Sources, Pathways, and Loadings Work Group Meeting June 3rd, 2002

Lester McKee
Watershed Program Manager
San Francisco Estuary Institute

Objectives of the Meeting

- Describe progress at Mallard Is. and seek SPLWG approval on how to proceed
- Present recent new Hg load estimates using C Foe data and seek SPLWG approval on a collaborative approach at the R2/ R5 boundary
- Summarize lessons learned and suggest where to go with mass budget modeling in the Bay
- Discuss the JOINT STORMWATER AGENCY Hg, PCBs, and OCs report
- Present the long awaited storm drain mapping report. Seek SPLWG input on recommendations
- Discuss the literature review of Urban Runoff Processes. Seek SPLWG input on and approval of recommendations

Mallard Island Again

Lester McKee, Jon Leatherbarrow, Don Yee, Jay Davis
SFEI
Neil Ganju and David Schoellhamer
USGS
Russ Flegal, Eric Grabowski, Sharon Hibdon, Genine Scelfo, Allison Leungen, Mara Ranville
UCSC

Why are Particle Loads Important?

- Most contaminant that are currently of concern in the Bay attach to particles
  - Mercury
  - PCBs
  - OC pesticides
  - PCBs
  - Other trace metals

- The Central Valley the largest pathway of particles and therefore contaminants to the Bay

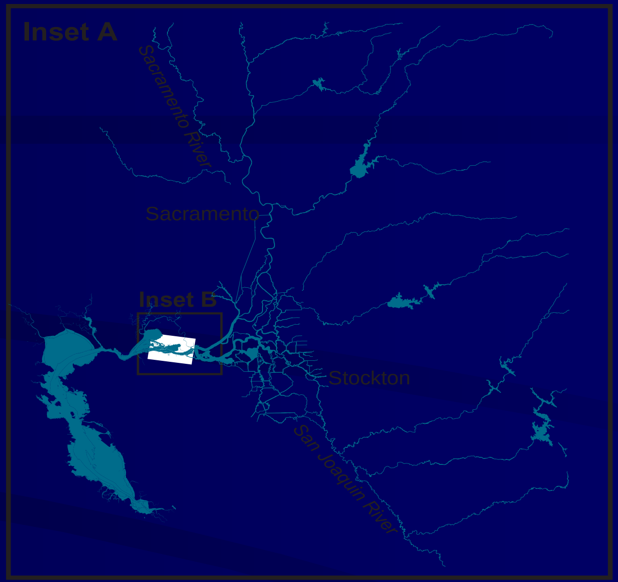
The Beginnings of the Mallard Island Study

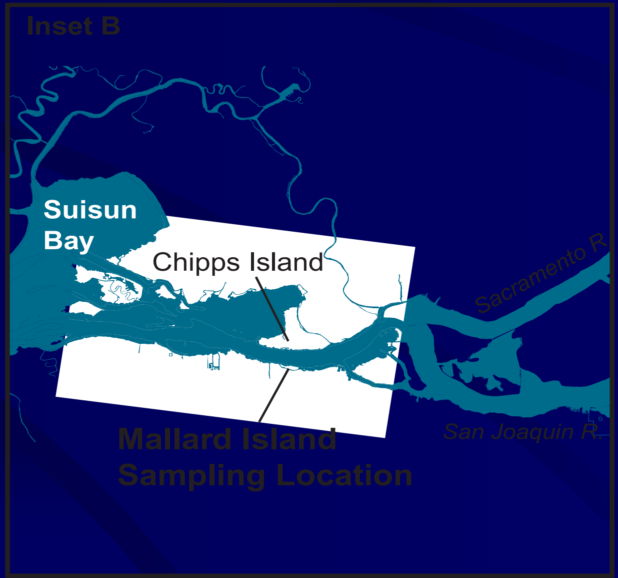
- Literature Review of Loading of Sediment Particles to the Bay from the Central Valley (McKee, Ganju, Schoellhamer, Davis, Yee, Leatherbarrow, Hoenicke)

Conclusions

- The data collected at Mallard Island by the USGS are suitable for estimation of suspended sediment and contaminant loads associated with particles
- The loads of suspended sediment entering the Bay from the Central Valley averaged $\underline{2.1 \pm 0.3\ \text{Mt}\ \text{y}^{-1}}$ for the water years 1995-98
- Data collected by the RMP is unsuitable for estimation of contaminant loads
- To improve accuracy of loads estimates new data focusing on floods must be gathered

Sampling Location





Sampling Team and Responsibilities

Suspended sediment sampling
- USGS

Contaminant sampling
- UCSC (2 persons)
- SFEI (1 person)

Laboratory analysis
- UCSC (Hg, TMs, and ancillary)
- AXYS (PCBs, PAHs, OCs)

Reporting and publishing
- SFEI
- UCSC
- USGS

Oversight
- SPLWG

Progress to Date

- o TRC approved funding for a three-year study at Mallard Is. Jan 2002: UCSC/ SFEI team begins sampling
- o Jan/ Feb 2002: Peer-review comments used to refine the study design

Issues raised

- Are the point samples collected at Mallard Is. representative of the whole cross-section
- Is there a better method for estimation of discharge

Solutions proposed

- Doppler profiler to qualitatively test water column variability
- Collaboration with a modeling group to generate discharge data at an hourly time step

Progress to Date Continued

- Field sampling began in January
  - Jan 9, 29, Feb 22, 23
  - 6 samples in total collected

Outcomes

- Learned about the team

- Learned about the system (tides, velocity, water clarity etc)

- Refined sampling procedure
  - 3 days heads up
  - Reaction discharge 40,000 cfs
  - 24 hour mobilization of the field team
  - Sample 2 times per day minimum

What to do this year?

Budget remaining

- o 140 hours of field time (LM, JL, DY)
- o 60 hours of data management time (DY)
- o 300 hours of project management and reporting (LM, JL)

Options

1) Perform an analysis on all existing chemical data and write up a formal report for peer-review. The objective: to develop hypotheses and conceptual models and to collate existing data and use it to develop contaminant models

- WY 1999, 2000 SSC data
- C Foe Hg, RMP, DWR/ IEP, CALFED, USGS data

2) Hold over non-fieldwork hours to 2003

Mercury loads entering San Francisco Bay from the Delta

Lester McKee
SFEI
Chris Foe
Central Valley RWQCB

Use of Existing Data

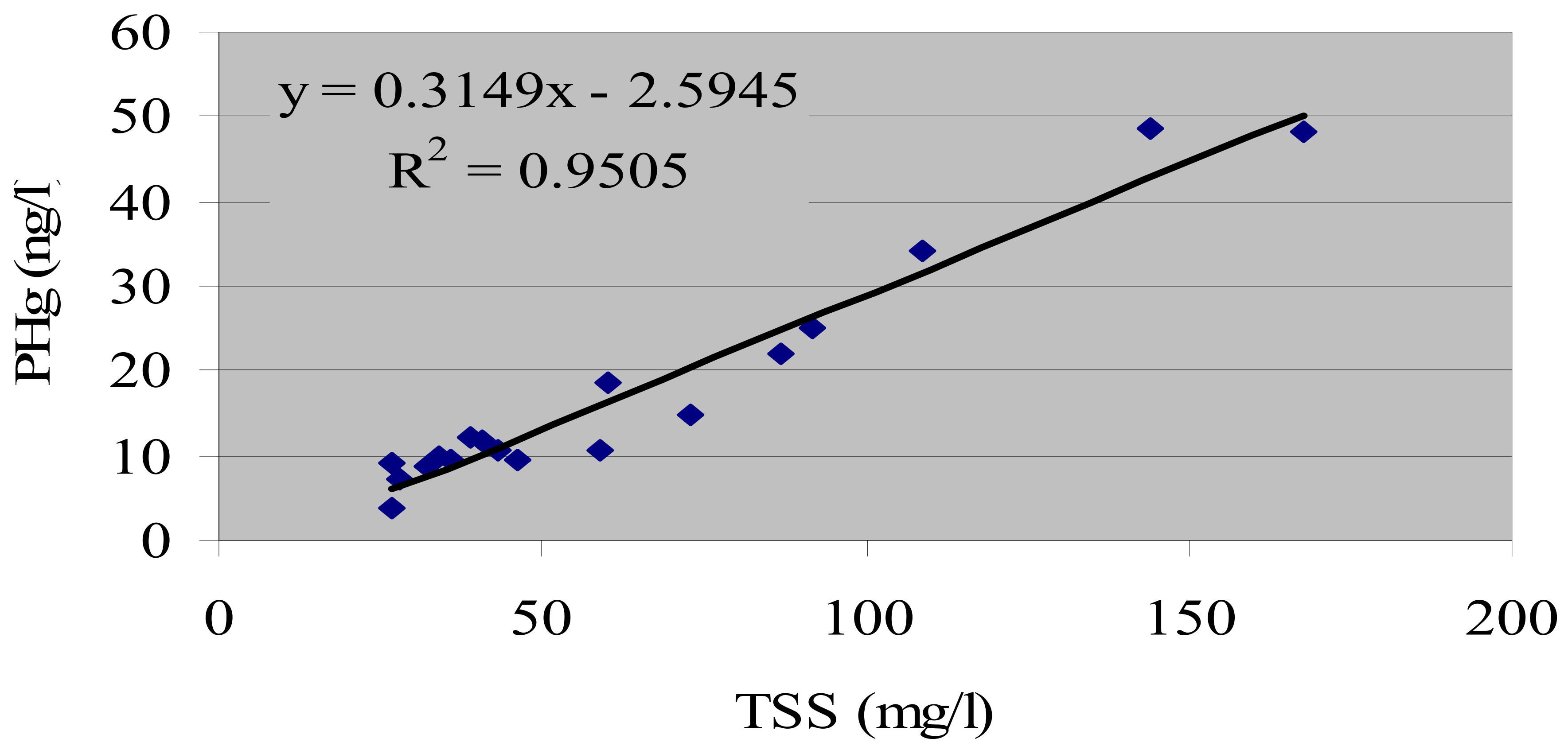
Data supplied by Chris Foe
(Region 5 RB)

- March 2000 to October 2001 Hg data at X2.
- Suspended sediment concentration and loads for water years 1995-98.
- Delta outflow using the DAYFLOW.

Issues

- Management actions will be sensitive to the accuracy of loads estimates.
- If loads estimated too high, efforts by Region 5 may have little impact on SF Bay contaminant budget.

The Regression Model



The Loads Estimates

Water year	Suspended sediment (Mt)	Particulate Hg (kg)
1995	2.6±0.4	701±154
1996	1.0±0.2	253±55
1997	2.2±0.4	612±134
1998	2.4±0.4	644±141
4-year average	2.1±0.3	552±121

Issues and Uncertainties

Laboratory Issues

- SSC versus TSS

Calibration space

- TSS concentrations collected at X2 were between 27 mg l^{-1} and 168 mg l^{-1}.
- USGS data, SSC estimated using OBS sensors between 5 mg l^{-1} and 420 mg l^{-1}.

The model

- The regression suggests that the relationship between SSC and Hg will remain constant under higher flow conditions.
  - It is known that source affects concentration
  - That the Delta appears to be a net source

Summary

- SFEI has a study structure and team that will collect data over the next 3 years to provide better estimates of contaminant loads.

- The data will help to improve management of contaminants in both R2 and R5 regions.

- The data provided by C Foe of R5 has been used to:

1. Build a hypothesis of Hg loads
2. Formulate questions on how to evaluate future data
3. May provide a great framework for building a consensus picture and collaboration between groups

Mass Balance Modeling

Jay Davis and Don Yee
SFEI

Joint Stormwater Agency Report KLI, 2002

Jon Leatherbarrow and Lester McKee

SFEI

Jon Konnan

EOA

Marty Stevenson

Kinnetic Laboratories, Inc.

The use of bed sediment concentrations as an indicator of relative watershed contamination

Normalization of organic contaminants to % fines

- Normalization to % fines assumes that :

1. The surface area to grainsize ratio remains constant
2. The distribution of grainsize in the grains finer than 0.62mm is constant or comparable between river systems

- Normalization of hydrophobic nonionic organic contaminants (PCBs, DDT, chlordane, etc.) to % fines assumes that sorption is :

1. Consistent between all samples
2. Independent of organic carbon

Bed sediment versus suspended sediment concentration:
Chemical evidence

- Differences in organic carbon characteristics between bed and suspended sediment, which influence their respective capacities to sorb contaminants.

1. Pereira et al. (1996) shows how concentrations of OC pesticides and PAHs may differ between bed and suspended sediment by as much as 55 times.

2. Hg data from sediments downstream from the Red Devil Mine Alaska (John Gray, USGS Denver), showed suspended sediment concentrations can be anywhere from 3.4 x more to 5 x less the bed sediment concentrations.

Bed sediment versus suspended sediment concentration: geomorphic considerations

- Typically sediment grainsize decreases in a downstream direction; the point of measurement may influence the characterization of that watershed as either contaminated or uncontaminated (This is called the enrichment ratio and is well documented in the literature).

- Some watersheds may store fine sediment, others may not, therefore two watersheds with equal contaminant sources may exhibit quite different contaminant signatures in bed sediments. (This mechanism was suggested in the Sacramento Basin studies as a reason why Cache Ck. (a known mine-contaminated watershed) exhibits similar bed sediment concentrations to the urban site (Arcade Ck.) (Domagalski, 1998)).

The use of bed sediment concentrations and the Simple Model for loads analysis

Bed sediment versus suspended sediment concentration: geomorphic considerations

- Concentrations on particles may vary between storm events and during storm events depending on the activation of watersheds sources.
- Concentration on particles that are deposited on the falling limb of the hydrograph may or may not be representative of either a flow-weighted mean concentration or an event peak concentration.
- Furthermore, Hg may leach out of bed sediments after deposition during dry periods that follow thus reducing sediment concentrations over time.

The Simple Model Again

- There is quantitative evidence that the Simple Model underestimated the suspended sediment load entering the Bay from small tributaries by 2-3 times.

1. FWMC calculated using USGS data for the Bay Area are in excess of 1,000 mg l^{-1} at 9 out of 17 locations and greater than 374 mg l^{-1} at all locations. Concentrations chosen for the Simple Model ranged between 90 and 157 mg l^{-1} for urban land uses, 2,068 mg l^{-1} for agricultural land use and 85 mg l^{-1} for open space land use

2. Estimates for Alameda Creek (45 t km^{-2} y^{-1}), Sonoma Creek (162 t km^{-2} y^{-1}), and Napa River near Napa (174 t km^{-2} y^{-1}) using USGS data are 2 to 3 times greater than estimates using the Simple Model (26, 66, and 55 t km^{-2} y^{-1} for each watershed respectively).

3. The summation of loads from watersheds totaling 45% of the total area of local tributaries is 361-415 thousand metric t y^{-1} compared to the Simple Model estimate of 320 thousand metric t y^{-1}.

Storm drain mapping

Eric Wittner and Lester McKee
SFEI

Urban Runoff Literature Review

Lester McKee
Jon Leatherbarrow
Jay Davis

SFEI

Climate and Hydrology

Lester McKee
SFEI

Summary of Findings

- The discharge of water from small tributaries is about 4% of the total runoff entering the Bay (about the same as the area ratio (5%))
- The ten largest watersheds (ranging in size from 105 to 1,662 km^2) make up 75% of the area (Alameda, Coyote, Guadalupe, San Francisquito, Sonoma, Napa, Wooden Valley, Walnut, San Leandro, and San Lorenzo)
- Rainfall in the region varies from about 250 to 2,000 mm, 90% wet season
- There is an average of 58 to 67 rain days per year (>0.1 in)
- Annual rainfall varies from 200% of normal to 40% of normal
- The region undergoes periods of drought and flood that can last 4-8 years
- There are also longer term flood dominated and drought dominated periods that can last for several decades or more

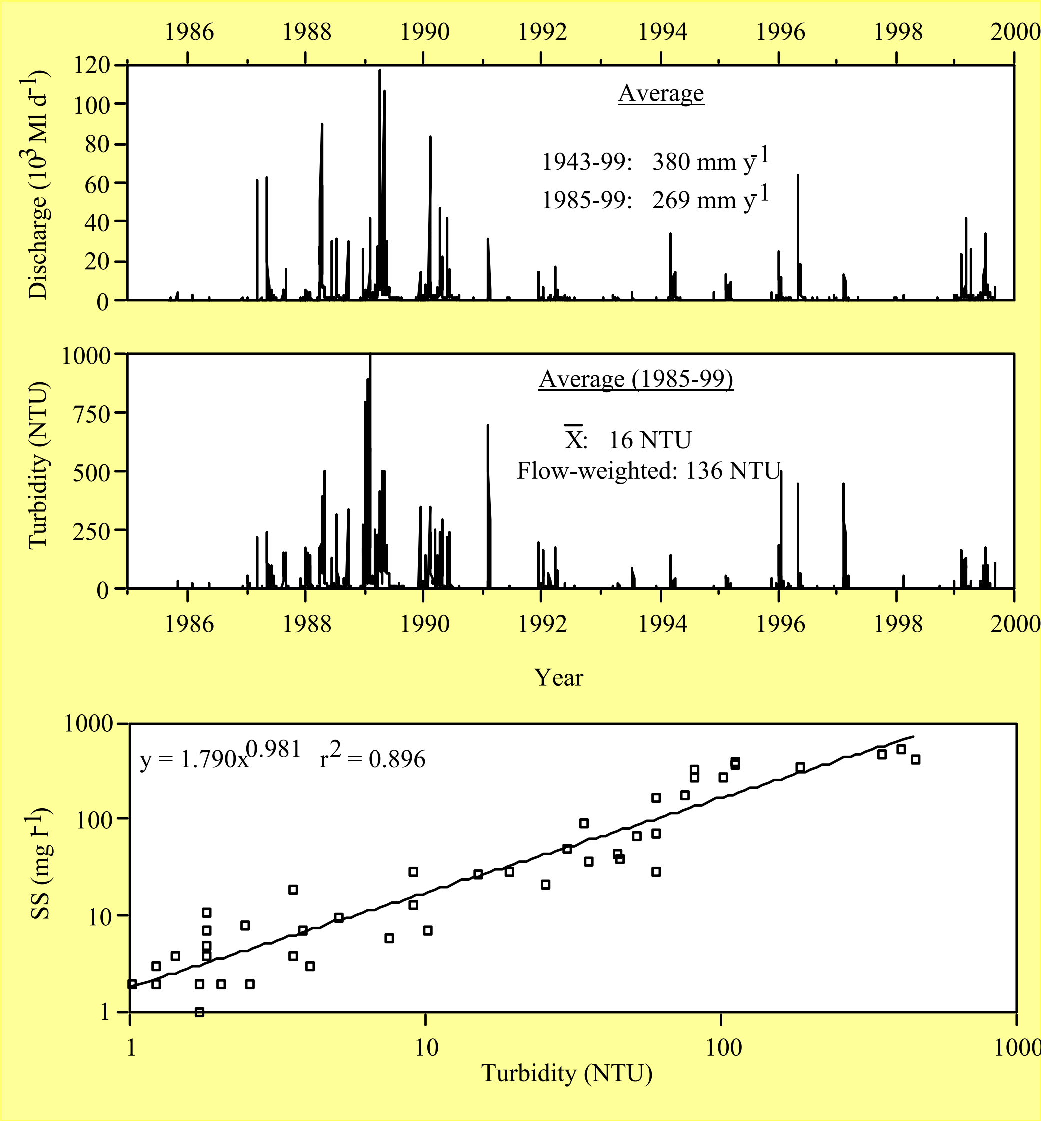
- Between 87 and 99% of the annual runoff occurs from November to April
- Runoff can vary from 0% of annual rainfall during drought years to 75% of annual rainfall during wet years
- Inter-annual runoff variation is amongst the highest in the world and urbanization further increases the "flashiness" of runoff response adding to the difficulties of field monitoring and subsequent modeling an extrapolation
- The response time of small tributaries ranges from about 5 hours (100 km^2) to more than 12 hours for Alameda Creek (1,662 km^2)
- Urbanization increases flow volume, peek flow, and decreases the response time although there are complexities associated with basin configuration
- A regional scale water budget was constructed using the last 30 years of data and shows that annual runoff volume varies from 180 to 3,930 Mm^3 and averages 918 Mm^3

Sediment Processes

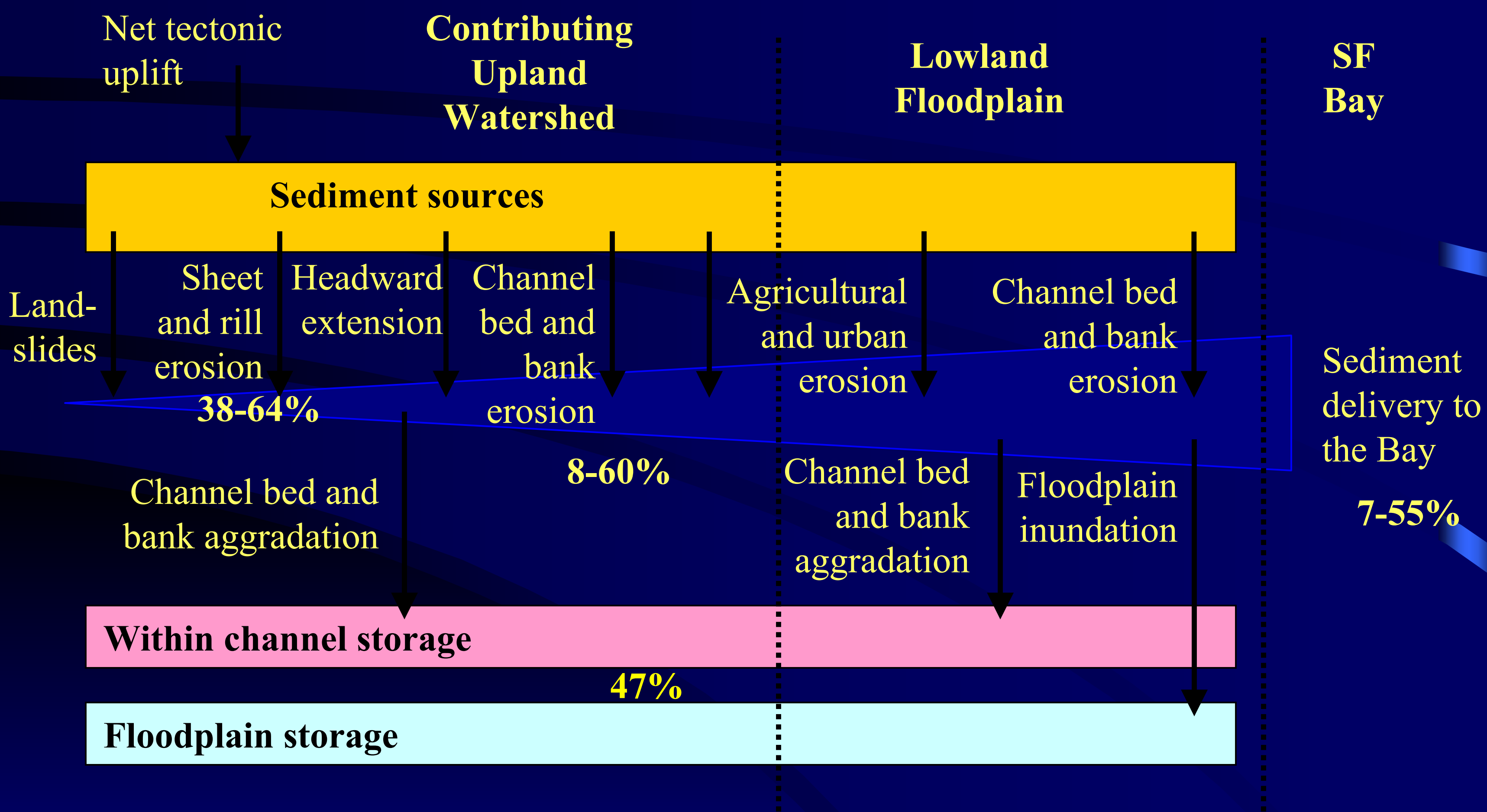
Lester McKee and Sarah Newland
SFEI

Why is an Understanding of Sediment Processes Important?

- Suspended sediment loads from local tributaries currently forms about 40% of the sediment load entering the Bay annually and this may be rising
- Suspended sediment carries with it contaminants such as Hg, PCBs, PAHs, and OCs
- There is a great relationship between SSC and turbidity



Conceptual Model



Available Local Existing Concentration Data

- The USGS has measured suspended sediment concentrations in streams within the nine-county Bay Area over the past 40+ years at 26 locations.

- Three locations in Alameda County have >15 years of data.

- 18 locations have one or more full wet season of data.

- USGS is presently monitoring six locations:

1. Alameda Ck. at Niles
2. Cull Ck. above Cull Ck. Reservoir
3. San Lorenzo Ck. above Don Castro Reservoir
4. Arroyo de la Laguna near Pleasanton
5. Alameda Ck. below Welch Ck. near Sunol
6. Crow Ck. near Hayward).

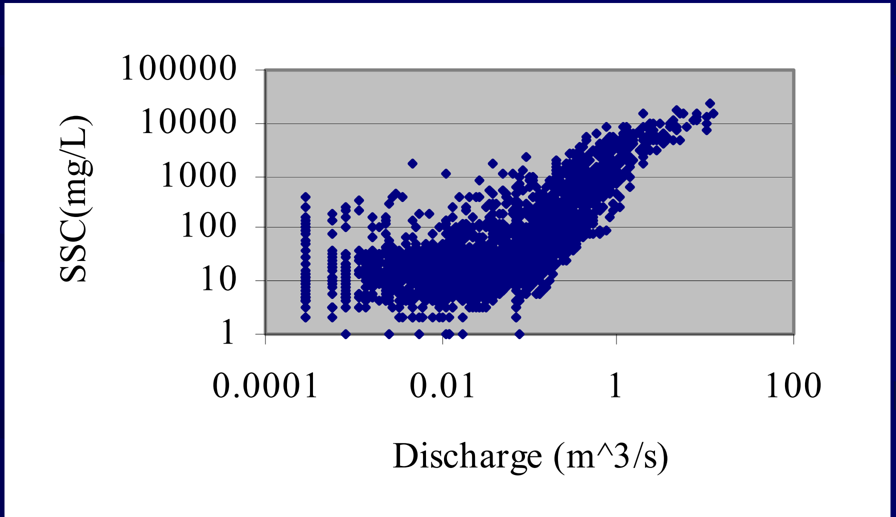
Suspended Sediment Character

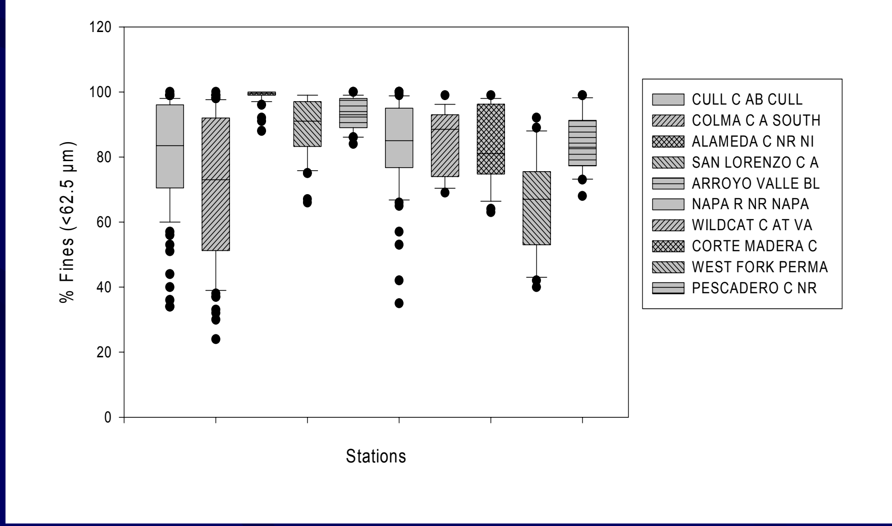
- Peaks in excess of 5,000 mg l^{-1} at 12 locations
- will make the use of surrogate techniques more difficult

- FWMC calculated in excess of 3000 mg l^{-1} at 2 locations, 1,000 mg l^{-1} at 9 out of 17 locations and are greater than 374 mg l^{-1} at all locations.

- At locations where there have been sufficient measurements, grains in suspension are between 67 and 100% finer than 0.62 mm (silts and clays).
- Surrogate technologies are likely to work well for these grain sizes

Cull Ck. above Cull Ck. Reservoir



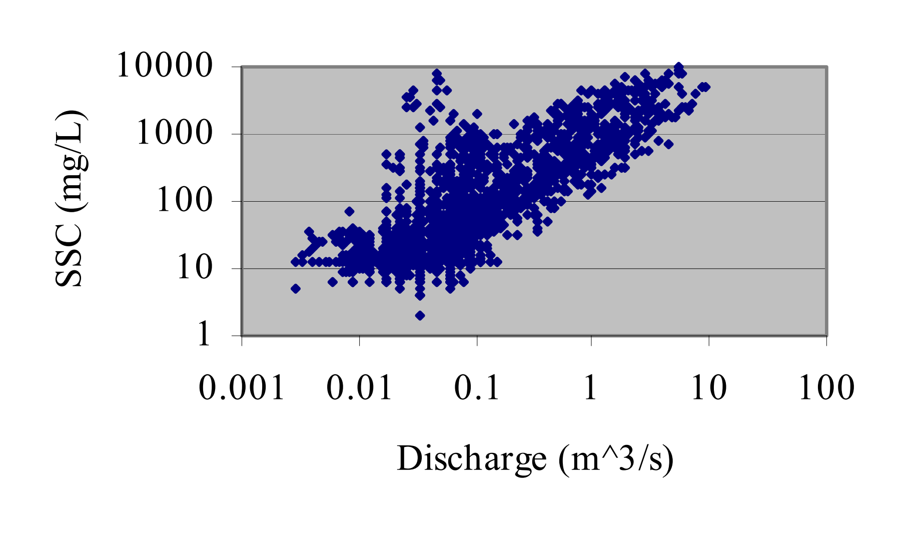


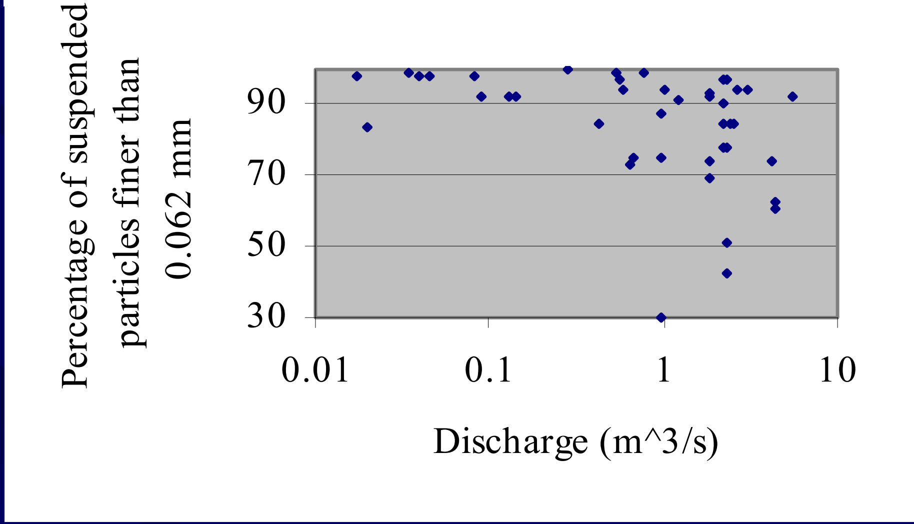
Seasonal Loads Character

	Cull Creek (wet season 1996-2000)	Napa River (WY 1979)	Wildcat Creek (WY 1978-1979)
October	(%)	(%)	0
November	0	0	0.3
December	0.1	3.1	2.4
January	4.2	7.4	40.8
February	53.1	76.7	74.9
March	96.4	89.5	96.7
April	99.8	99.6	99.99
May		99.9	99.995
June		99.92	99.997
July		99.95	99.998
August		99.97	99.999
September		99.99	100

Inter-annual Loads Character

Colma Ck., South San Francisco





- Non urban / less urban watersheds

- 3 to 4 orders of magnitude annual variation

- Urbanized areas (if Colma Ck is a good indicator)

- 1 to 2 orders of magnitude annual variation

- Colma Ck. has low discharge variability, and high and variable SSC

Summary and Ramifications for Sampling Contaminants

- Peak SSC are high but a turbidity threshold sampling technique can overcome this problem.
- Grain sizes vary during floods but are in the range of acceptability for surrogate techniques.
- Existing USGS sediment gauging provides an opportunity to sample for contaminants.
- Several long term data collection sites could be used to interpret less intensive sampling sites and for testing the best extrapolation methods
- Studies that select for a certain time (for example 3 years) may fail to sample the range of sediment and contaminant response to climatic variation and therefore fail to estimate the average or range of annual loads.

- The solution is to selectively sample certain floods for contaminants over a less defined period of time (for example – it may take 4 years or five years

Mercury Literature Review

Lester McKee
Jon Leatherbarrow
Jay Davis

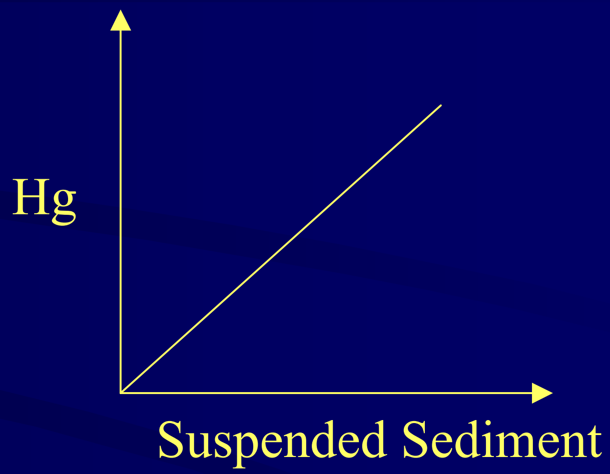
SFEI

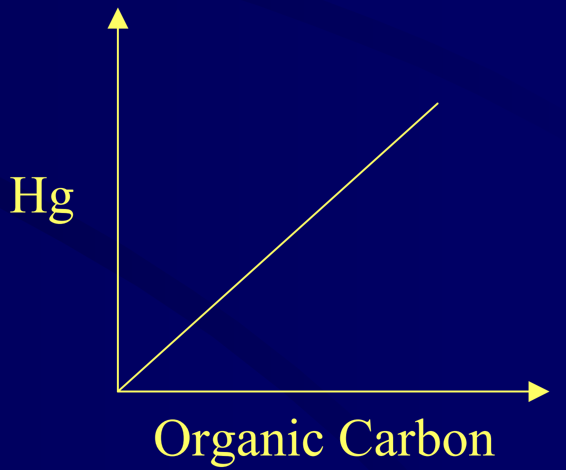
Hg Sources in the Watersheds

- There are 16 historic mine locations in the Bay Area.
- Ultramafic serpentinite rocks that are found in all nine counties.
- Hg is used in the urban environment in common everyday products and devices. This suggests that urban areas with high population will also be likely to have high mercury loads.
- Hg is transported from naturally occurring deposits and contaminated locations in dissolved, colloidal, and particulate forms.
- Particulate mercury is conventionally reported as the mass that does not pass through a 0.4 or 0.45µm filter paper. The colloidal fraction can be partitioned out using ultra-filtration leaving the truly dissolved fraction that passes through 0.0015-0.005 µm pore size

Hg Transport in the Watersheds

- Based on studies in other parts of the US, particulate Hg is between 69 and 99% of total Hg in the water column of contaminated streams.
- In agricultural watersheds particulate Hg may only form 37-50% of the total mercury load and organic carbon seems to play a role in transport.
- Given that colloidal transport make up part of the "dissolved phase" and colloidal material is detectable using optical sensors, surrogate techniques are likely to be applicable to loading studies for Hg under most circumstances.
- Field and laboratory techniques must be "Clean". This issue will pose a challenge or potential barrier to the use of automated field sampling for mercury. Manual collection be necessary, and extrapolation using relationships with suspended sediment or turbidity are likely to be appropriate.



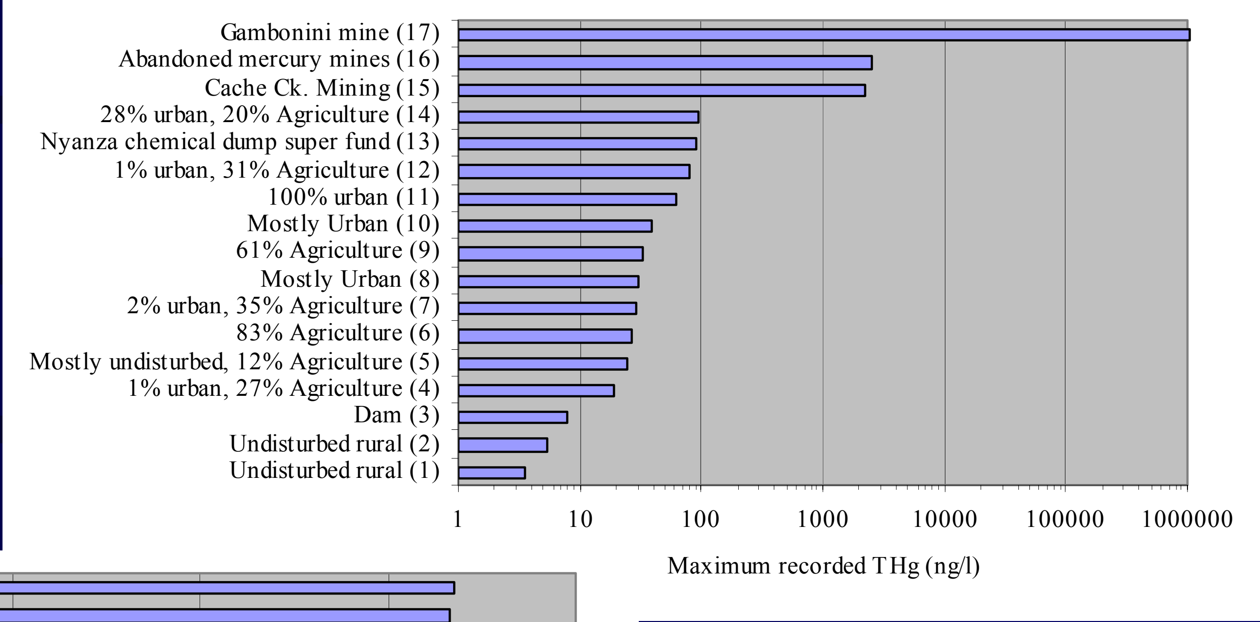


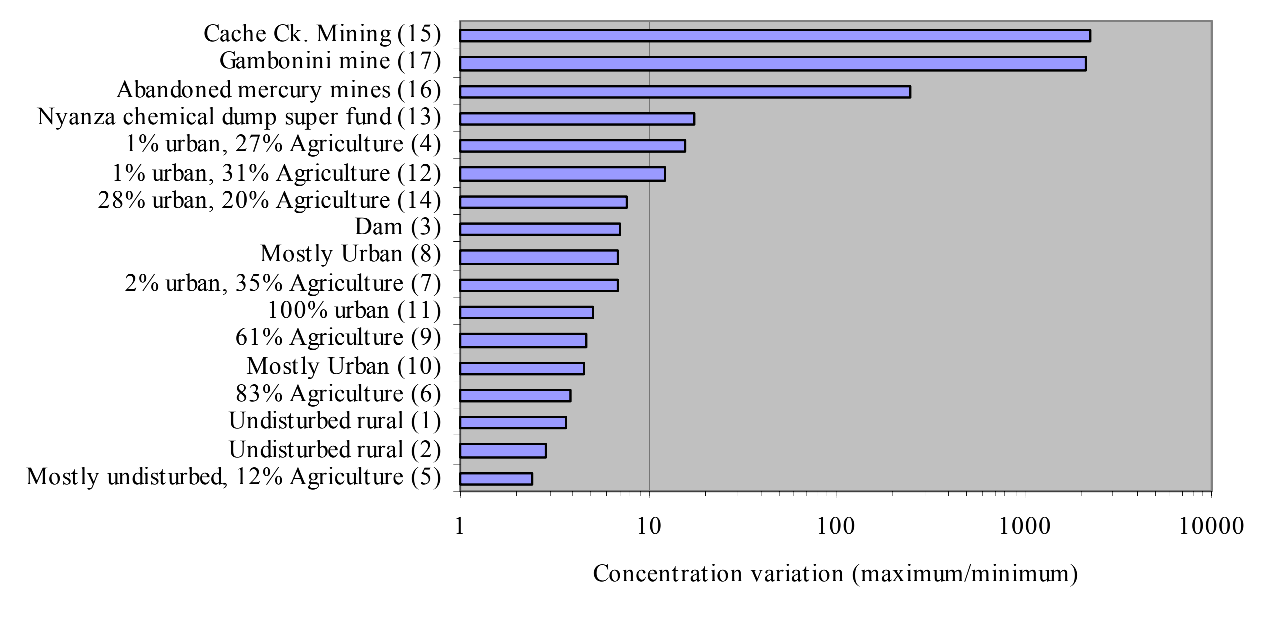
Hg Transport in the Watersheds 2

- Catastrophic events such as large rainstorms, and landslides or tailings dam failures can occur. These “rare events” may cause the majority of loads.
- Total mercury concentration can be expected to vary by 2-3 orders of magnitude during storm events.
- Total mercury concentrations in undisturbed rural watersheds are likely to be 3-10 ng l^{-1}.
- Hg concentration is likely to be 30 times greater in urban and mixed urban and agricultural watersheds and more than 500 times greater at historic mine sites

Hg Character for Different Land Uses

Concentration in different land uses



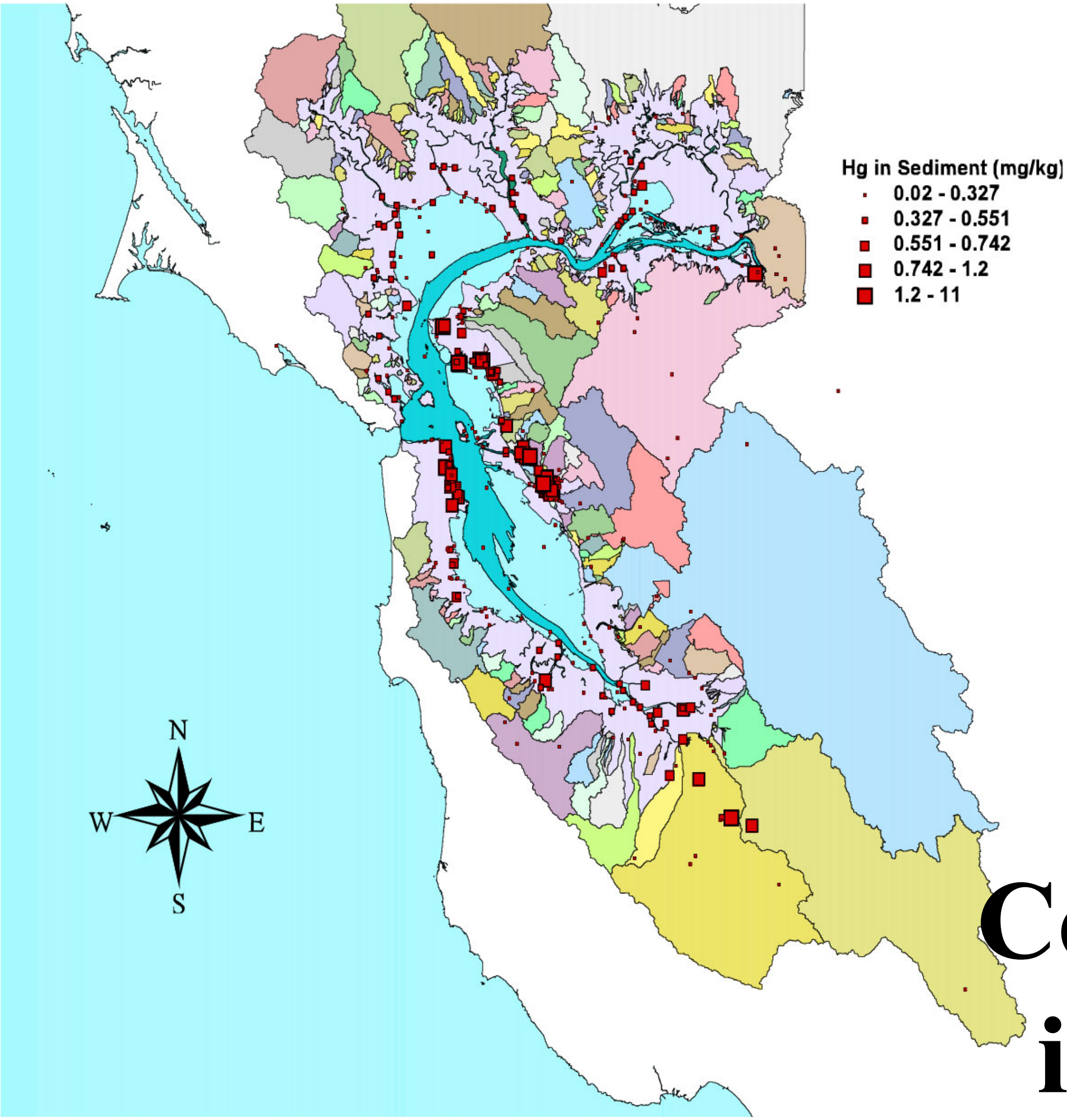


Concentration variation in different land uses

Loads Variation

- Monthly loads in the Central Valley have been found to vary by 129 to 292 times from the wettest month to the driest month.
- Daily loads in watersheds can vary by upward of 1000 times.
- Given the relationship between Hg and suspended sediment, it is likely that 90% or more of the annual load will be transported during the wet season during short lived flood events.

DRAFT Average concentrations of mercury in sediment (mg/kg).
Pilot RMP 1991-1992, RMP 1993-1999, BPTCP 1994-1997, BADALEMP 1994-1997, Stormdrain Sediment Study 2000 (Gunther et al. 2001, KLI 2001), San Leandro Bay Study 1998 (Daum et al. 2000), CALFED 1999.



Concentrations in Sediments

Chlorinated Hydrocarbons

Variability in relation to watershed processes

Polychlorinated Biphenyls (PCBs)

Organochlorine (OC) Pesticides:

DDT, chlordane, and dieldrin

Jon Leatherbarrow

San Francisco Estuary Institute

History of Uses

- PCBs - banned in 1979, except for enclosed applications; primary uses in industry, some for res/comm and non-urban.
- DDT - banned in 1972, except for emergency health purposes; primary uses in agriculture, some for public health and mosquito abatement.
- Chlordane and dieldrin- agricultural use banned in 1970s; continued use for urban applications (e.g., subsurface termiticide) until late 1980s.

Properties

- Hydrophobic organic contaminants – low water solubility, high affinity for organic material (i.e., high K_{ow}, K_{oc}, K_{om}).
- Persistent in soils and sediment and accumulate in lipids of biota.

Sources

- Areas of past and current use and manufacturing.
- Local sediment studies - higher concentrations in urban areas (especially industrial) compared to non-urban locations.
- National sediment studies - higher concentrations of PCBs, dieldrin, chlordane at urban sites, DDT at cropland sites.
- High chlordane concentrations in areas of urban use even in areas of historic agricultural use.

Pathways

- Tributaries (including storm drains) and atmospheric deposition
- Monitoring strategies based on variability:
  - Partitioning
  - Spatial Variability
  - Temporal Variability

Atmospheric Deposition

- SIGNIFICANCE - net deposition to watershed surface from wet and dry deposition
- Concentrations consistent with patterns of use
- Dry deposition and accumulation during summer
- Wet deposition scavenges particles
- Urbanization - less retention of contaminants from increased impervious cover and modified flow

Atmospheric Deposition (cont)

Depositional Fluxes
$g\ km^{-2}\ yr^{-1}$

	Dry	Wet	Total
PCBs	0.13-5.3	1.4-8.1	6.4
DDT	0.43	1.5	1.94
Chlordane	0.23	0.5	0.75
Dieldrin	0.54	0.45-1.3	0.79

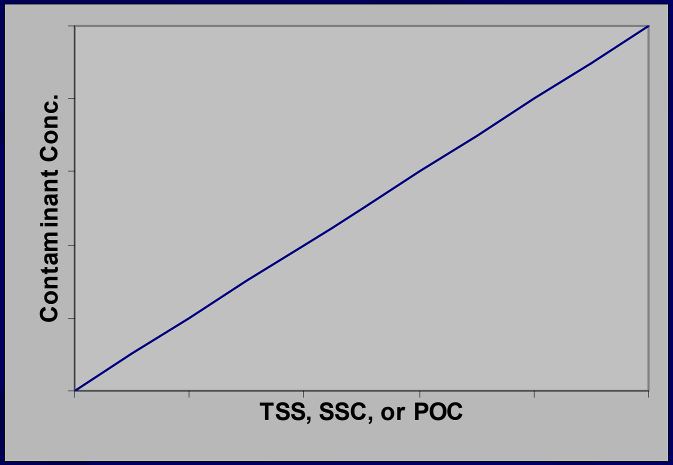
Refs: Tsai et al. 2001, Park et al. 2001, Chan et al. 1994.

IMPLICATIONS FOR MONITORING

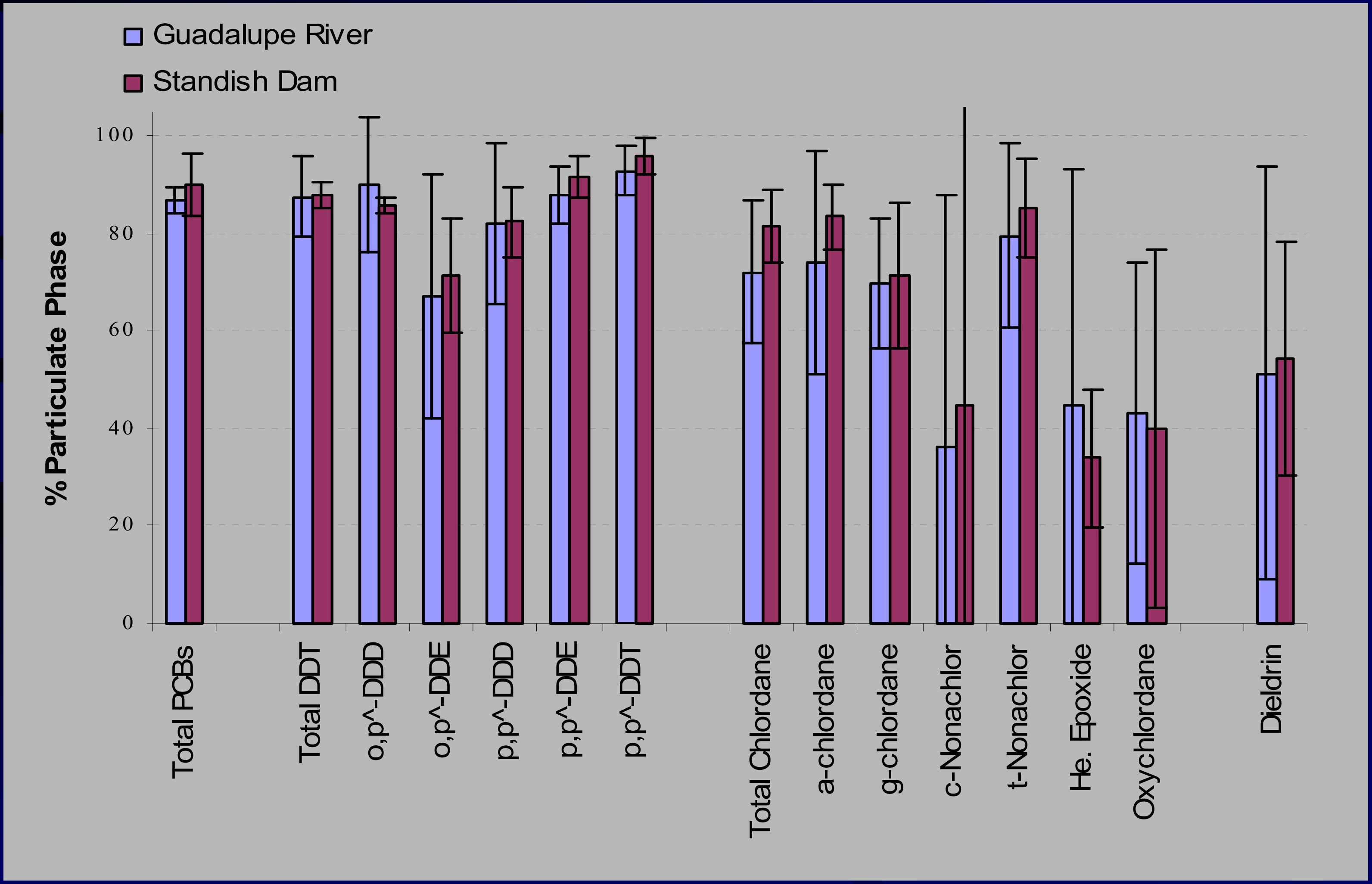
- First Flush Effects - monitor initial storm events of wet season
- Urbanization - may enhance first flush effects

Tributaries - Partitioning

- High affinity for particulate phases, such as organic carbon in soils and sediment
- Some association with dissolved and colloidal phases, which pass through the watershed
- Linear relationships with suspended particulate matter (e.g., POC, TSM, TSS, SSC)



Tributaries - Partitioning (cont.)



Tributaries - Partitioning (cont.)

STRATEGIES FOR MONITORING

- Measure total concentrations to account for dissolved, colloidal, and particulate phases.
- Measure concentrations of variables that influence contaminant fate and transport, including POC, DOC, and SSC.

Tributaries - Spatial Variability

Between Watersheds

- Hot spots - local sediment survey; 3 orders of magnitude between max conc. of PCBs in urban (26,000 µg kg^{-1}) and non-urban locations (29 µg kg^{-1}).
- Hydrology and sediment transport

Within Watersheds

- Varying sources of contaminants, sediment, and organic material from erosion of soils, and mobilization of floodplains, banks, and bed sediment.
- Heterogeneous watershed characteristics, such as land uses, hydrology, and sediment transport.

Tributaries - Spatial Variability (cont.)

STRATEGIES FOR MONITORING

- Prioritize monitoring locations based on contaminants data, hydrology, sediment transport, etc.
- Monitor downstream of contaminated areas
- Monitor near the bottom of the watershed to integrate inputs from various sources

Tributaries - Temporal Variability

- Greatest variability in response to discharge of suspended sediment and organic material.
- First flush vs. seasonal effects
- Urban Storm Drain - 100-fold increase in PCB concentrations on hourly time scale preceded peak discharge.
- Watershed - 5 to 25-fold differences on daily, monthly, and seasonal scales.

Tribs - Temporal Variability (cont.)

STRATEGIES FOR MONITORING

- Monitor initial storms of the wet season to capture first flush effects.
- Monitor at more frequent time intervals during the wet season.
- Explore the use of surrogate techniques for continuous monitoring of suspended material to augment discrete measurements.

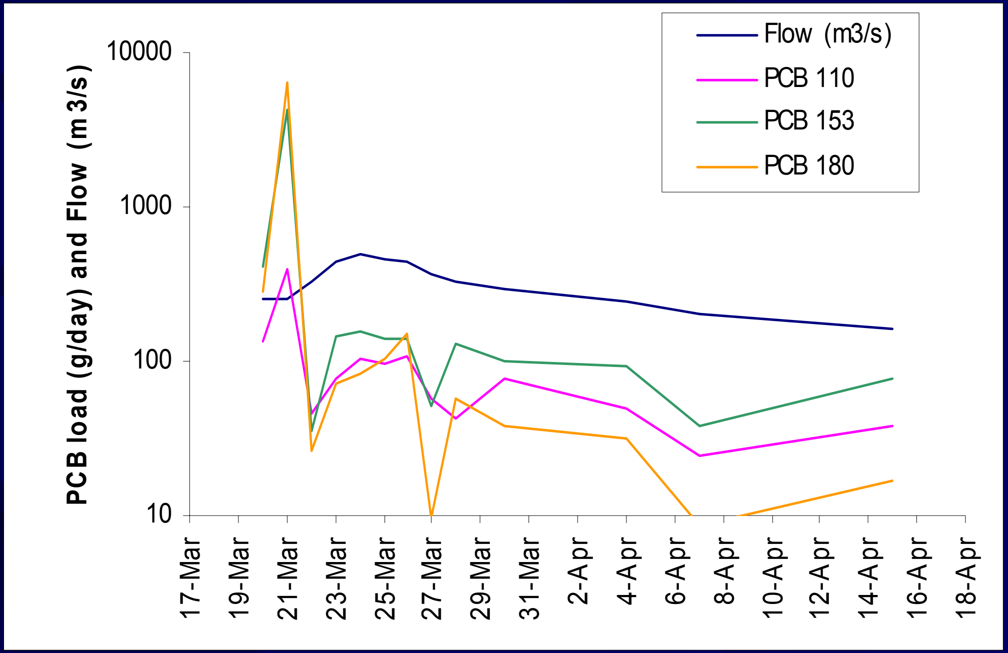
Loading

- Spatial Variability - Urban vs. agricultural rivers in Chesapeake Bay ($g\ km^{-2}\ yr^{-1}$) (*Foster et al. 2000a*).

	Area (km2)	Percent Urban (%)	PCBs	DDT	Chlordane	Dieldrin
Anacostia River	440	60	9-10	2.87	17.8	0.67
Susquehanna River	70,160	5	2.7	0.58	0.44	0.17

Loading (cont.)

- Temporal Variability - similar to patterns of fluctuations in concentrations
- Loading peaks precede peak discharge
  - Urban Storm Drain - > 60-fold increase in instantaneous loading on hourly time scale.
  - Larger Watershed - order of magnitude changes in loading on daily scales.



Summary

- Measure total concentrations to account for dissolved, colloidal, and particulate phases.
- Measure variables that influence contaminant fate and transport (POC, DOC, SSC).
- Prioritize monitoring locations based on existing contaminant data and watershed characteristics.
- Monitor near the bottom of the watershed to integrate inputs from varying sources of contaminants, sediment, and organic material.
- Monitor first significant storms of the wet season to capture first flush effects.
- Monitor at more frequent intervals during the wet season.
- Explore the use of surrogates to augment monitoring.

Recommendations

Lester McKee
Jon Leatherbarrow
Jay Davis