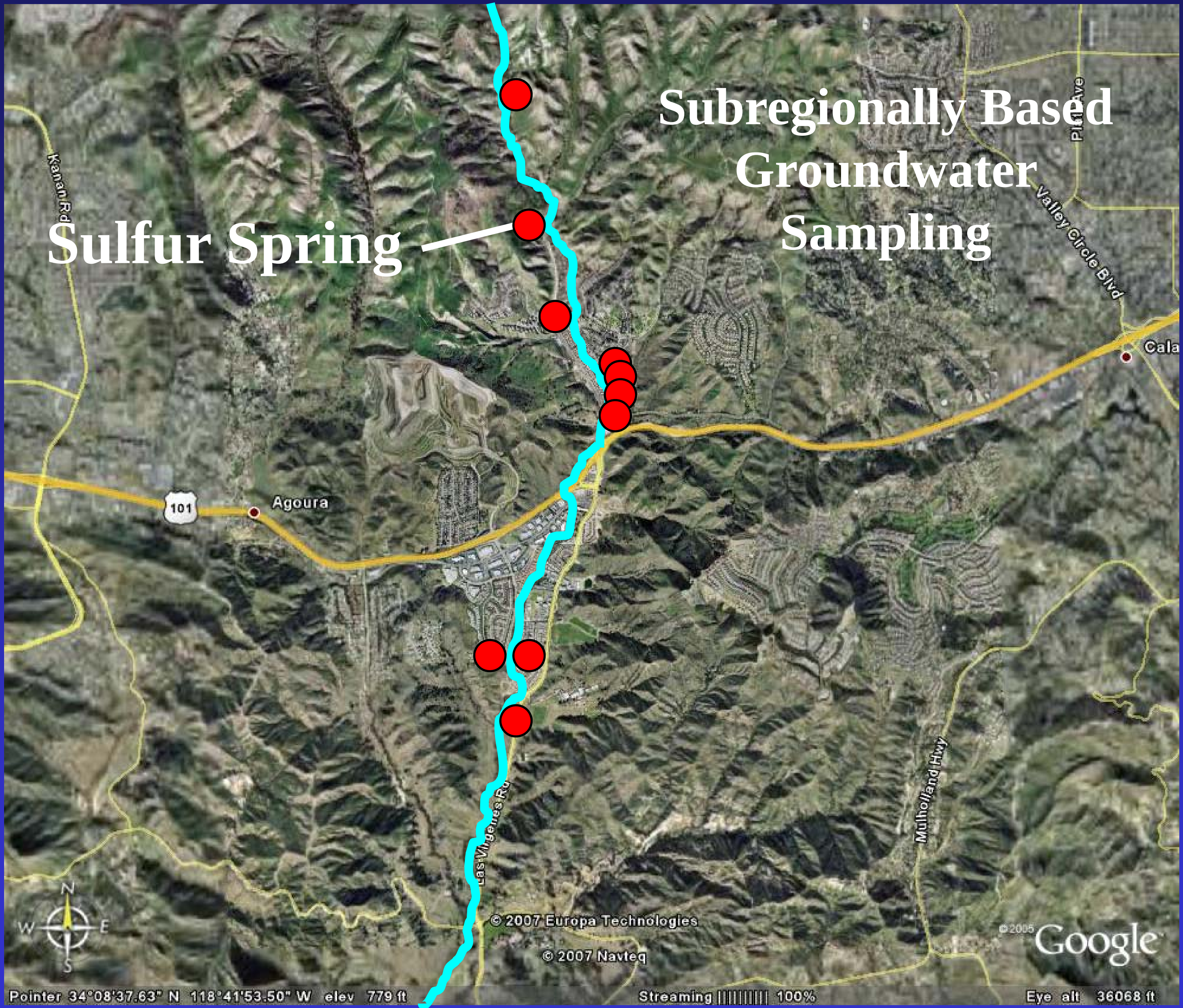
Sample Name	EC (uS/cm)	SO4 (mg/L)	NO3-N (mg/L)	Diss. Se (ug/L)
Urban Subdrain 1	960	272	1.2	1.6
Plate Flow	3732	1600	0.2	0.3
Dewatering Unit	3396	1688	3.1	41.5
Urban Subdrain 2	4021	2078	3.7	95.4


Nitrate and Selenium Levels at LV Sites
Nitrate as N (mg/L)
Selenium (mg/L)
Nitrate-N (mg/L)
Selenium (mg/L)
3.5
3
2.5
2
1.5
1
0.5
0
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Downstream
LVG
LVF
LVE
LVD
LVC
LVII
LVI
LVB
LVA
Sites
(Data provided by Horns-Kim/Calabasas)

Question:

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

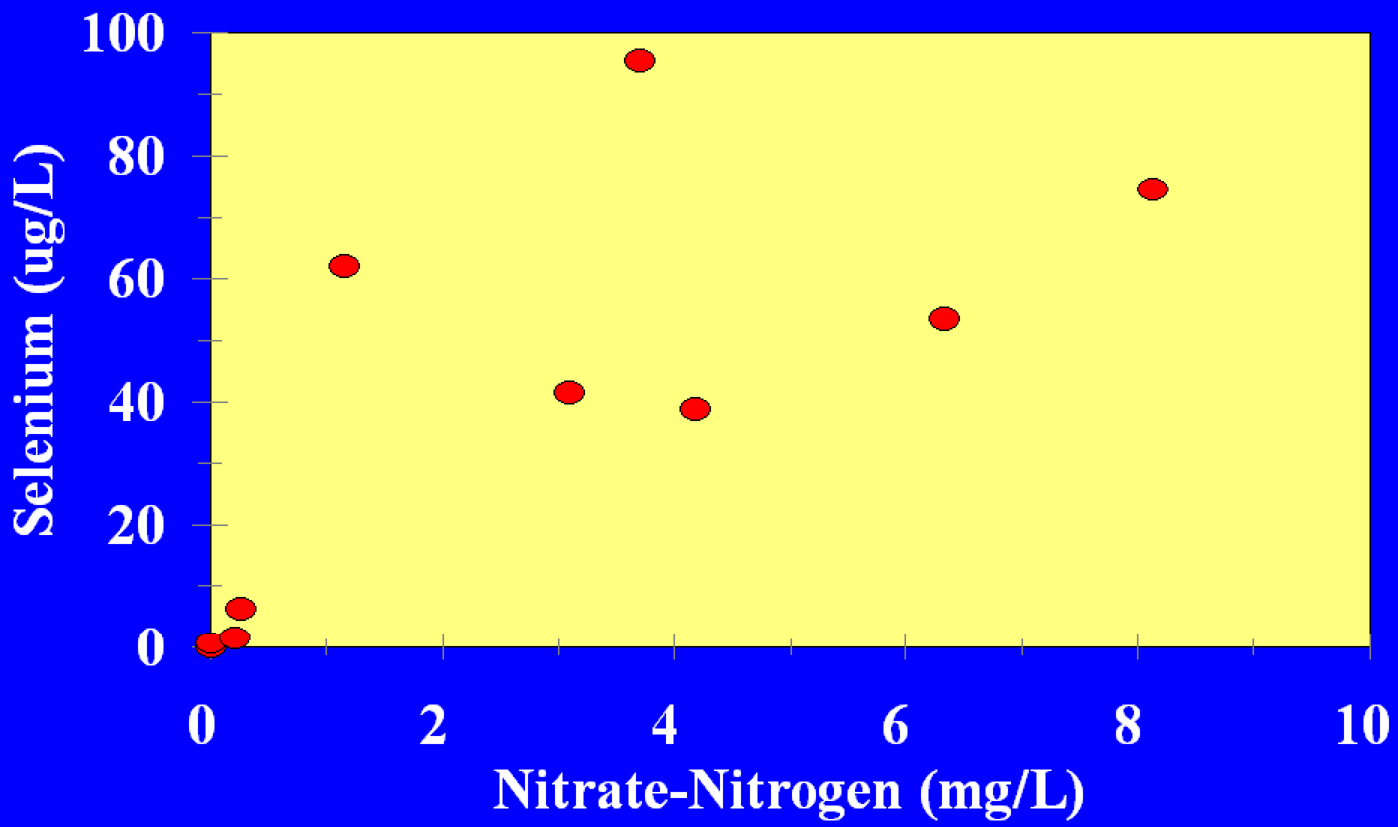
Study Area Location Map



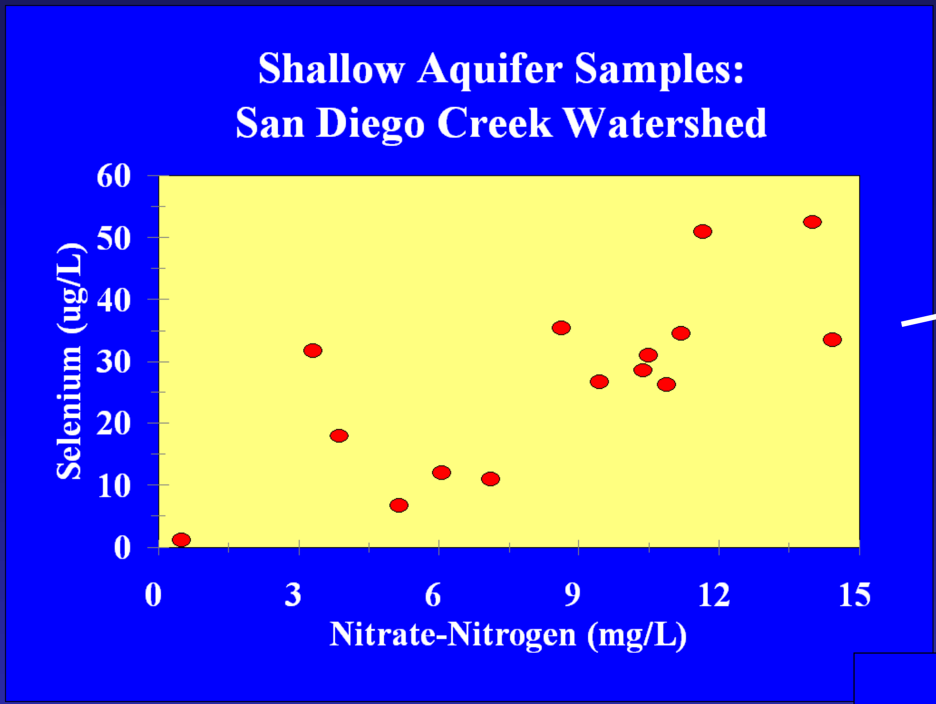
Explanation

Groundwater Sample

Shallow Aquifer Samples: Las Virgenes Creek Watershed

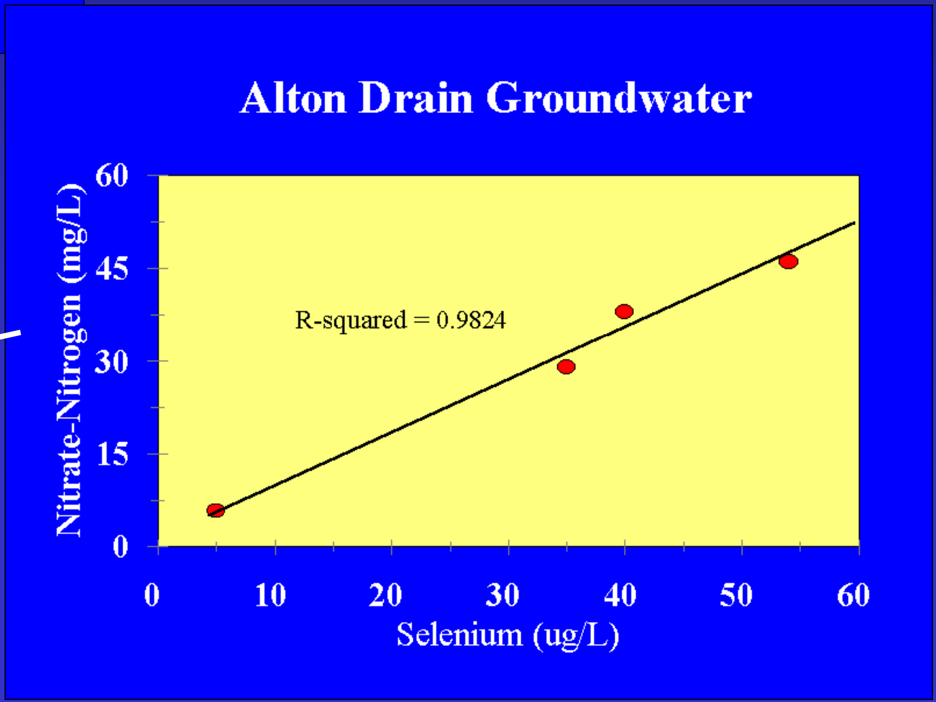


Los Angeles Basin: Areas Found with High Selenium And Nitrate in Streams

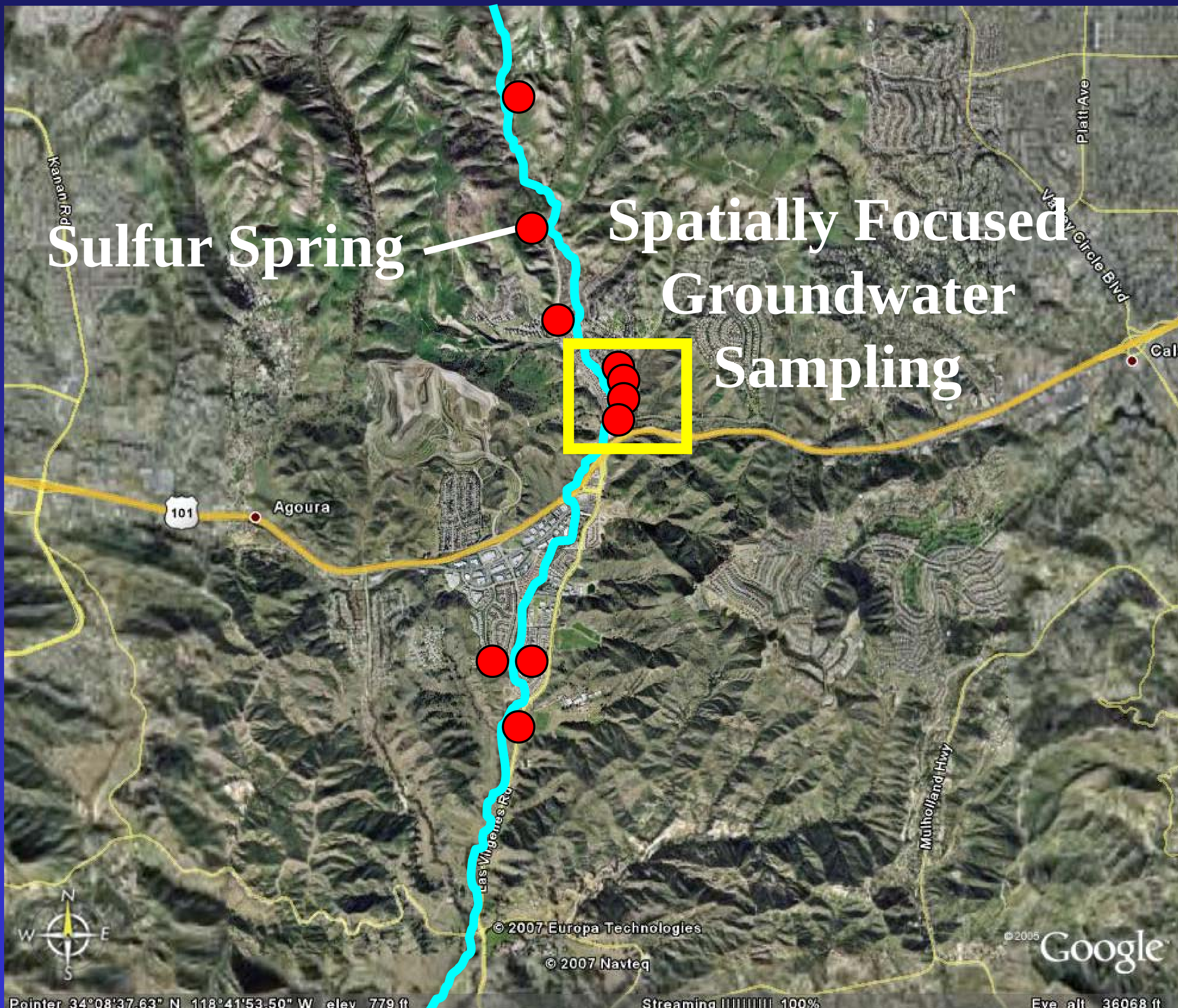


Regionally based groundwater sampling

Spatially focused groundwater sampling

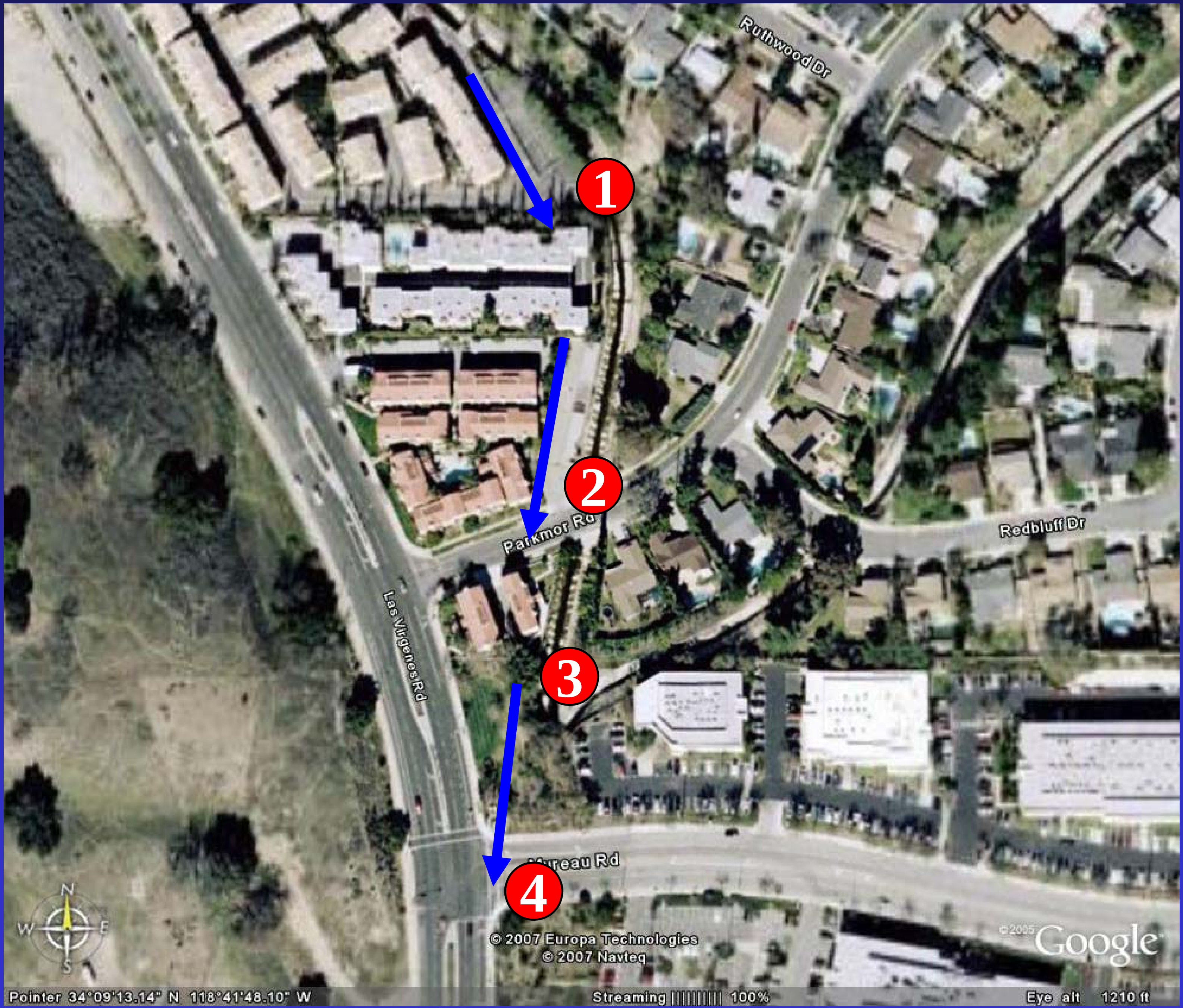


Study Area Location Map



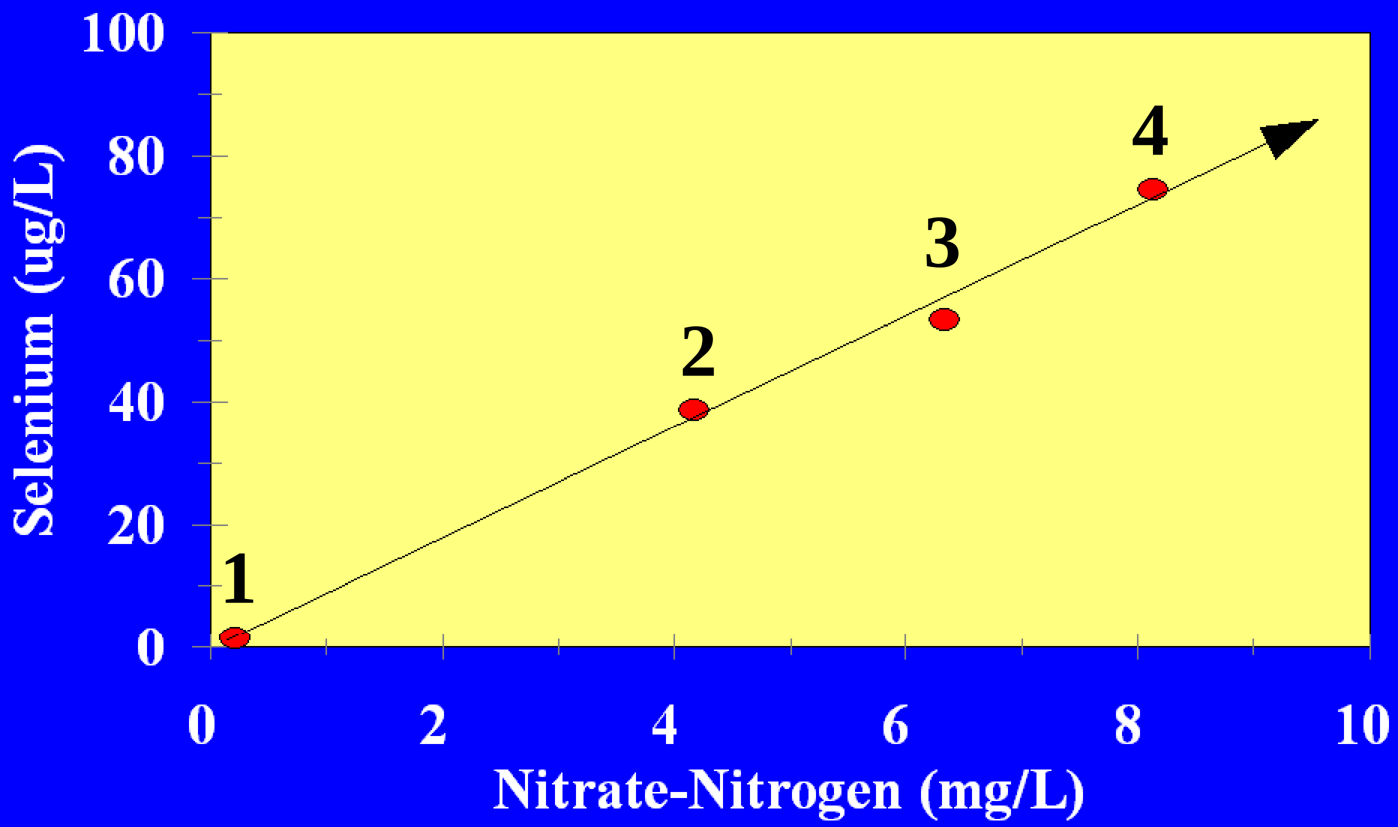
Explanation

Groundwater Sample



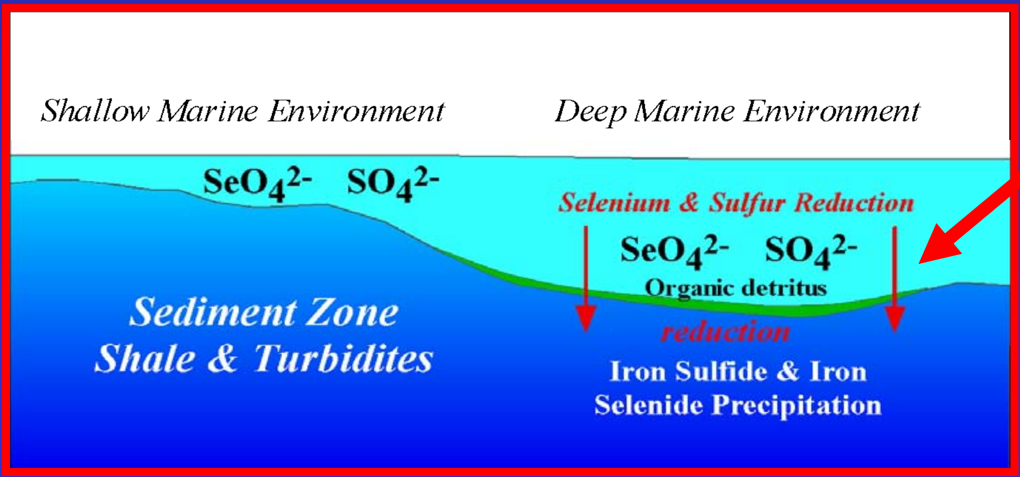
Ruthwood Dr
1
2
Parkmor Rd
Redbluff Dr
Las Virgenes Rd
3
Mureau Rd
4
© 2007 Europa Technologies
© 2007 Navteq
Google
Pointer 34°09'13.14" N 118°41'48.10" W
Streaming |||||||||| 100%
Eye alt 1210 ft

Shallow Aquifer Flowpath Samples: Las Virgenes Creek Watershed



Possible Hydrochemical Links Between Selenium and Nitrate

Origin of Iron Selenides and Iron Sulfides in Marine Rocks and Sediments in Los Angeles Basin



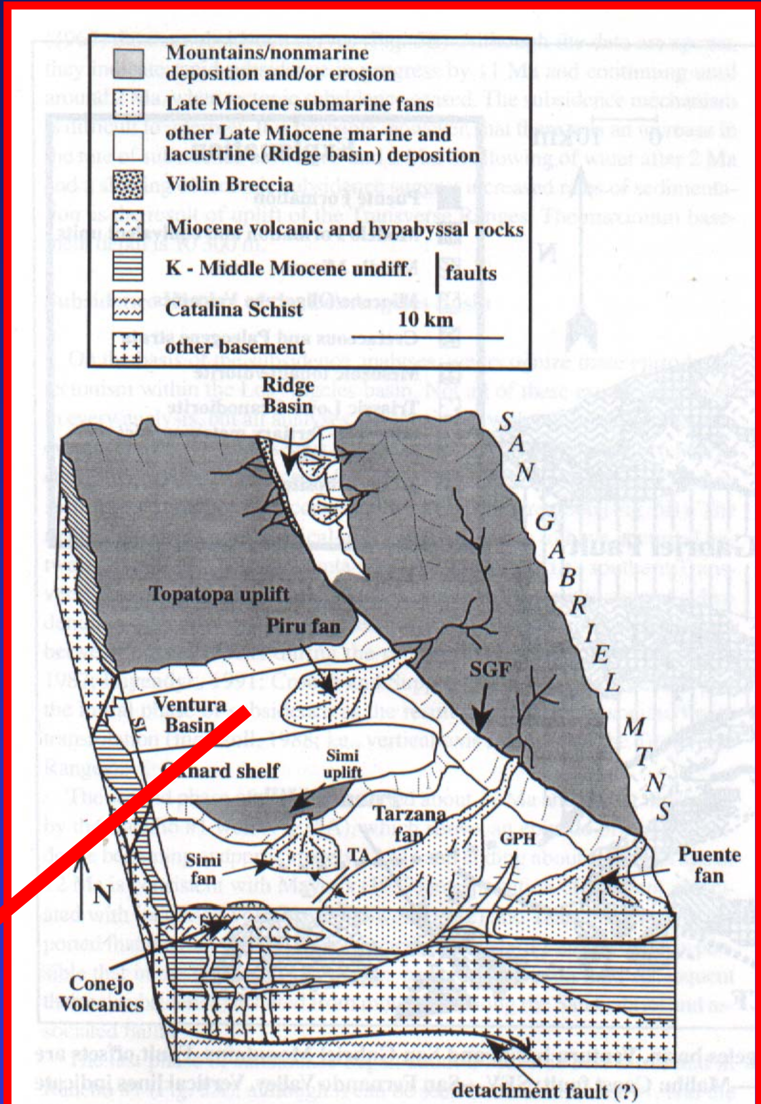


Figure 8. Paleogeographic block diagram of northern Los Angeles and eastern Ventura basins during deposition of middle member of Modelo Formation. TA—Topanga anticline; SGF—San Gabriel fault; SL—sea level; GPH—Griffith Park high. See text for discussion.

Many Foothills in LA Basin Consist of Marine Shales and Siltstones, Containing Selenium

Puente Formation – selenium bearing shale

Selenium bearing deposits eroded from foothills

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 (W. Wright, USGS, Journal of Environmental Quality, 1999)

Oxidation Reactions

nitrate as oxidant of iron sulfide and iron selenide via denitrification

$$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 7N_2 + 10SO_4^{2-} + 5Fe^{2+} + 2H_2O$$

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

Hypothesis

nitrate acts as an oxidant of selenium (and sulfur) where content of reduced forms of selenium and sulfur (metal selenides, elemental selenium, selenite, and metal sulfides) in geologic deposits is high

Oxidation Reactions

nitrate as oxidant of iron sulfide and iron selenide via denitrification

$$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 7N_2 + 10SO_4^{2-} + 5Fe^{2+} + 2H_2O$$

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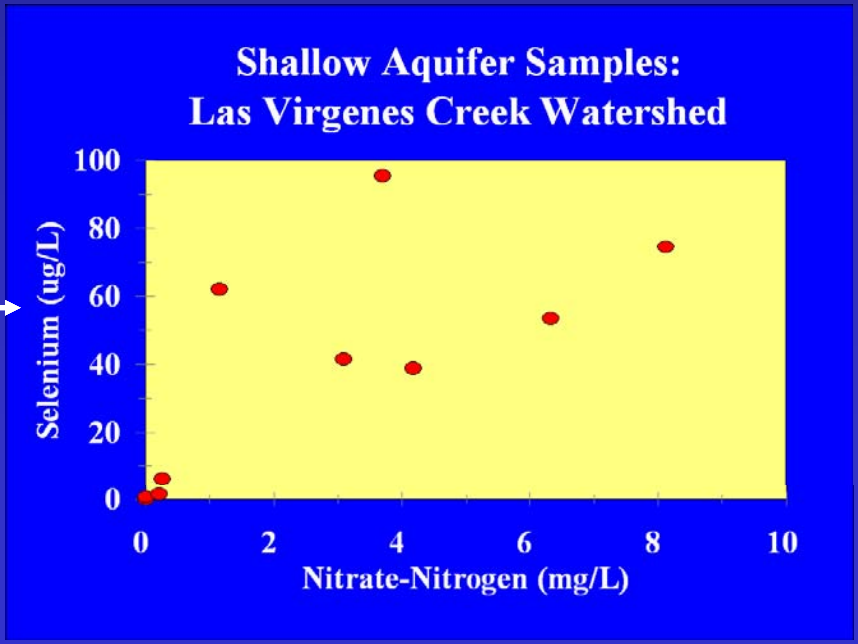
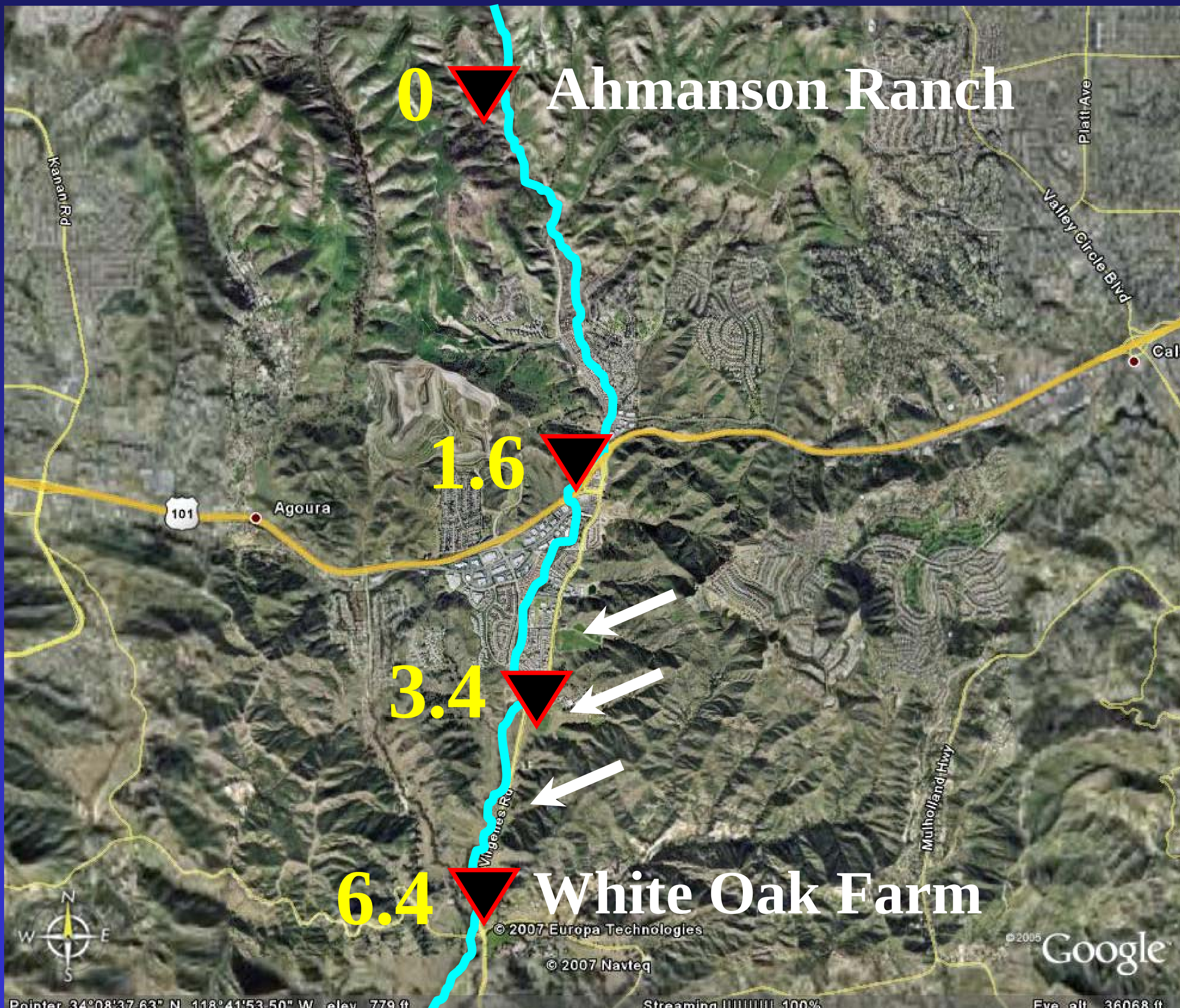
Discussion of Scatter of Points



Source(s) of Nitrate in Groundwater and Surface Water?

Nitrate-Nitrogen at Surface Water Stations (mg/L)



Explanation

▼ **Surfacewater Sample**

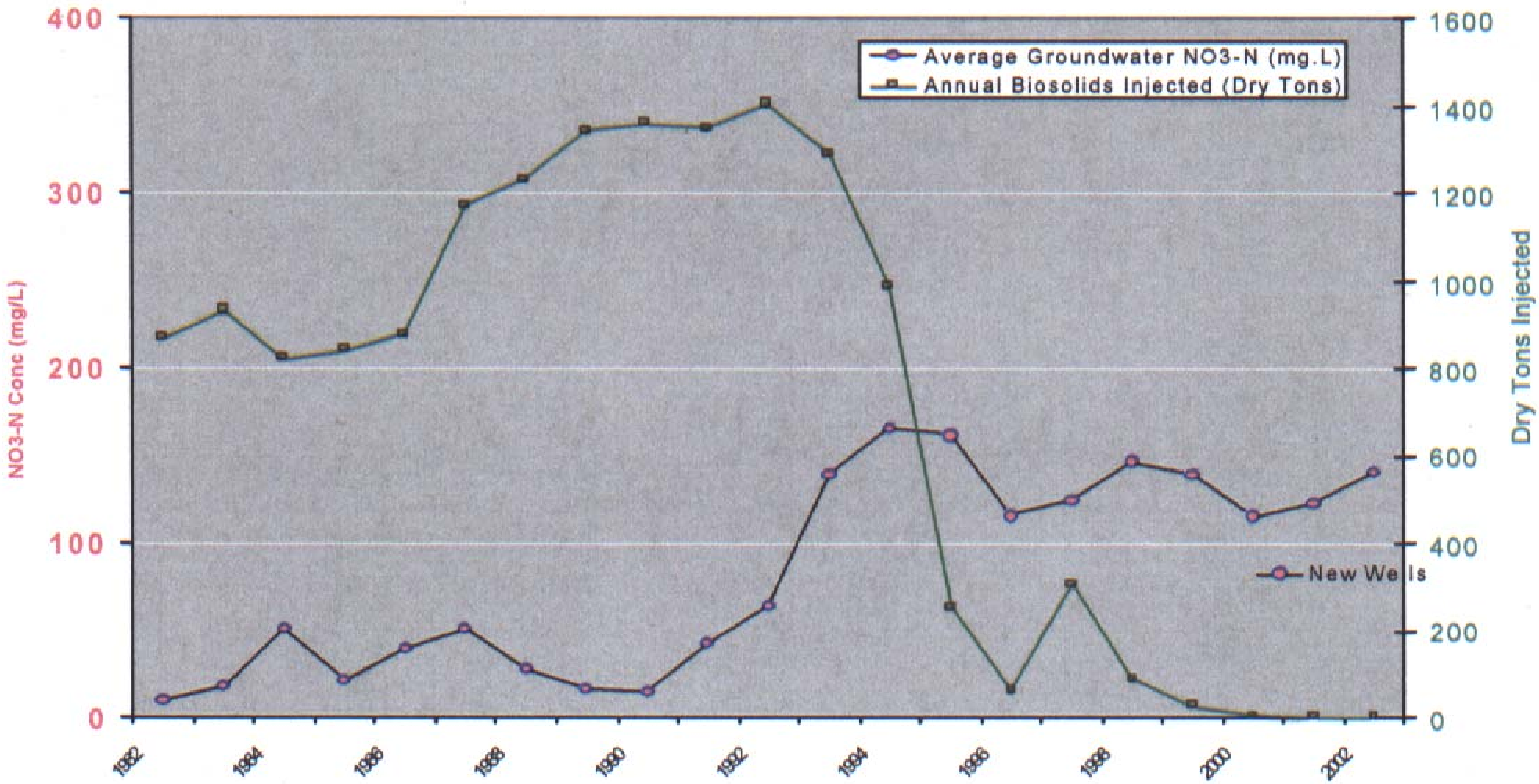
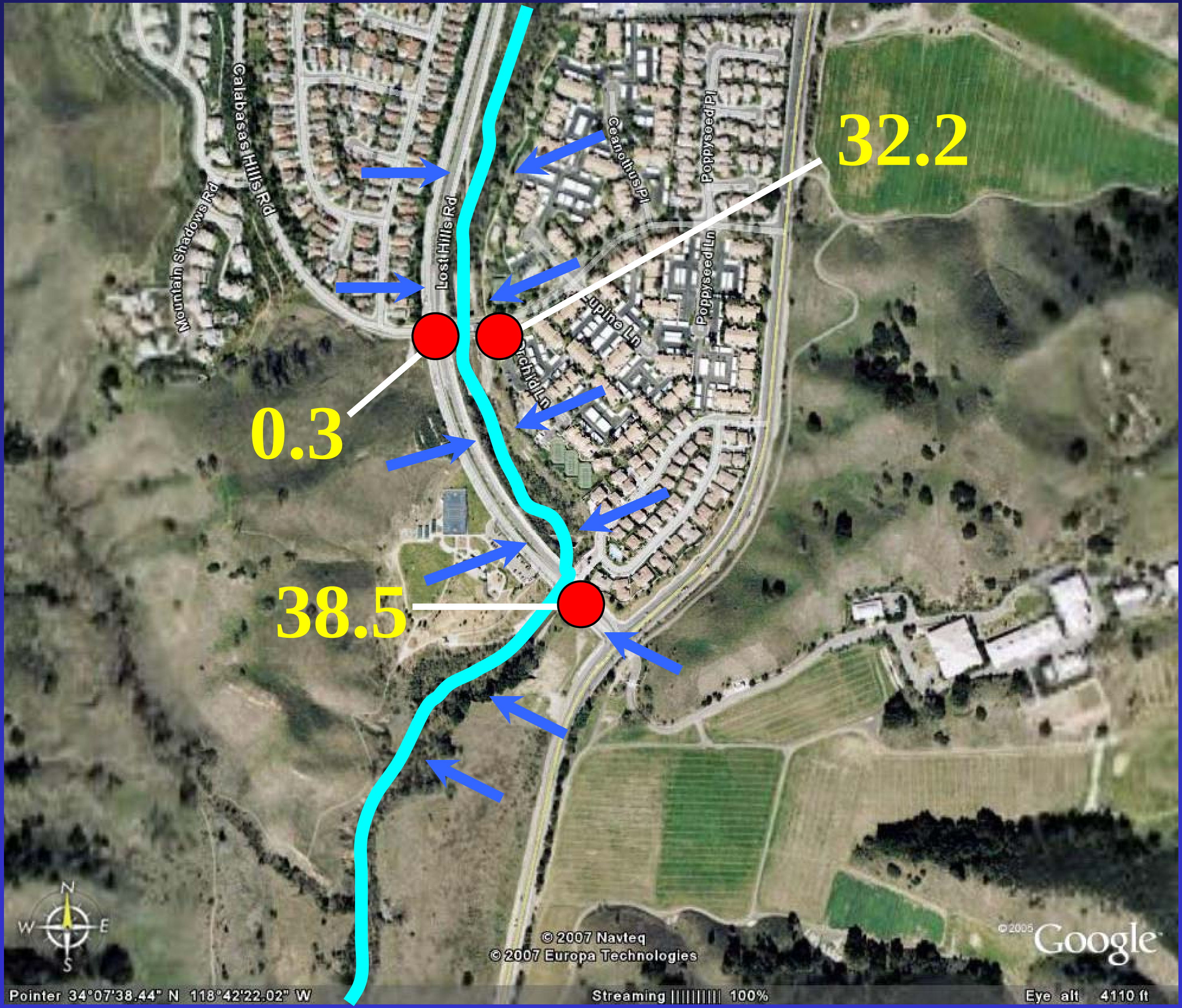


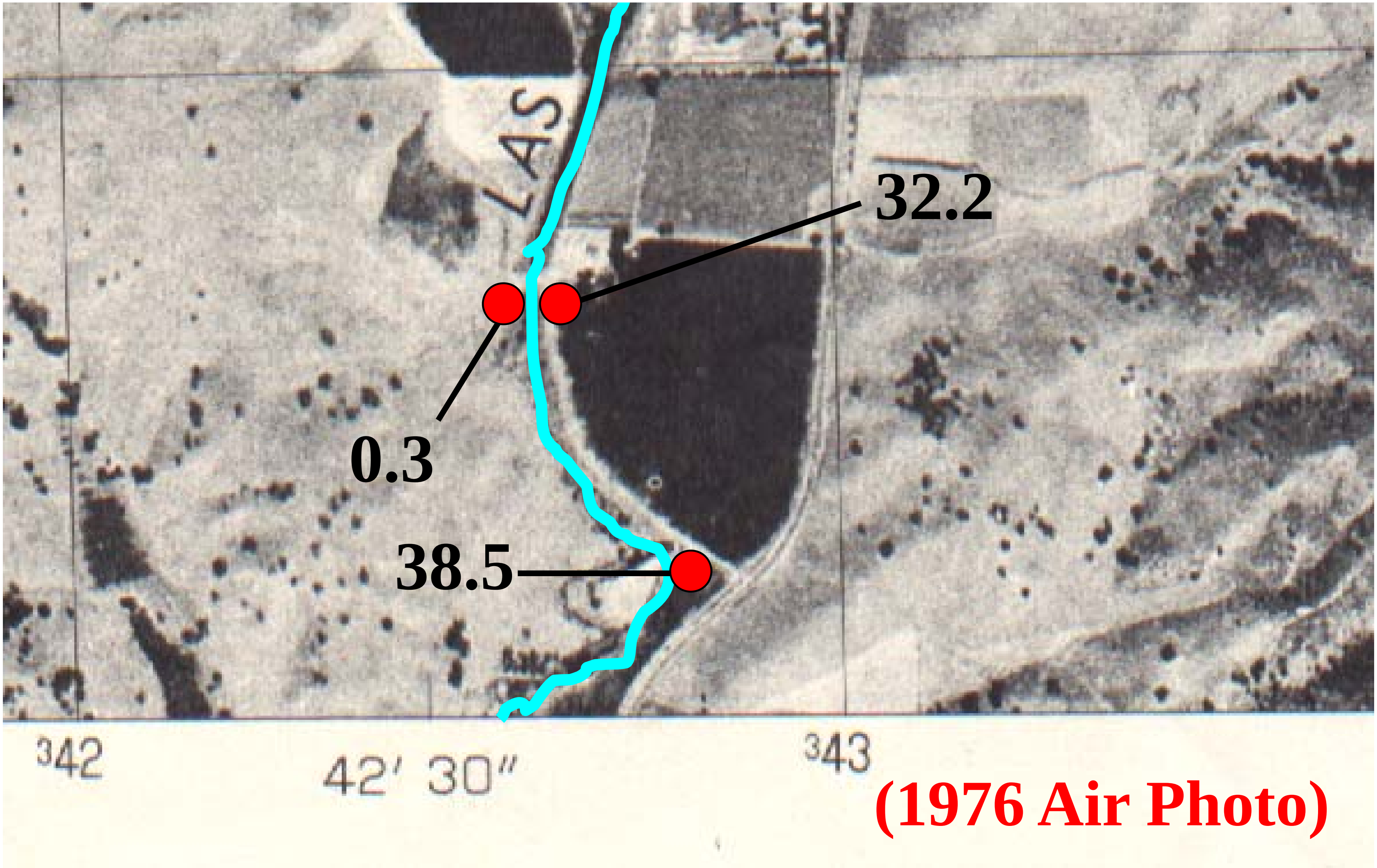
Fig. 10. Nutrient loading and groundwater well Nutrient levels at Rancho Las Virgenes Farm

Nitrate-Nitrogen at Select Springs (mg/L)



Explanation

● **Groundwater Sample**



Nitrate-Nitrogen at Select Springs (mg/L)

Treated wastewater applied to nurseries may recharge groundwater

Treated wastewater applied to planted riparian areas may recharge groundwater

Relationship Between Nitrate, Selenium, and Groundwater

- Selenium bearing strata in the shallow aquifer connected to Las Virgenes Creek shows a nitrate-selenium correlation.
- Nitrate may be a relic from historic agriculture, septic tanks, ranch animals, and sludge injection; furthermore, nitrate may be loaded today from wastewater application.
- Groundwater with high selenium and high nitrate flows into Las Virgenes creek, potentially compromising the habitat.

Policy Impacts and Technical Recommendations

- What is the hydraulic relationship between shallow aquifers and streams? (i.e., do streams gain baseflow from groundwater seepage or intentional discharge or do streams recharge shallow aquifers?)
- What is the nature of the geology? Where are selenium bearing rocks and sediments located and where have their erosion products been deposited?
- 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 wastewater at green-belts and other vegetated areas