

# **Characterization of nutrients in surface waters and modeling at the watershed scale**

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# Objectives

- To discuss watershed nutrient processes
- To demonstrate linkages between land management and concentrations and loads
- To describe several models available for characterization of nutrients, metals and organics at the watershed scale
- Demonstrate the use of the “Simple Model” in the San Francisco Bay Region

# Nutrients in Watersheds

# Overview

- Life support system of the biosphere
- N & P are essential for cell processes – life limiting
- Pristine watersheds = low N & P conc

## Natural sources of nitrogen

- Atmosphere
- Fixed by symbiotic and non-symbiotic microbes
- Fixed by lightening
- Rainout
- Dissolution from rocks (small relative to P)

# Overview (continued)

## Natural sources of phosphorus

- Common in igneous rocks
- Weathering and dissolution from rock and soils
- Atmospheric sink (small relative to N)

# Why are we concerned

- Degraded watersheds = high N & P conc
- Blooms of aquatic plants
- Algal blooms and toxicity
- Smell of rotting aquatic vegetation
- Low oxygen and fish kills
- Loss of aquatic habitat (e.g. sea grass)
- Changes in community structure
- Loss of recreational amenity
- Loss of recreational and commercial fisheries
- Loss of water supply (or high treatment costs)

# Laboratory analysis of forms of N in surface waters

- Nitrate ( $\text{NO}_3$ )
- Nitrite ( $\text{NO}_2$ )
- Ammonium and Ammonia ( $\text{NH}_3$  and  $\text{NH}_4^+$ )
- Organic nitrogen
- Total Keldahl N (TKN)
- Particulate nitrogen (minor)
- Total nitrogen

# Laboratory analysis of forms of P in surface waters

- Phosphate ( $\text{PO}_4$ )
- Organic phosphorus
- Particulate phosphorus
- Total phosphorus



# SF Bay Water Quality Control Plan

## Water quality objectives for municipal supply

- $\text{NO}_3 + \text{NO}_2$  10 mg/L
- $\text{NO}_2$  1 mg/L

## ■ Water quality objectives for agricultural supply

- $\text{NO}_x + \text{NH}_4^+$  (threshold) 5 mg/L

# California EPA guidelines

## ■ Ammonia (mg/L)

1998 update: [http://www.epa.gov/waterscience/standards/nh3\\_rpt.pdf](http://www.epa.gov/waterscience/standards/nh3_rpt.pdf)

pH	Acute (salmonids present)	Acute (salmonids absent)	Chronic
6.5	32.6	48.8	3.48
7.0	24.1	36.1	3.08
8.0	5.62	8.40	1.27
9.0	0.885	1.32	0.254

# Summary

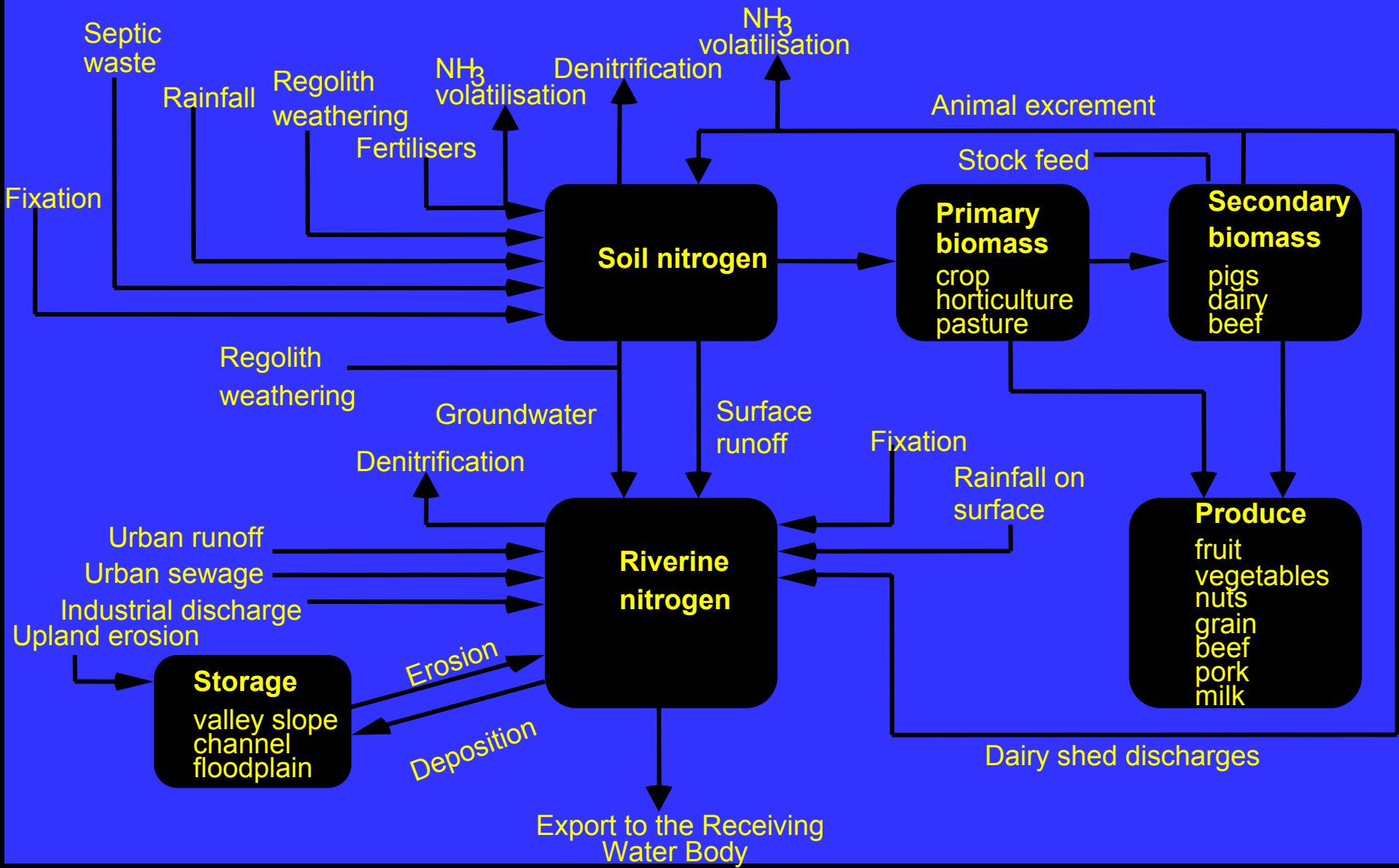
- Nutrients are life-limiting
- Natural sources N – atmosphere, P-geosphere
- Excess nutrient cause reduction of beneficial uses
- Nitrate, nitrite, ammonium and phosphate concentrations are indicators of degradation
- RWQCB and EPA set and enforce guidelines



# Sources, Processes and Fate

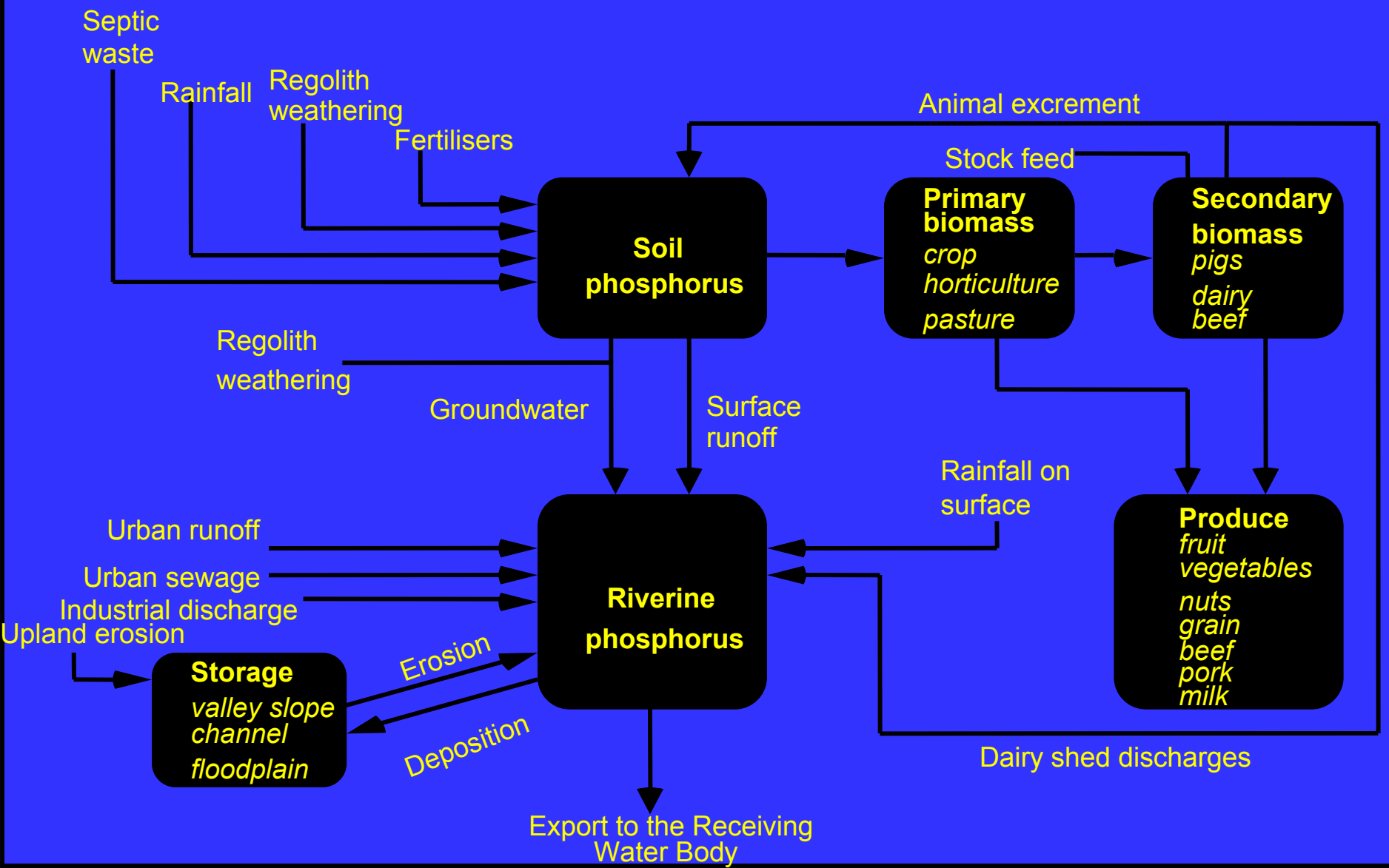
# Conceptual model: Nitrogen

(McKee and Eyre 2000)



# Conceptual model: Phosphorus

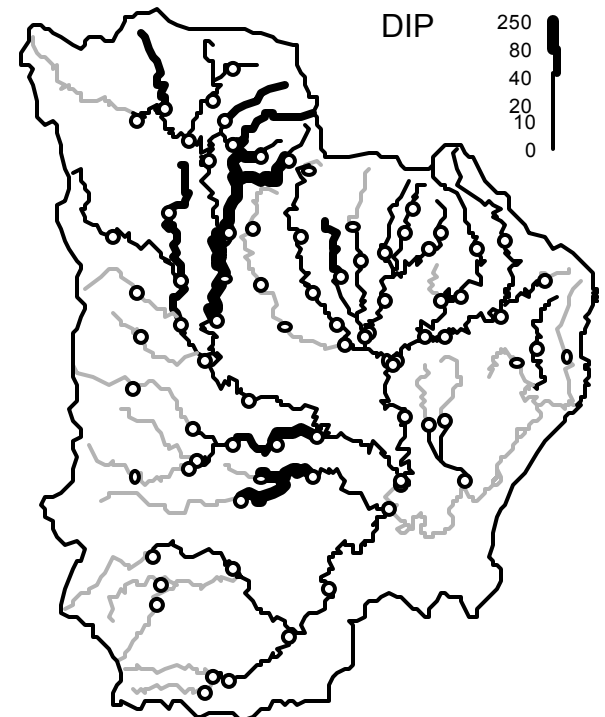
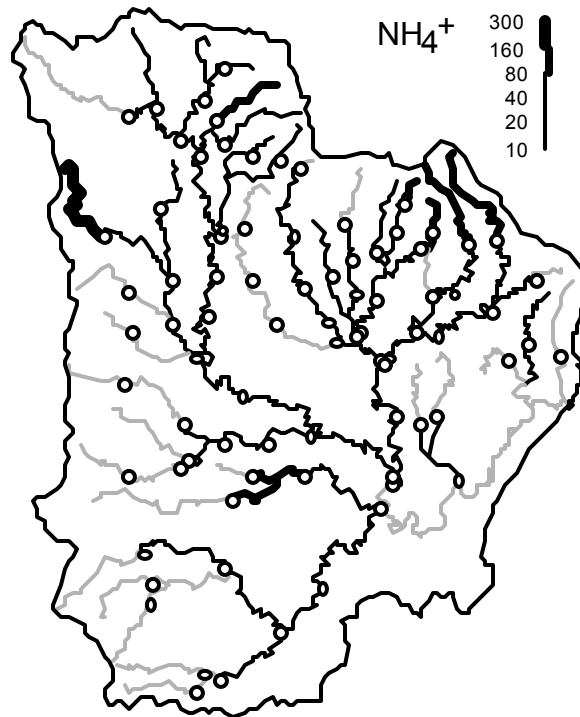
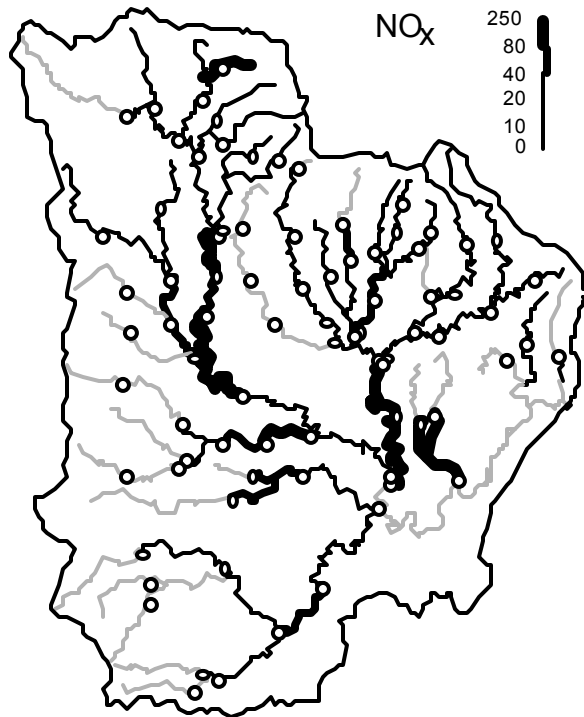
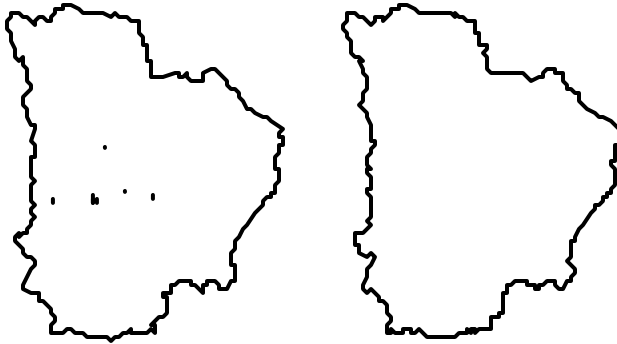
(McKee and Eyre 2000)



# Mapping water quality: low flow

Crop

Dairy



# Sources and sinks of nutrients:

## Low flow

### Sources

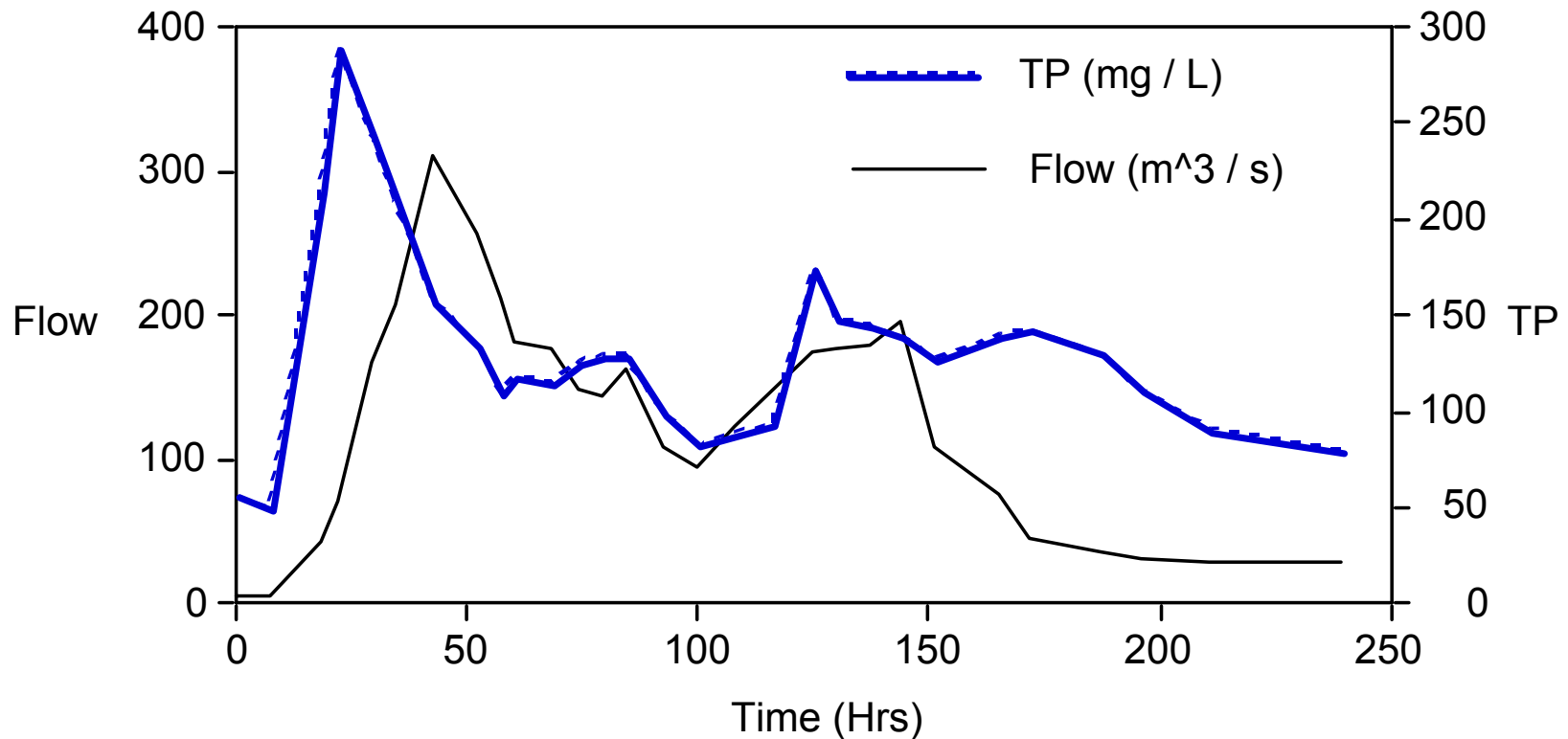
- Nutrients enter the stream from groundwater of point sources

### Sinks

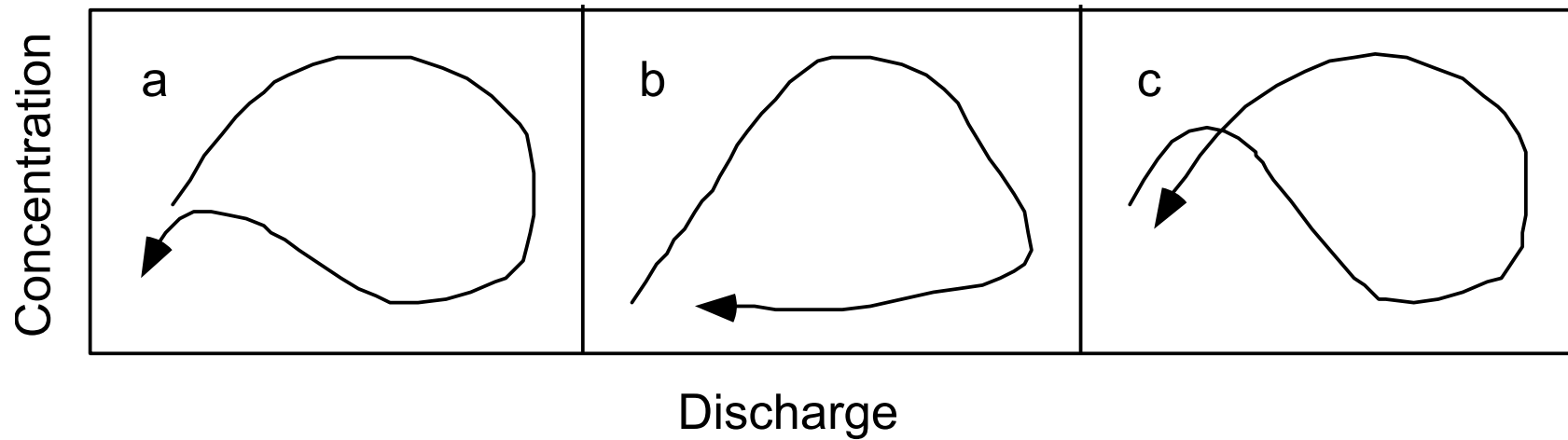
- Phosphorus can adsorb to sediments
- Macrophytes and algae can increase in biomass
- Ammonia is volatilized or oxidized to nitrate
- Nitrogen can be denitrified



# Transport of nutrients during floods (McKee 1999)



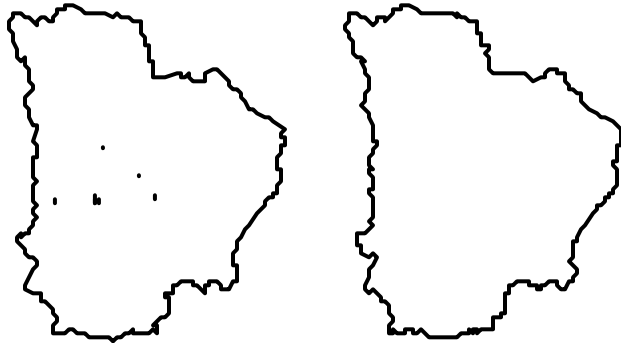
# Hysteresis



# Mapping water quality: high flow (McKee et al. 2001)

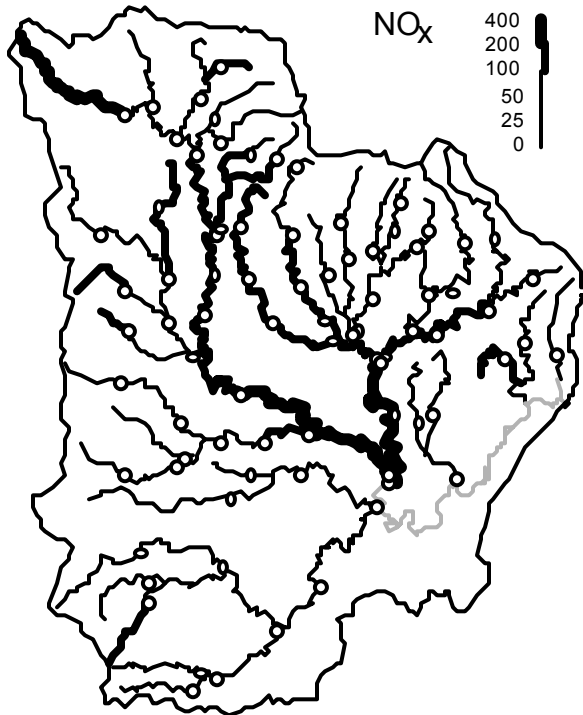
Crop

Dairy



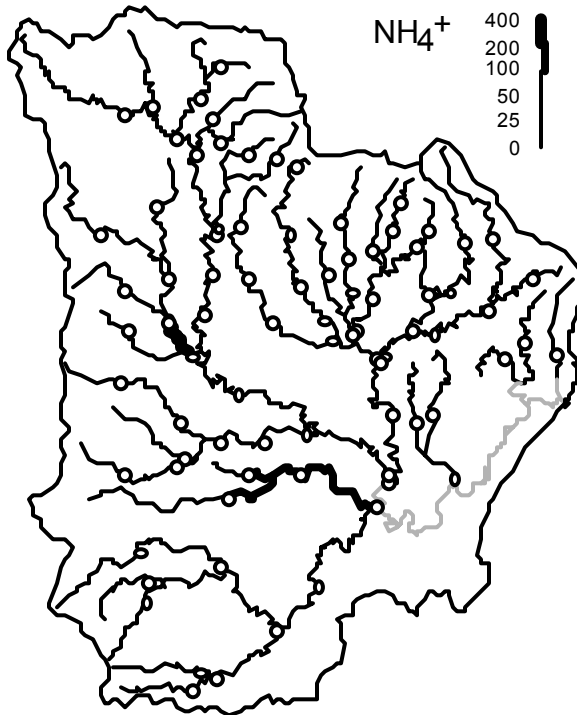
$\text{NO}_x$

400  
200  
100  
50  
25  
0



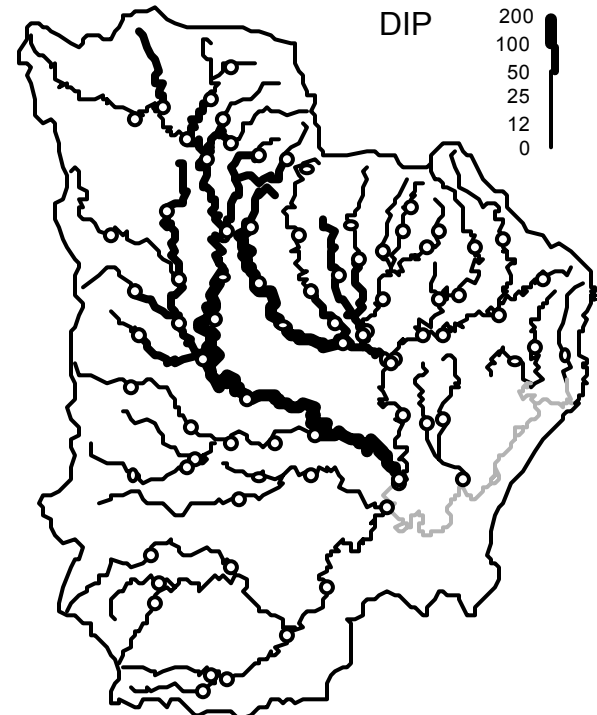
$\text{NH}_4^+$

400  
200  
100  
50  
25  
0



DIP

200  
100  
50  
25  
12  
0



# Sources and sinks of nutrients:

## High flow

### Sources

- Nutrient are sourced from watershed surfaces, bed and bank storage

### Sinks

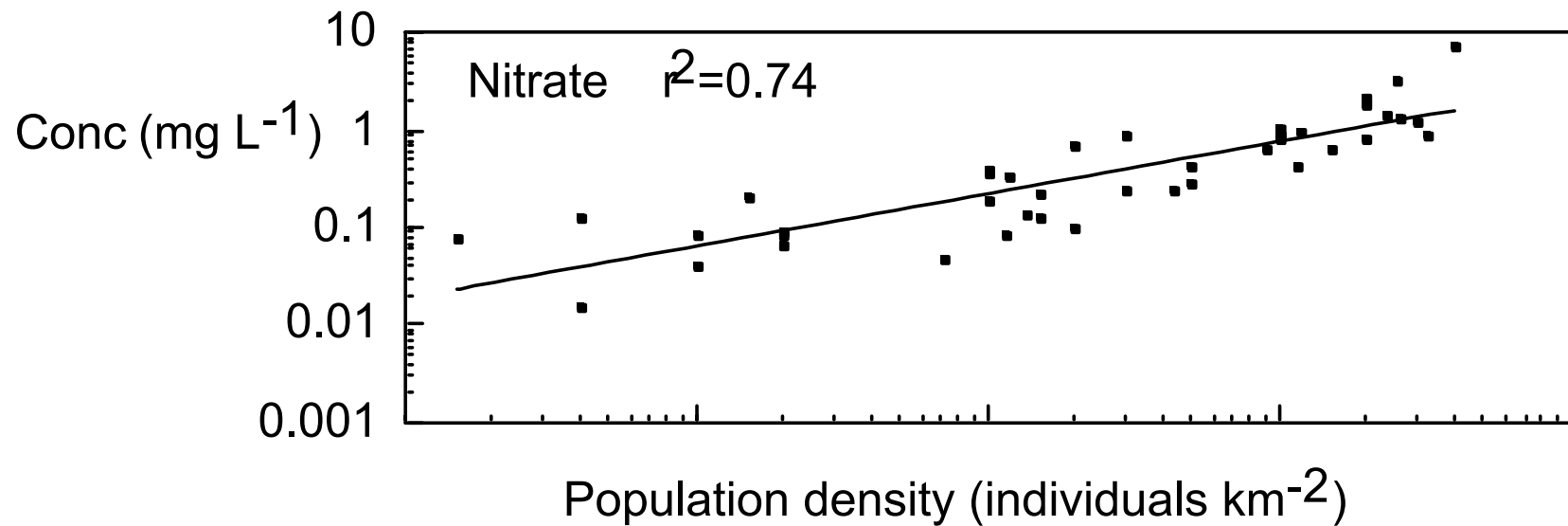
- Banks and floodplain

# Summary

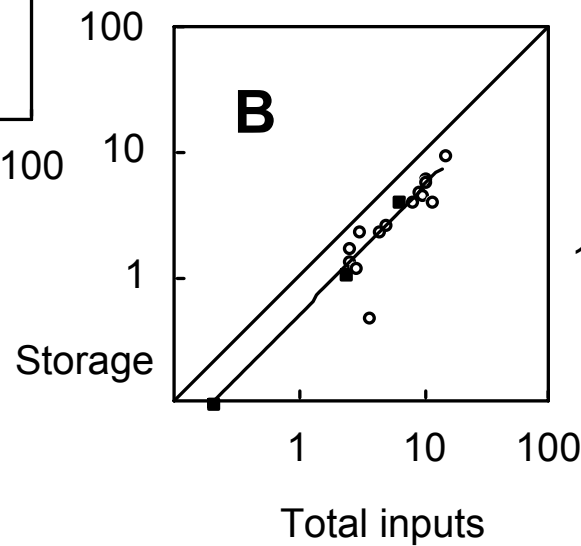
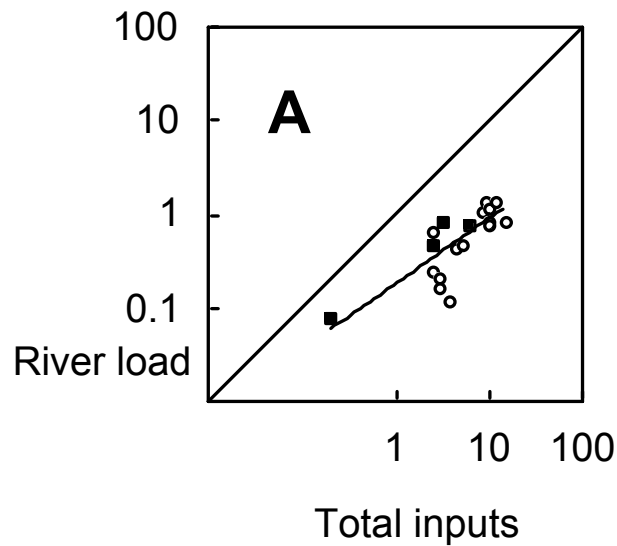
- Nutrients undergo complex pathways
- Sources vary between seasons
- There is some storage and loss during dry times
- Concentrations may or may not peak at the same time as discharge
- >90% of nutrient are transported during floods
- Flood storage occurs on floodplains and on the waning stage in channels and on banks

# Linkages between land and water management and nutrients in surface waters

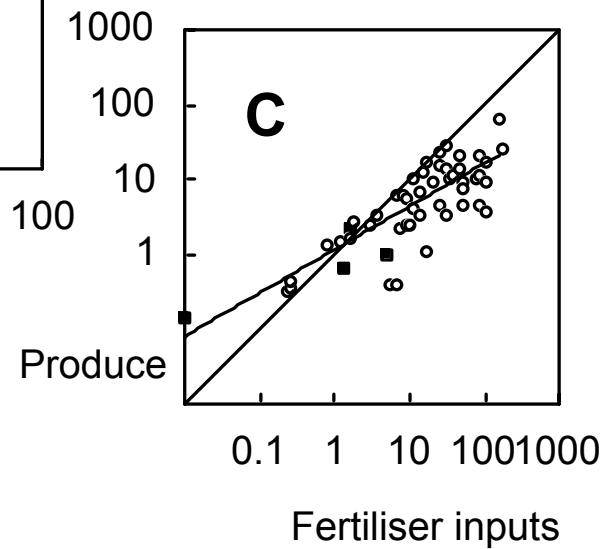
# Cole et al. 1993; Caraco 1995



# Frissel 1978



## Phosphorus





# Summary

- Humans have a massive impact on riverine concentrations and watershed nutrient budgets
- Management options may include:
  1. Timing of fertilizer applications
  2. Reduction in sediment erosion
  3. Sewage treatment
  4. Urban runoff treatment
  5. Use of phosphate free detergents
  6. Riparian zone management
  7. Ensuring environmental flows



# Modeling

**Fact:** Field data  
collection cost heaps!

# What is a model?

- ❑ Models are simulations of the real environment that allow us to:
  - 1) Interpolate between temporal sampling points.
  - 2) Extrapolate spatially to other areas that are not sampled.
- ❑ When suitably parameterized, calibrated, and verified, models can predict (with accuracy and precision) concentrations and loads in space and time where and when empirical sampling data are not adequate for locally determined needs.
- ❑ In reality, at watershed scales, no model can simulate perfectly, the complex hydrological and biogeochemical processes that occur in watersheds with heterogeneous physical properties and heterogeneous rainfall patterns.

**Fact:** Models cost heaps of money also!

# Types of models

- Conceptual or “planning level” models (e.g. PLOAD, SIMPLE model)
  - low data inputs (land use, pollutant generation rates)
  - Minimum time step: 1 year
- Assessment models (e.g. SWAT, GWLF, QUAL2E)
  - moderate data inputs such as rainfall, soils, land use, topography
  - Use empirical equations such as MUSLE and SCS curve numbers
  - Minimum time step: 1 day and sometimes event
- Complex conceptual models (e.g. HSPF)
  - high data inputs
  - Account for hydrological variability and in-stream processes through calibrated and field verified, concentrations, processes, and discharge data
  - No minimum time step
- Process models have extreme data requirements (e.g. SHE)

# Choosing the right combination of model and empirical observation

**Fact:** Even though models can not simulate the environment perfectly, the right combination of a model and observations will reduce long term costs and provide input into local and regional level needs

- Accuracy
- Time step
- Compliance monitoring
- Cost
- Technical expertise
- Logistical issues
- Computer hardware requirements
- Field equipment and personal requirements
- Management questions (water quality, toxic effects, loads, trends)

# EPA Basins

Better Assessment Science Integrating Point and Non-point Sources

- BASINS addresses three objectives:
  - (1) to facilitate examination of environmental information
  - (2) to provide an integrated watershed and modeling framework
  - (3) (3) to support analysis of point and non-point source management alternatives

# How does BASINS work?

- It includes a national data base of environmental and GIS data
- It allows for additional local data input
- It combines a number of modeling components that allow the user to:
  - 1) Model instream, interflow and groundwater processes at a range of scales and time steps
  - 2) Tools for classifying data and watershed areas
  - 3) Tools for assessing changing management and future scenarios
  - 4) Tools for analysis and output
- The user selects the components depending on management questions

# PLOAD

(Annual estimates of point and non-point source loads) Developed by CH2MHILL

- Virtually the same as the SIMPLE model
- Combines:
  1. Land use
  2. Event mean concentrations
  3. SCS curve numbers
  4. Impervious percentages
  5. Average annual rainfall
  6. Aerial delineations
  7. Simple BMPs
- Low computing power screening tool



# QUAL2E (in-stream water quality model)

[http://smig.usgs.gov/SMIC/model\\_pages/qual2e.html](http://smig.usgs.gov/SMIC/model_pages/qual2e.html)

- Used for modeling the impacts of a waste stream
- Assumes constant flow of both waste and non-point source load
- Can combine 15 water quality parameters dynamically to determine diurnal algal growth, DO, BOB
- Model can determine the optimal waste inputs in order to maintain desired water quality criteria
- Useful for point source TMDLs

- Dissolved Oxygen
- Biochemical Oxygen Demand
- Temperature
- Algae as Chlorophyll a
- Organic Nitrogen as N
- Ammonia as N
- Nitrite as N
- Nitrate as N
- Organic Phosphorus as P
- Dissolved Phosphorus as P
- Colifoms
- Arbitrary Nonconservative Constituent
- Three Conservative Constituents

# SWAT (soil and water assessment tool)

- Assessment tool for relative risk or impacts
- Not intended to be calibrated
- A long term yield model (no flood simulation)
- Continuous simulation (daily time step)
- Inputs include:
  - 1) SCS curve numbers
  - 2) USLE
  - 3) Rainfall, land use, soil and topography
- PC compatible

# GLWF (generalized watershed loading function)

Haith and Shoemaker, 1987

- Estimates of monthly and annual loads without calibration
- Capable of relative loads given land use changes
- Includes loads from:
  - 1) Point source (local data)
  - 2) Rural runoff (land use, SCS curve, USLE, concs for each land use (mg/g and mg/L))
  - 3) Groundwater (water balance model and concs)
  - 4) Urban runoff (daily accumulation rates and exponential washoff functions)

# HSPF (Hydrological simulation program – fortran)

- Comprehensive simulation of quantity and quality of water for each land use and sub-catchment
- Water and chemical fluxes are routed to the watershed outlet
- Includes point sources
- Includes in stream and surface processes:

Hydrolysis

Oxidation

Biodegradation

Volatilization

Sorption

Others can be added

- Requires a lot of data for calibration
- New modules allow BMP analysis (e.g. veg swales, riparian buffers, land use change, wet and dry detention ponds)
- High computing power for large basins or small time steps

# Summary

- There is a range of models available
- Models achieve a process of organized thinking and analysis
- Many people make the mistake of having a model as a product rather than the means to get to a product
- The choice of “organized thinking structure” is based on the management or scientific question

# The “Simple Model” and its use in the Bay Area

# Assembly Bill 1429

- **AB 1429 (Shelley) WATER QUALITY**
- **Status: Chaptered 97-0899**
- **Summary:** This bill requires the State Water Board, to the extent that funds are available for that purpose to prepare, and complete on or before January 1, 2000, an inventory of existing water quality monitoring activities within state coastal watersheds, streams, bays, estuaries, and coastal waters, as prescribed. This bill would require the submission of a report by July 1, 2001 to implement a comprehensive monitoring program

# Assembly Bill 1429 (continued)

- San Francisco Estuary Institute (SFEI)
- Southern California Coastal Water Research Project (SCCWRP)
- California State University Moss Landing Marine Laboratories (MLML)
- Directed by the legislation to collaborate and produce a report for the State Water Resources Control Board (SWRCB) detailing current information for the whole California Coast



# Good Planning Tool

- As an impetus for collating a data inventory
- Data gaps and prioritizing data collection
- For building a hypothesis of loads
- For educating people about human impacts
- Making predictions of RELATIVE change in impact GIVEN FUTURE LAND USE OR MANAGEMENT CHANGES
- May give accurate loads estimation under certain circumstances in spite of assumptions

# The Model

## A simple rainfall / runoff model

$$W = \sum_{j=1}^n (C_j * r_j * i * A_j)$$

### Where

W = Contaminant load from a hydrologic unit

C = Stormwater contaminant concentration for land use  $j$

r = Runoff coefficient for land use  $j$

i = Average rainfall for the hydrologic unit

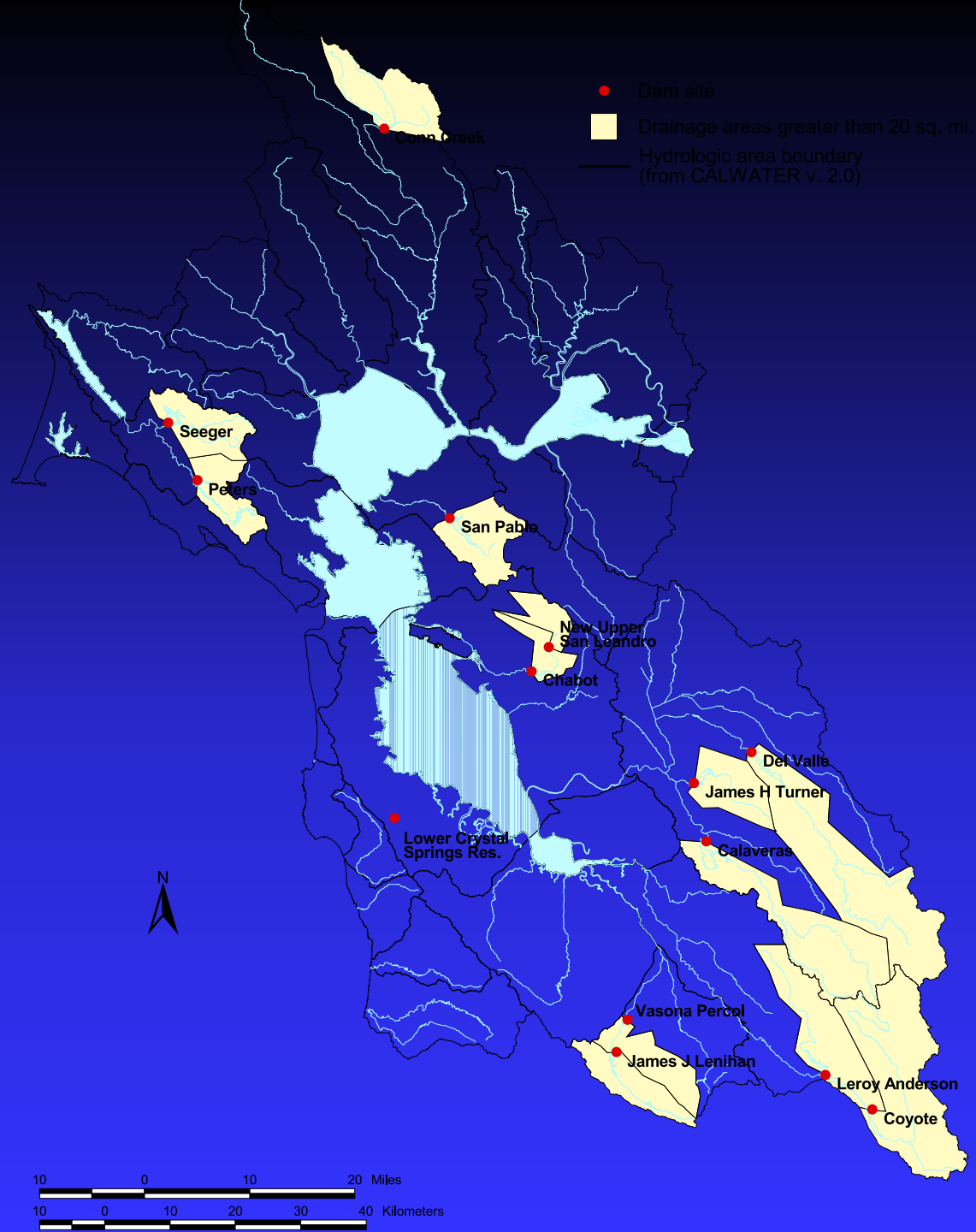
A = Area of land use  $j$  in the hydrologic unit

Defining  
the  
modeling  
space:

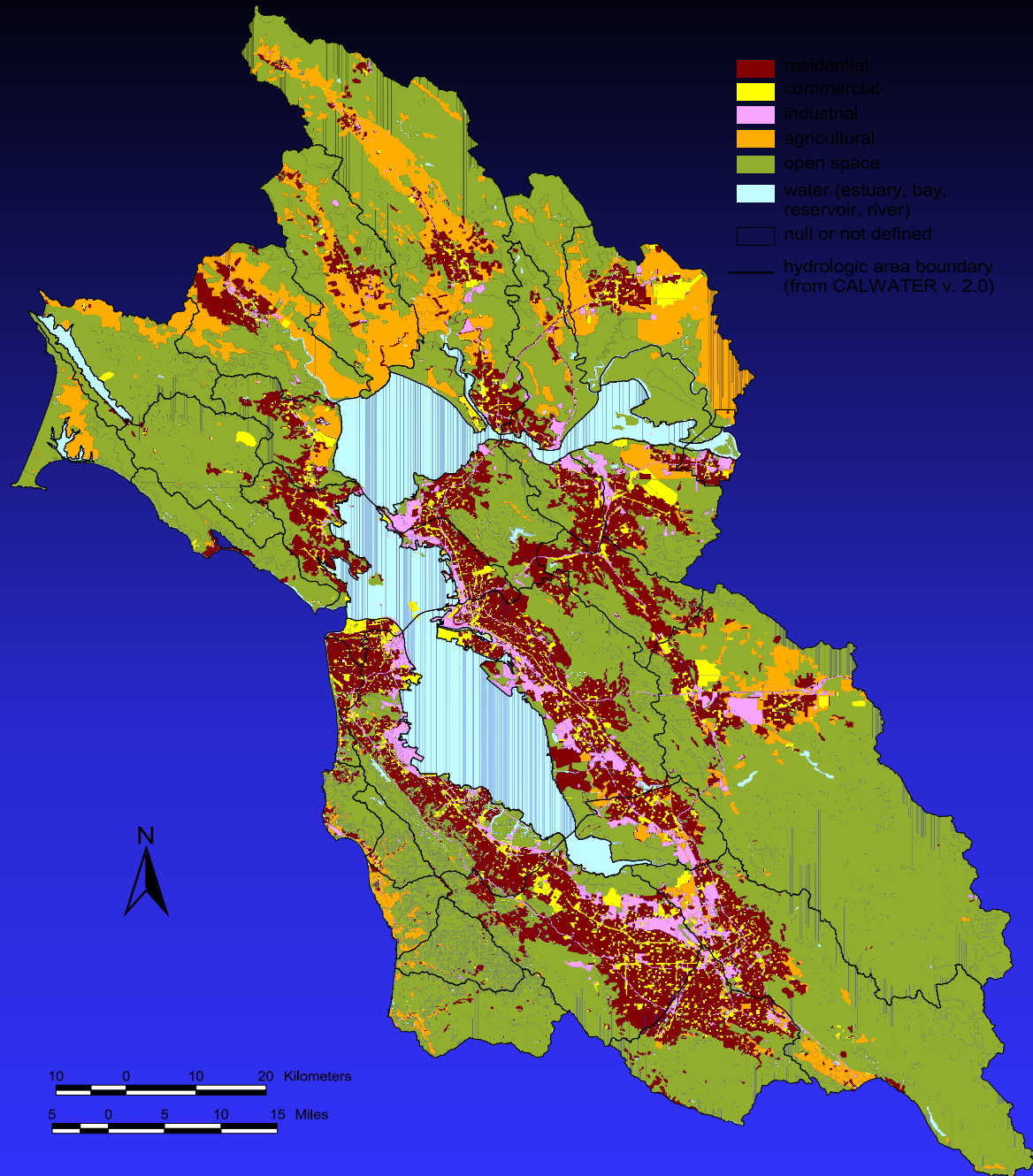
Hydrologic  
areas  
CALWater  
map



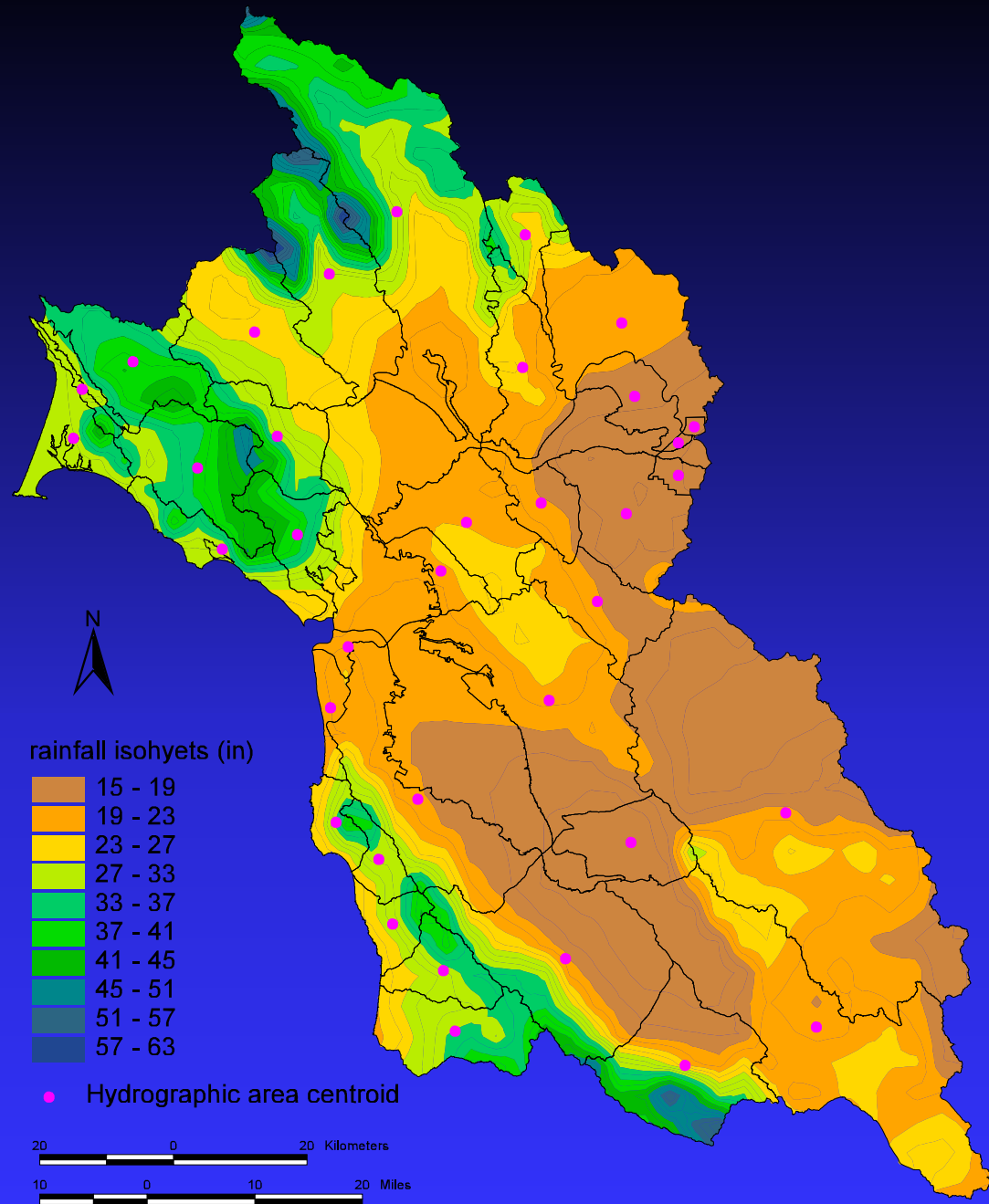
Drainage  
areas that  
were  
disregarded  
in the  
modeling  
process



# Land use input into the model (ABAG)



# Rainfall input into the model (PRISM)



# Bay Area Characteristics

## Drainage area – 8,552 sq km

- Residential – 21%
- Commercial – 5%
- Industrial – 4%
- Agricultural – 13%
- Open Space – 56%

# Runoff Coefficients

	Low	Best	High
Residential	0.20	0.35	0.50
Commercial	0.60	0.90	0.95
Industrial	0.60	0.90	0.95
Agricultural	0.05	0.10	0.20
Open Space	0.10	0.25	0.50



# TSS concentrations (mg/L)

	Low	Best	High
Residential	28	90	286
Commercial	30	98	312
Industrial	49	157	502
Agricultural	646	2068	6618
Open	27	85	272

# Nitrate concentrations (mg/L)

	Low	Best	High
Residential	0.22	0.70	2.2
Commercial	0.22	0.70	2.2
Industrial	0.19	0.60	1.9
Agricultural	3.1	10	32
Open	0.063	0.20	0.64

# Phosphate concentrations (mg/L)

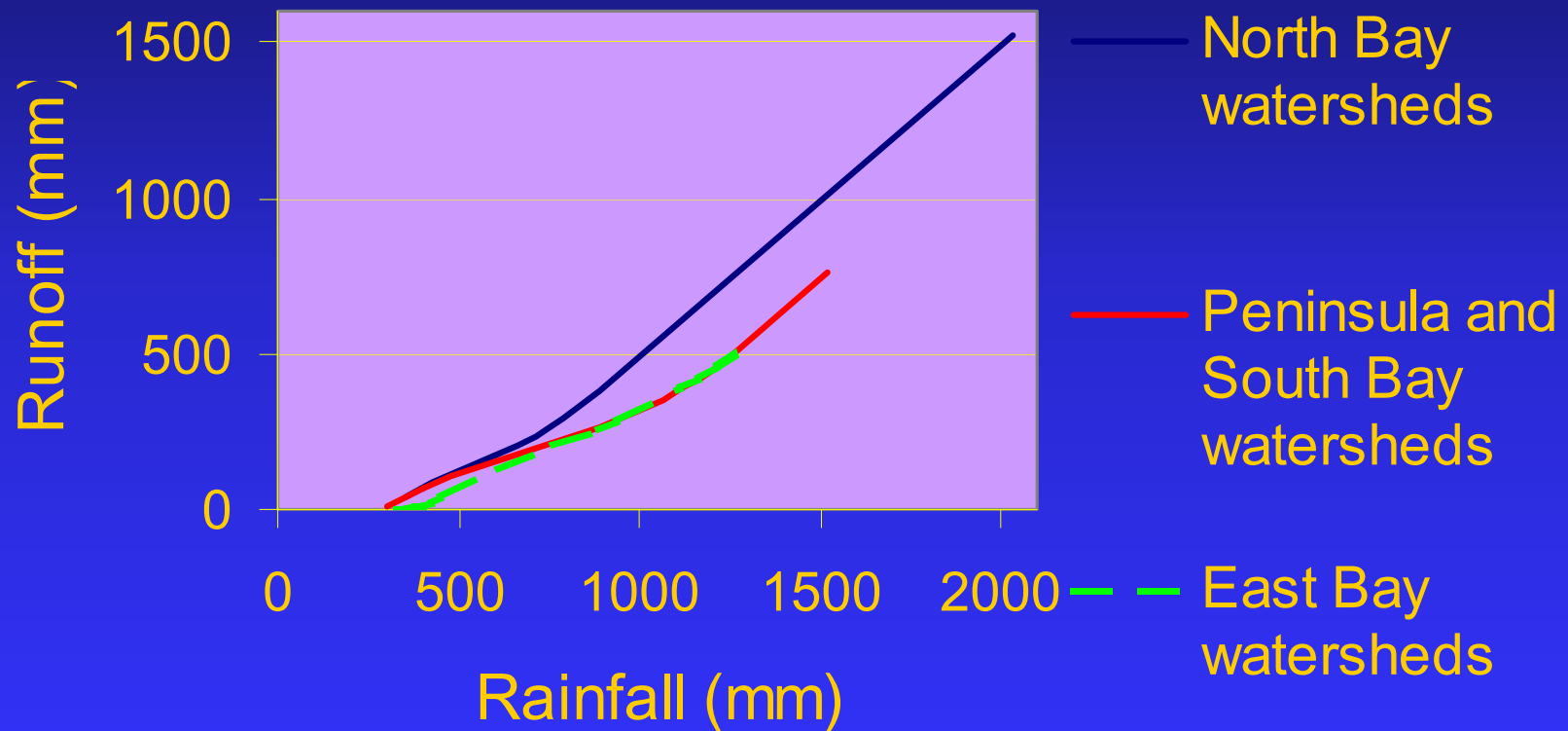
	Low	Best	High
Residential	0.094	0.30	0.96
Commercial	0.094	0.30	0.96
Industrial	0.22	0.70	2.2
Agricultural	0.18	0.57	1.8
Open	0.059	0.19	0.61

# Major Assumptions?

- That the runoff response to rainfall is linear
- That rainfall variability accurately characterizes runoff and loads variability
- That the delivery ratio of pollutant load to coastal waters is 100% (i.e. no in-stream processes or losses)
- That concentration is a function of land use and that that function is constant over the annual cycle (there are no hysteresis patterns)

# Rainfall vs Runoff in the Bay Area

(Modified from Rantz 1974)



# Categorizing land use into five strata

open	74	Bare Exposed Rock	open	62	Nonforested Wetlands
open	72	Beaches	open	174	<b>Open Space-Urban</b>
open	172	<b>Cemeteries</b>	open	762	Other Transitional
open	321	Chaparral	open	173	<b>Parks</b>
open	322	Coastal Shrub	open	422	Pine
open	41	Deciduous Forest	open	1712	Racetracks
open	42	Evergreen Forest	open	421	Redwood and Douglas Fir
open	423	Evergreen Mix	open	63	Salt Evaporation Ponds
open	171	Extensive Recreation	open	73	Sand Other than Beaches
open	61	Forested Wetlands	open	32	Shrub and Brush Rangeland
open	1711	<b>Golf Courses</b>	open	77	Mixed Sparsely Vegetated Land
open	31	Herbaceous Rangeland			
open	43	Mixed Forest			
open	33	Mixed Rangeland			
open	76	Transitional Areas			

# Estimated Mass Loads From Storm Water Runoff (t/y)

	Lower bound	Upper bound	Best estimate
Suspended solids	170,000	670,000	310,000
BOD	8,600	25,000	16,000
Nitrate	810	3,200	1,500
Phosphate	280	850	510

# Estimated mass loads from storm water runoff (t/y) (continued)

	Lower bound	Upper bound	Best estimate
Cadmium	1.3	3.7	2.3
Chromium	22	64	40
Copper	36	110	66
Lead	44	150	81
Nickel	27	78	49
Zinc	150	470	280



# Contaminants Not Quantified

- COD
- Nitrite
- Ammonia
- Mercury
- Selenium
- Total PCBs
- Total PAH
- Total DDT
- Total Chlordane
- Dieldrin
- Chlorpyrifos
- Diazinon
- Dioxins
- Total coliform
- Fecal coliform
- Enterococcus
- MTBE

# Comparisons Of The Pathways

	Total load (t)	Runoff %	Effluent %	Atmosphere %	Dredge %
SS	320,000	98	2.4	-	-
Nitrate	4,500	33	67	-	-
PO4	1,500	34	66	-	-
Cd	2.4	95	3.4	1.5	0.0
Cr	57	70	2.3	1.6	26
Cu	74	89	8.0	1.5	1.6
Ni	64	76	7.5	0.9	15
Zn	320	87	11	-	2.5

# Comparisons of Local Pathways With Central Valley Loads

	Local Bay (t)	Central Valley (t)	Relative Magnitude
SS	320,000	3,500,000	11x
Nitrate	4,500	43,000	10x
PO4	1,500	6,400	4x
Cd	2.4	1.6	0.7x
Cr	57	550	10x
Cu	74	270	4x
Ni	64	410	6x
Zn	320	428	1.3x

# Recommendations

- a. **Watershed characterization** using factors that relate to storm water transport of priority contaminants
- b. **Conceptual model development** (sources, transport, transformations, pathways, loadings, and losses)
- c. **Development of evaluations strategies** for classes of contaminants with similar properties
- d. **Establish a regional network of observation watersheds**
- e. **Extrapolate to other watersheds**

# What has happened since AB1429?

- SWAMP / RMAS
- Better characterization of Central Valley loads
- Urban literature review
- Conceptual model development

# Summary

- The simple model was used as a tool for:
  - 1) Inventory
  - 2) Data gap analysis
  - 3) Comparing loads from different sources
  - 4) A framework for determining monitoring needs for the future