

**National Water Quality Monitoring Council:
Working Together for Clean Water**

Monitoring Trace Metals

Russ Flegal

Environmental Toxicology

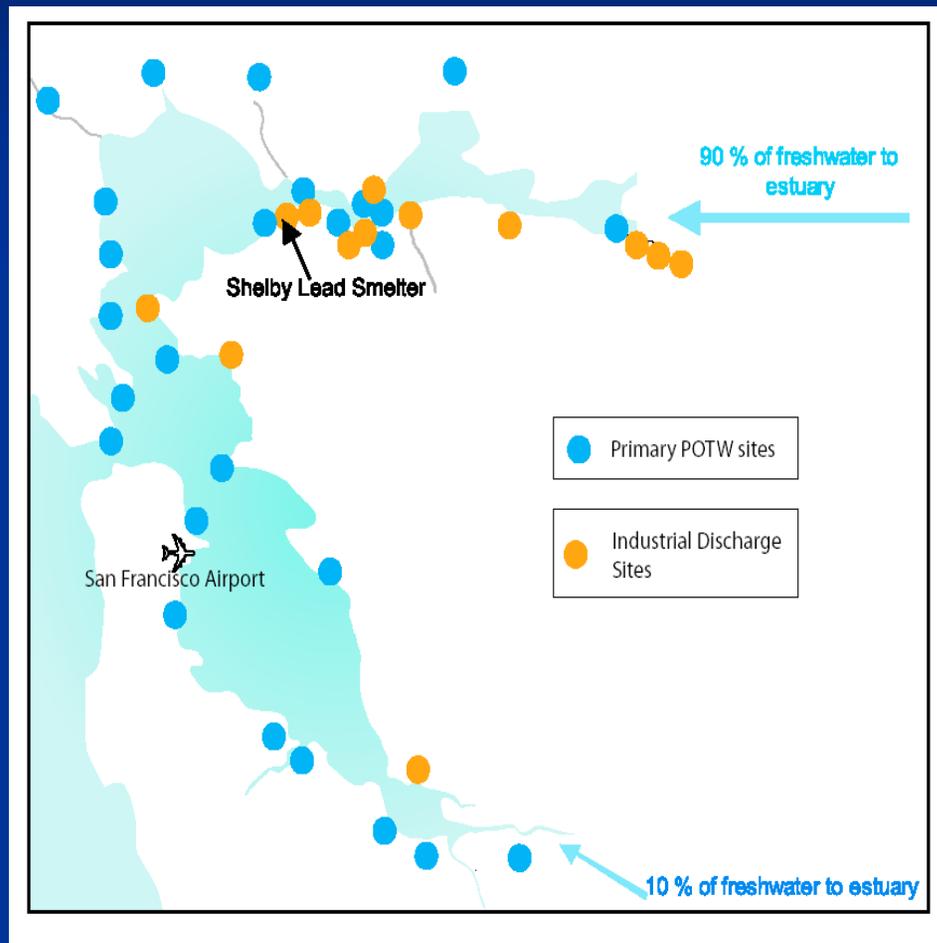
University of California, Santa Cruz

SF Regional Monitoring Program

Spatial Variation in Contemporary Inputs



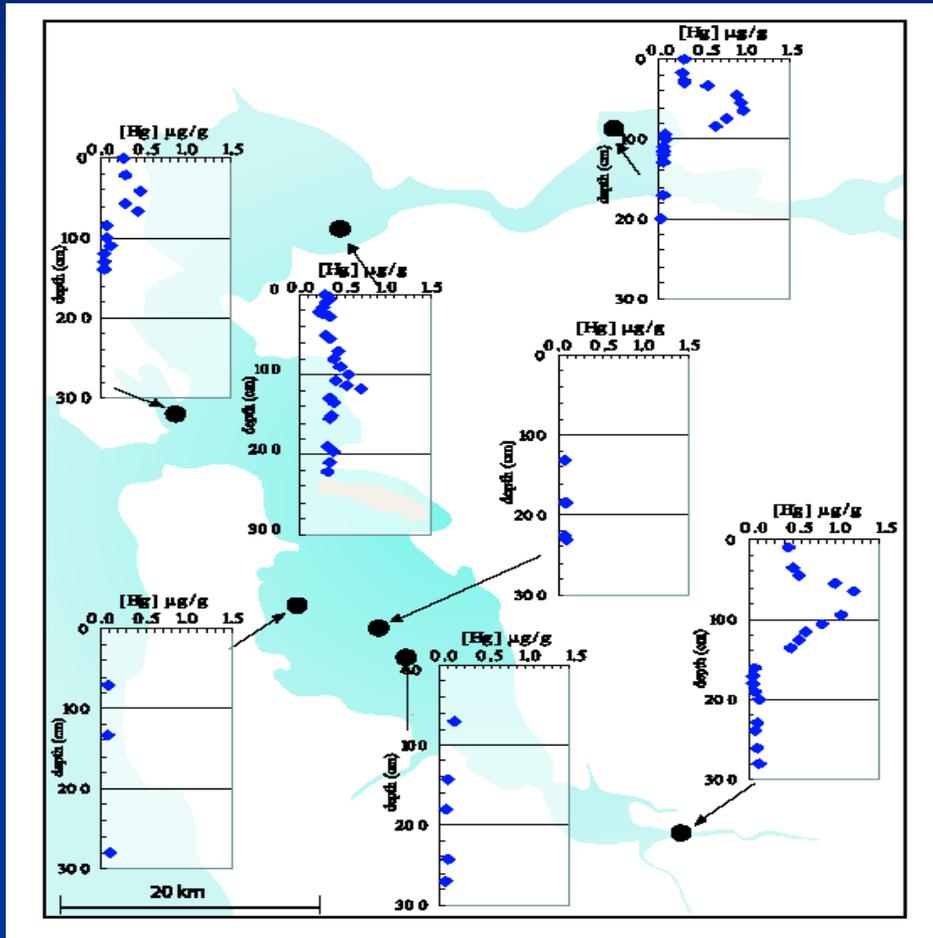
sampling sites



sponsors

Spatial Variation in Legacy Pollutants

Example: Mercury in Sediment Cores



Northern reach

← hydraulic gold mining

Central Bay

← industry ?

← gold mining ?

← mercury mining ?

Southern reach:

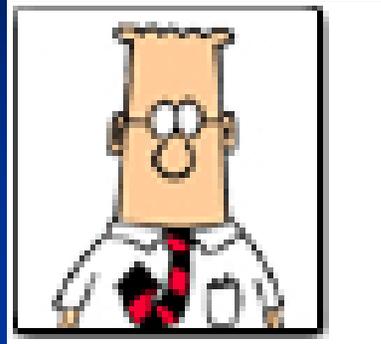
← New Almaden mines

(Conaway et al., 2004)

National Water Quality Monitoring Council: “Working **Together** for Clean Water”



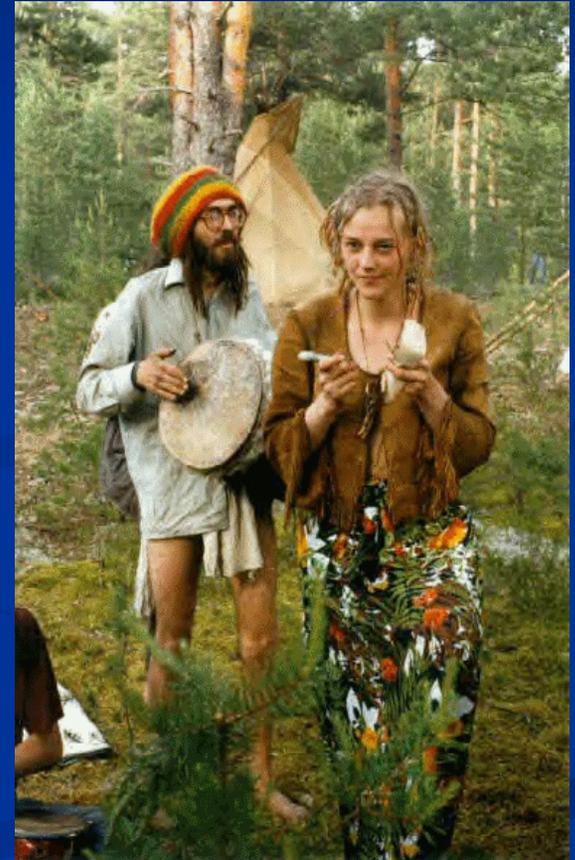
**Scientists
(Research)**



**Managers
(Bottom Line)**

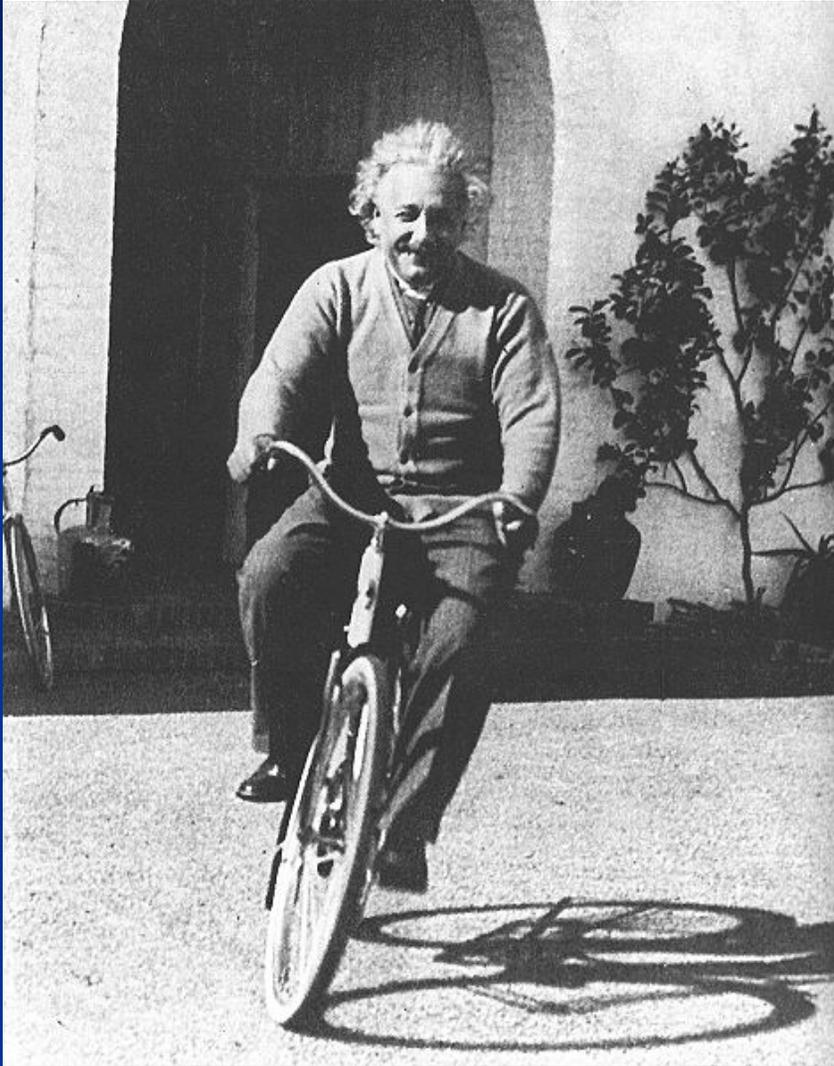


**Regulators
(Numeric Goals)**



**Environmentalists
(Natural at Any Cost)**

One Scientist's Bias *



(* some other guy)

Benefits:

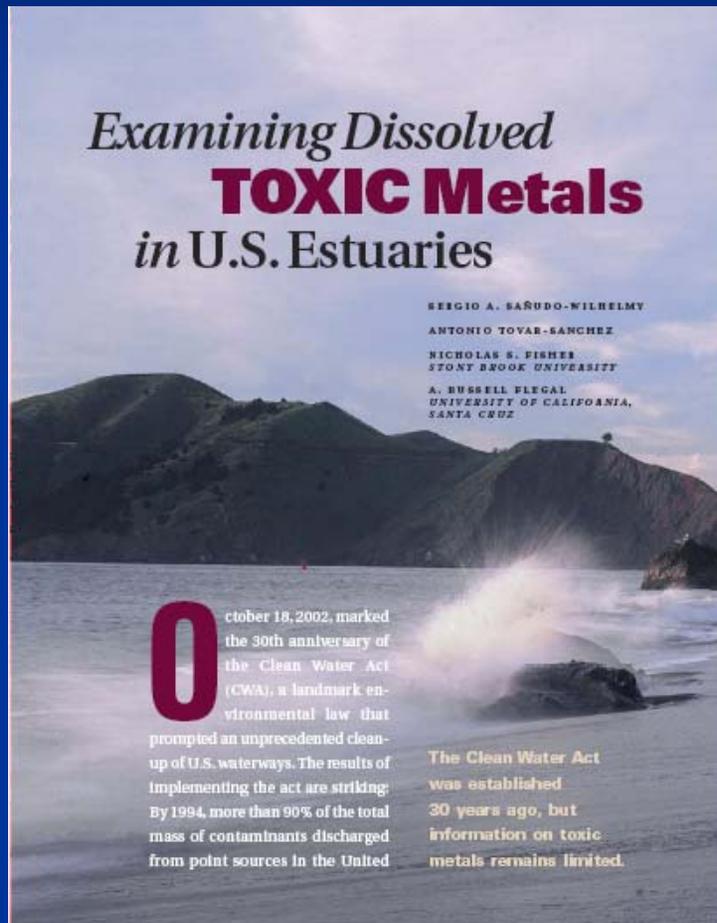
Long-Term Monitoring
temporal variability

Systematic Monitoring
spatial variability

Expanded Monitoring
science behind measurements

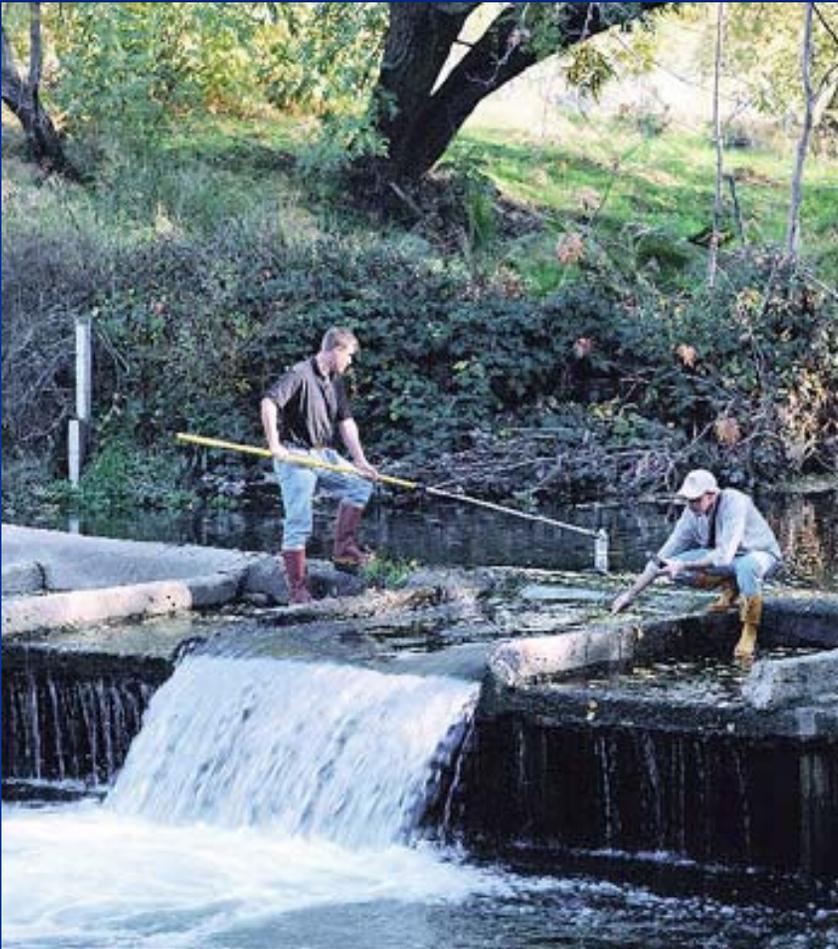
Evolving Measurements
evolving science

SF Bay : National Model for Metals (Please correct me if I am misinformed)



(Sañudo-Wilhelmy et al., 2004. Environmental Science & Technology)

Consequences: Quantity & Quality of Trace Metal Data



No data:

no measure of cost/benefits

Limited data:

limited assessment

incorrect assessment

Sufficient data:

focus on real problems

& emerging problems

Problems of Limited Data

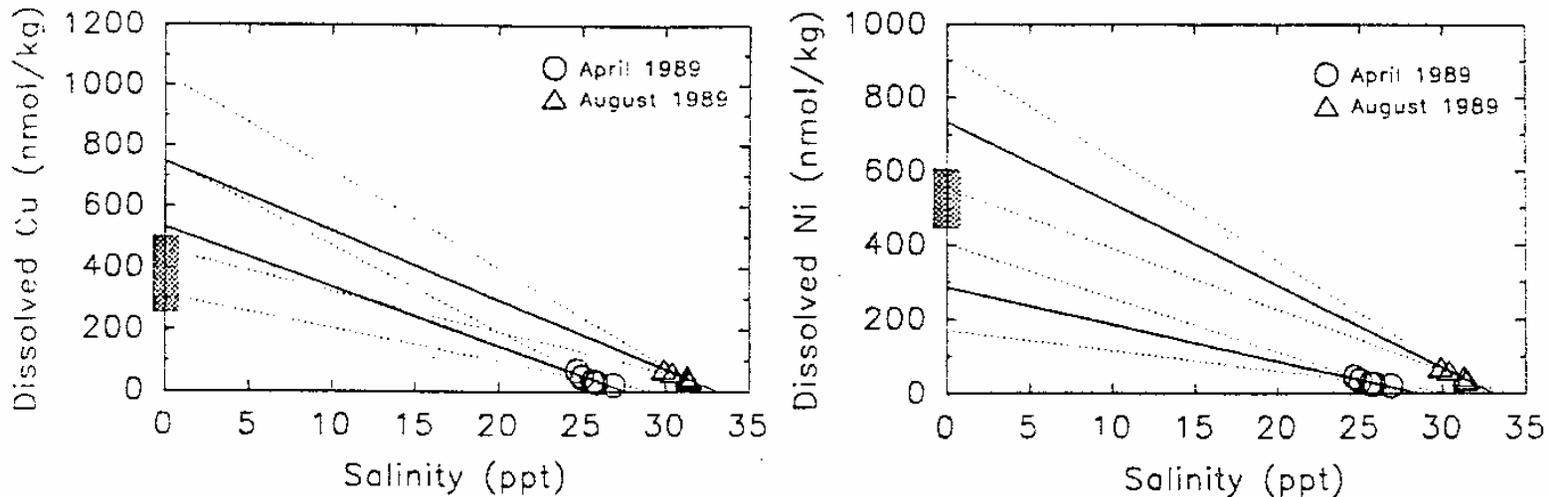
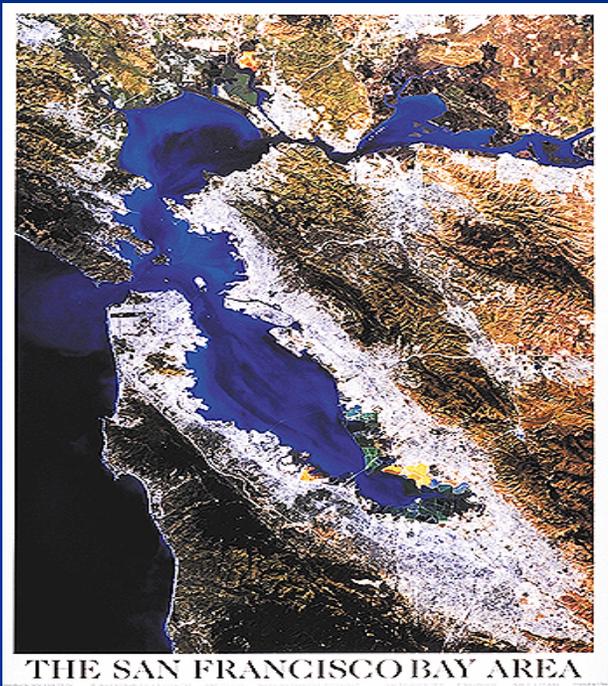


Fig. 7. Extrapolations of dissolved copper and nickel concentrations (mean \pm 95% confidence limits of simple linear regressions) in the South Bay to zero salinity. Cross-hatched areas at zero salinity represent reported concentrations of copper and nickel in municipal waste-water discharges to the estuary (from Gunther et al., 1987).

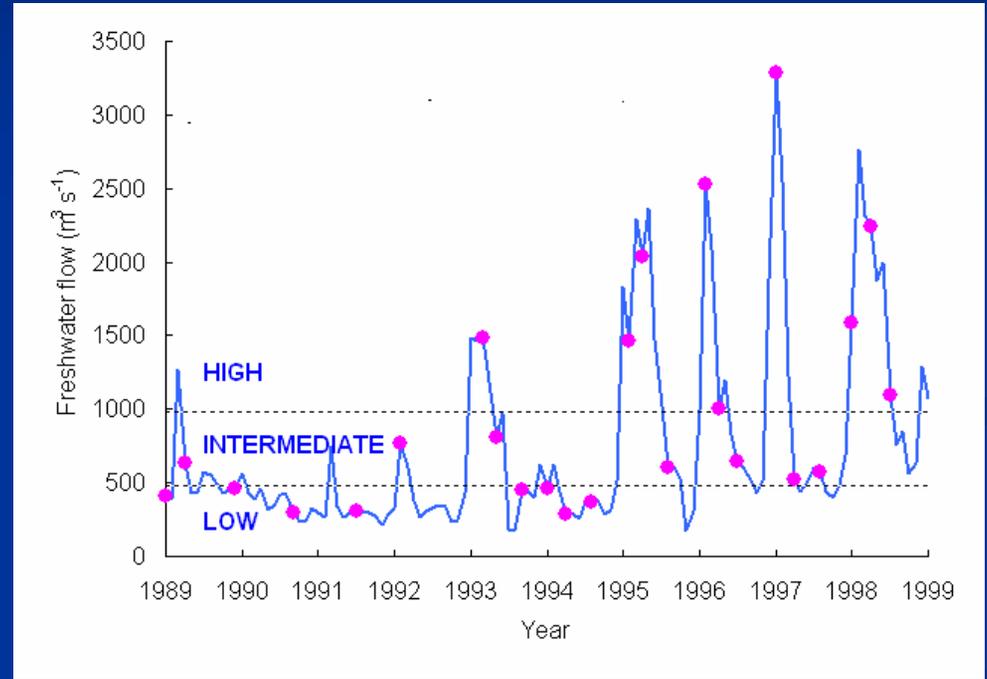
(Flegal et al., 1991)

Limited data enables gross extrapolations & misinterpretations
ex. San Jose POTWs are polluting SF Bay (Flegal et al., 1991)

Benefits of Long-Term Data: Resolve Temporal & Spatial Variability

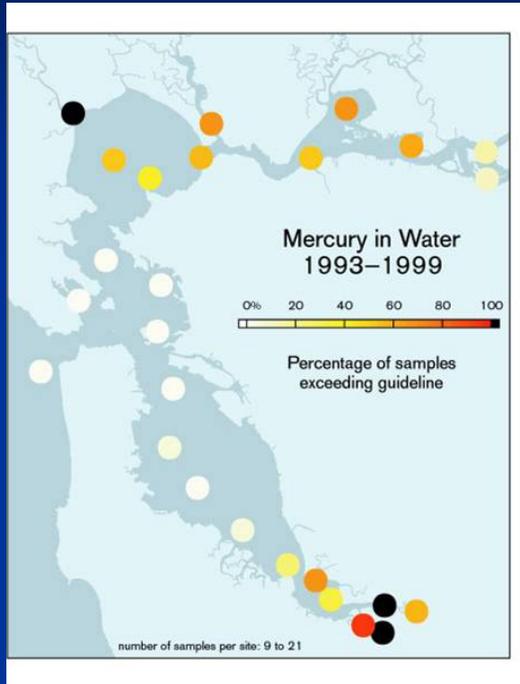


Physical Complexity

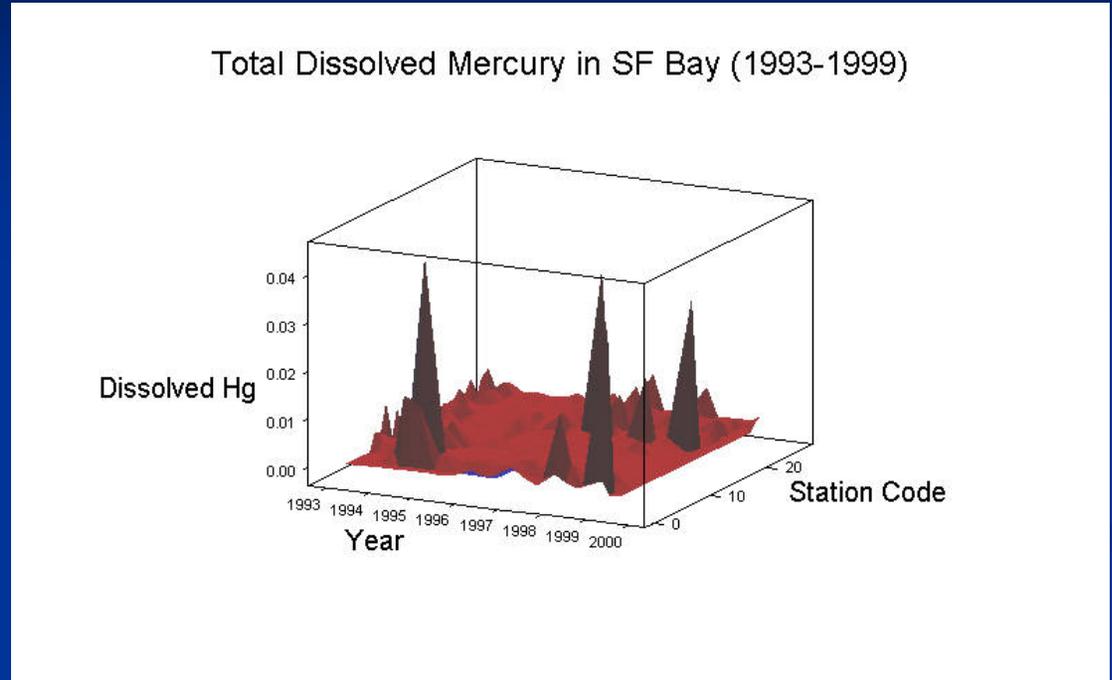


Hydrologic Complexity

Benefits of Long-Term Data: Identify Causes of Temporal Variability



(SFEI Report)



(UCSC Time Series Data)

Temporal & spatial variations of mercury contamination in SF Bay waters
fn: non-point source inputs & fresh water discharges
≠ fn: POTW discharges

» Reducing POTW Hg discharges will have little measurable benefit

Benefits of Long-Term Data: Quantify Temporal Changes & Sources

Example: Lead & Silver in South SF Bay
Observed & Modeled Changes (1989-2000)

Dissolved Metal Concentrations

Ag: 40% decline *

Pb: no decline **

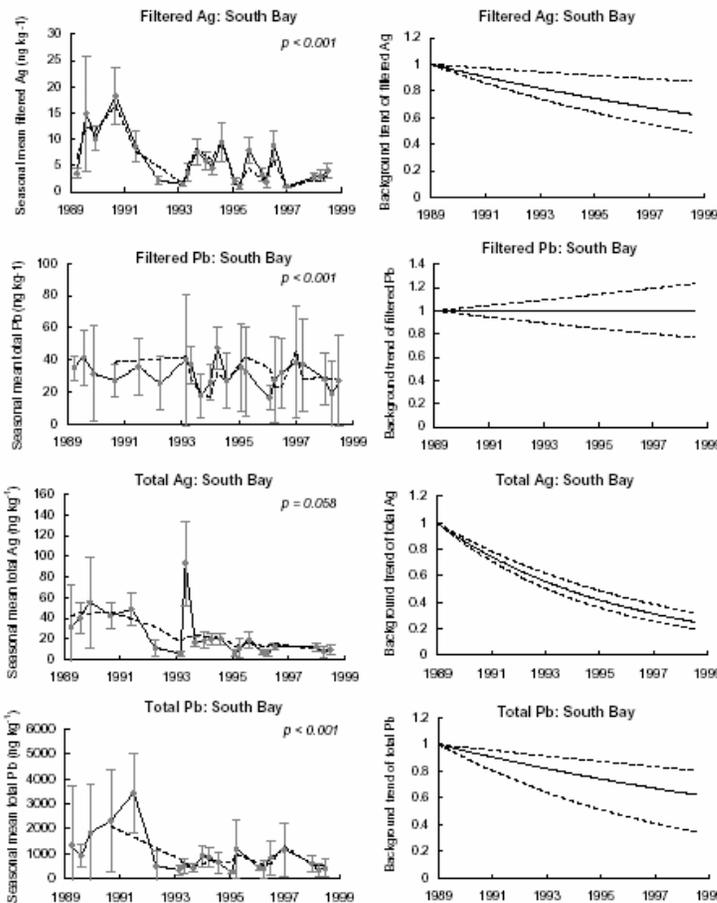
Total Metal Concentrations:

Ag: 70% decline *

Pb: 40% decline **

* Successful Regulation of POTW Ag discharges

** Predominance of non-point source Pb inputs



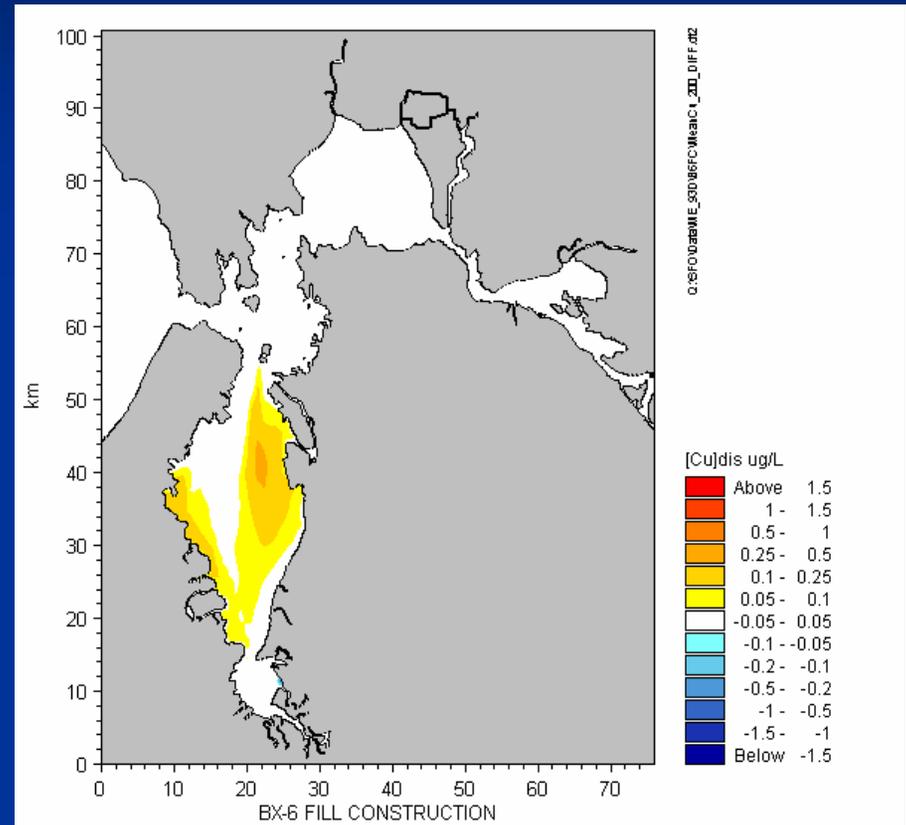
Squire et al., 2002)

Benefits of Long-Term Data: Creditable Extrapolations

INDEPENDENT PEER REVIEW PANEL FINAL REPORT ON:

Predicted Changes in Hydrodynamics,
Sediment Transport, Water Quality, and
Aquatic Biotic Communities Associated with
SFO Runway Reconfiguration Alternative
BX-6, A3, and BX-R

Prepared for the Proposed Runway Reconfiguration at
San Francisco International Airport



Modeled changes in dissolved
copper concentrations are much
lower than feared (Cook et al., 2004)

Benefits of Evolving Measurements: More Appropriate Assessments

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A.R. FLEGAL ET AL.

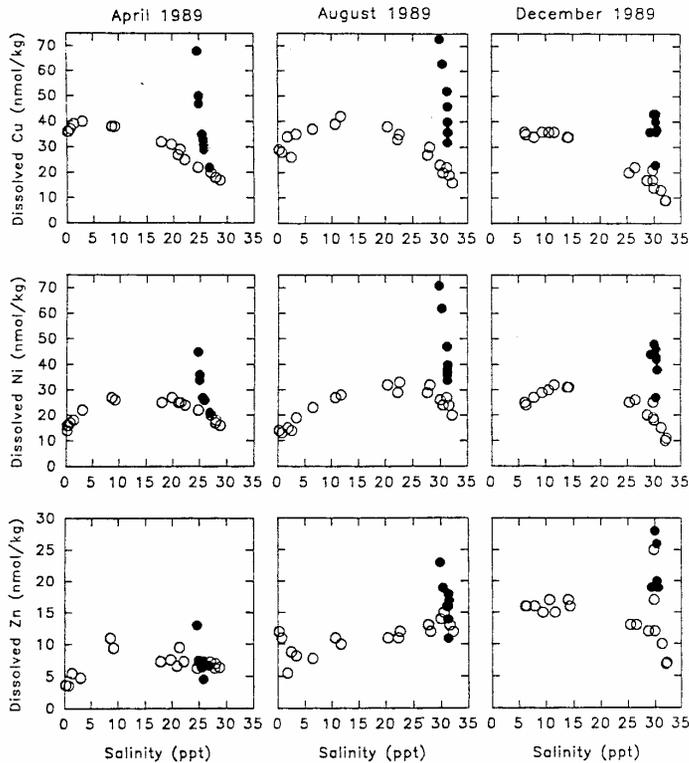


Fig. 3. Dissolved copper, nickel, and zinc vs. salinity in San Francisco Bay estuary for April, August, and December 1989. Open circles represent stations 9-27 in the main estuary, and filled circles represent stations 1-8 in the South Bay.

First accurate analyses (1989)

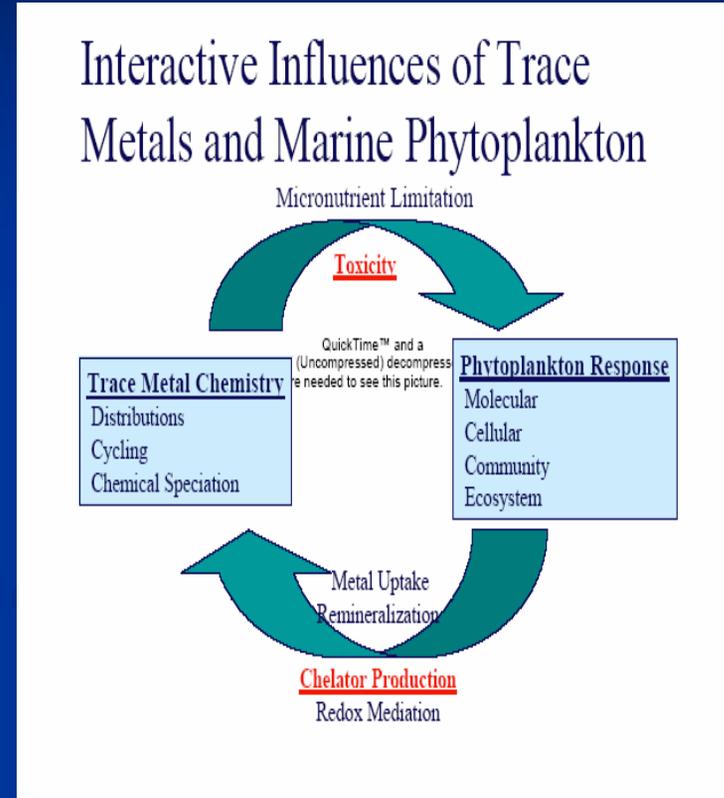
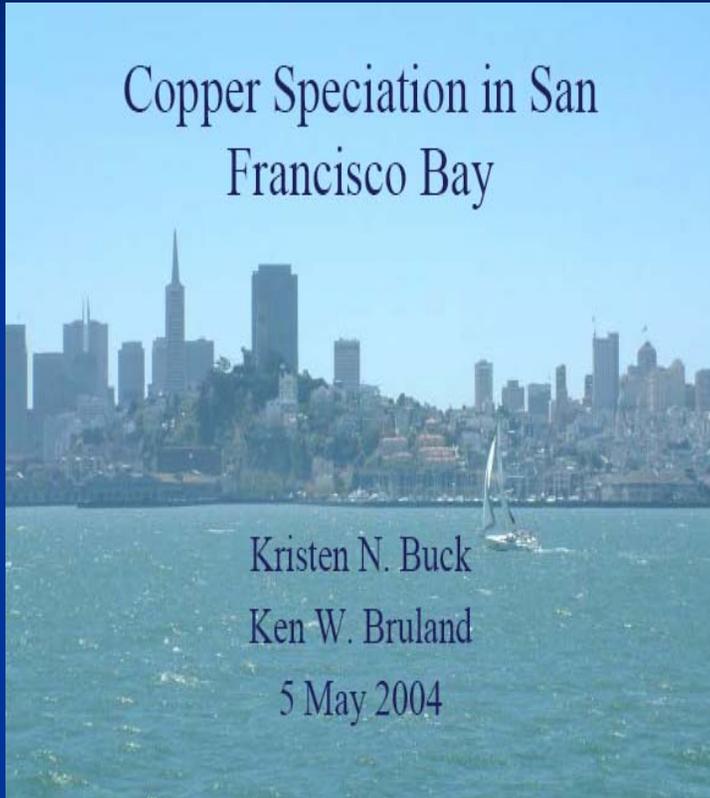
- trace metal clean techniques
- disproved previous data
by orders of magnitude

[Cu] and [Ni] still > WQC

- only in extreme South SF Bay
- only during low flow periods
- BUT...

(Flegal et al., 1991)

Benefits of Evolving Measurements: More Appropriate WQC



Total dissolved copper concentrations > WQC

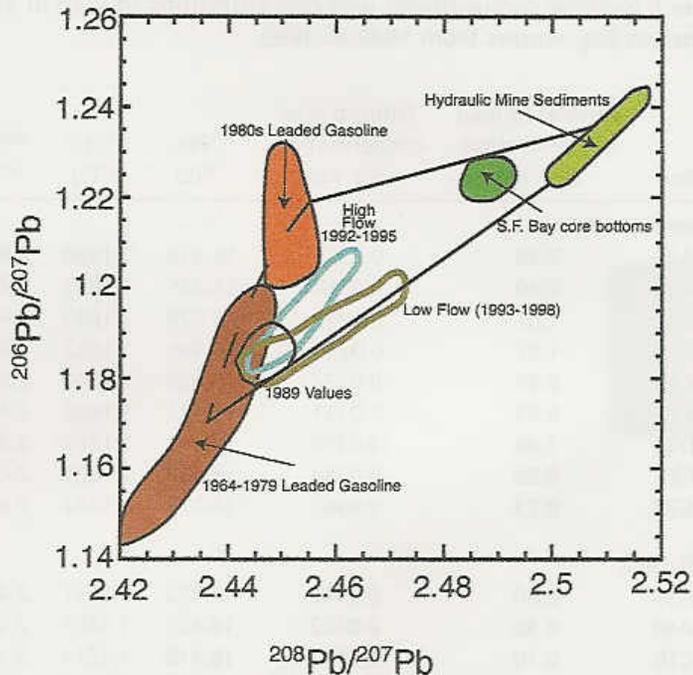
- but most Cu is strongly bound to refractory organic ligands

≠ bioavailable → new, more valid WQC for SF Bay

Benefits of Evolving Measurements: Source Identification

Lead Isotopic Compositions

- Sources in SF Bay waters
 - Natural sedimentation
 - Hydraulic mining
 - Leaded gasoline emissions
- ≠ current POTW discharges



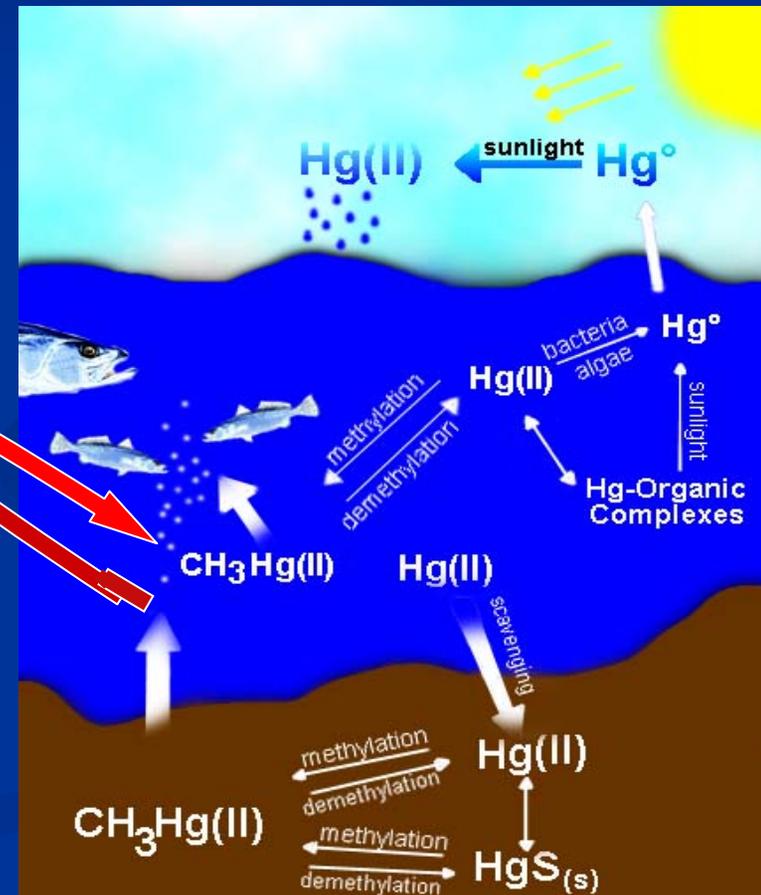
(Steding et al., 2000)

» Reducing lead in POTW discharges will have no measurable effect on lead concentrations in SF Bay waters.

Benefits of Evolving Measurements: Evolving Instrumentation & Science

MeHg concentrations can increase over 100,000 fold between water and phytoplankton (Mason et al., 1995)

Subtle differences in sampling can cause 1,000-fold differences in MeHg measurements in sediments (Horvat et al., 2004)



(Gary Gill's website)

Benefits of Evolving Measurements: Pollutants Do Not Recognize Boundaries

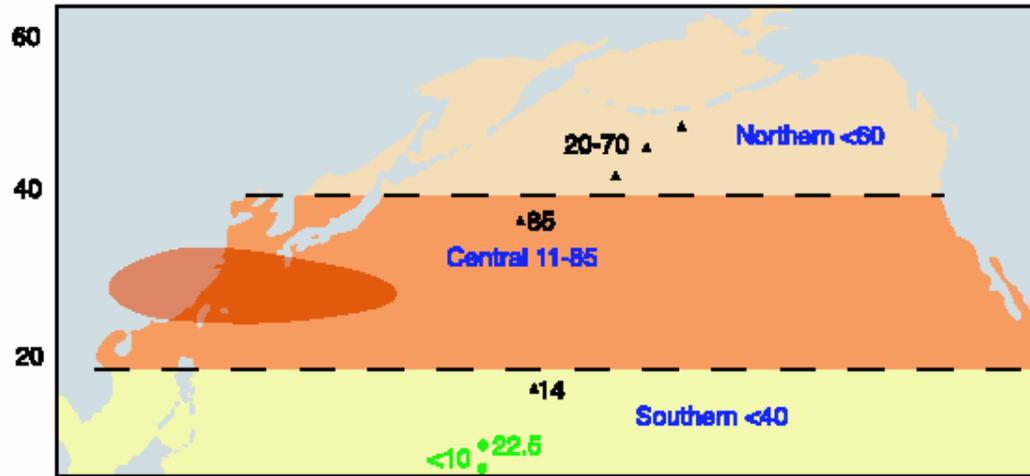


Figure 4. Relationship between storm tracks and Hg concentrations at Long Marine Lab. Storm tracks have been sorted into three categories, represented by dashed lines. Concentrations (pM) are given in blue for each category, with peak concentrations associated with the midlatitude storm tracks. For comparison, previous measurements of Hg in rainwater in the Pacific are given; circles are from *Mason et al.* [1992], triangles from SEAREX [*Fitzgerald*, 1989]. In addition, the area of maximum ozone production and export is plotted [*Mauzerall et al.*, 2000], which corresponds to the peak Hg concentrations observed in this study. See text for discussion.

(Steding and Flegal, 2002)

Approximately half of the mercury precipitation in SF Bay and its drainage basin is derived from Asian industrial emissions

Concerns with Evolving Measurements: Accuracy v. Precision

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K. Ndung'u et al./Analytica Chimica Acta 481 (2003) 127–138

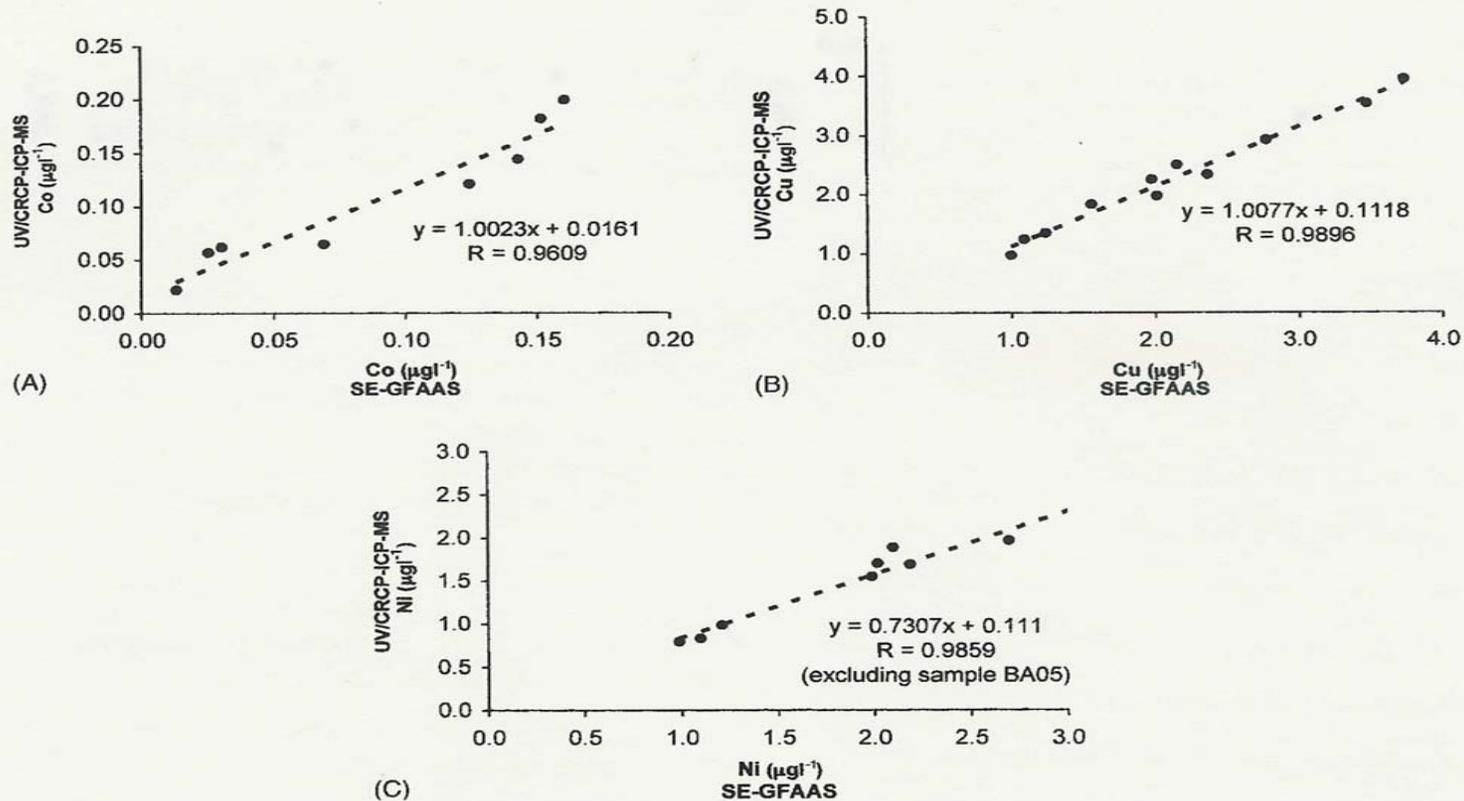


Fig. 4. Comparison of (A) cobalt, (B) copper, and (C) nickel (excluding sample BA05) concentration measured by the on-line CRCP-ICP-MS method and, after UV digestion, by SE-GFAAS. Copper and nickel samples were collected in 1995 and cobalt samples in 1993 (Table 1).

“I don’t care if the data are accurate, as long as they’re precise”
(retired EPA administrator, personal communication)

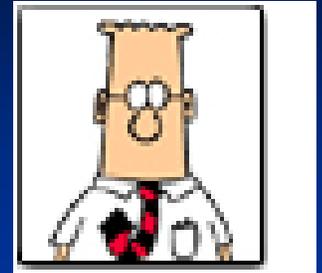
One Last Comment on Evolving Measurements: If Published in Peer-Reviewed Scientific Journals



It stands up in court

Conclusions

Systematic, long term monitoring is cost effective:
resolve temporal & spatial variations
identify & quantify sources of contamination
→ address current & emerging problems



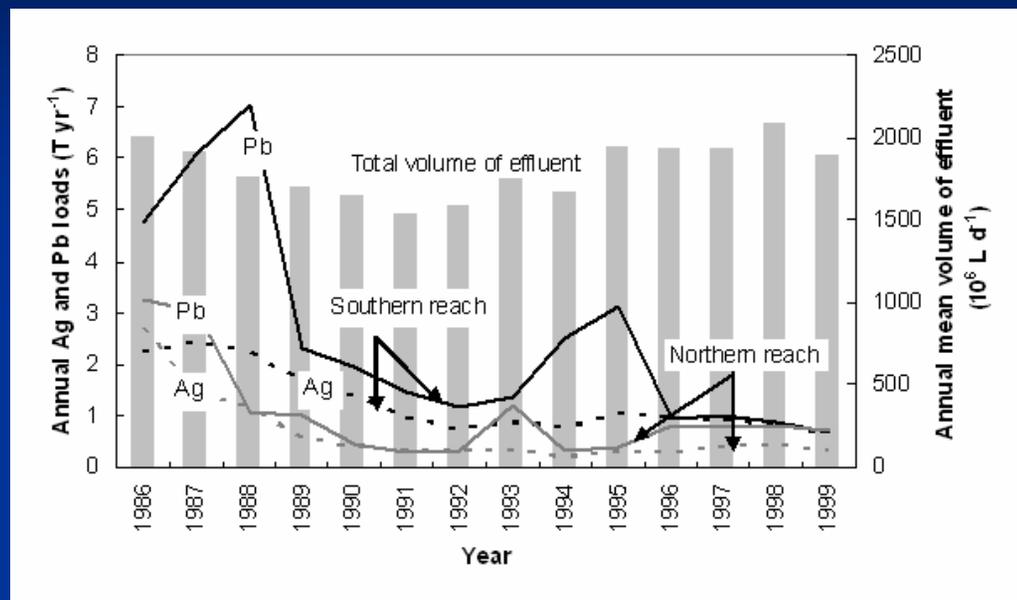
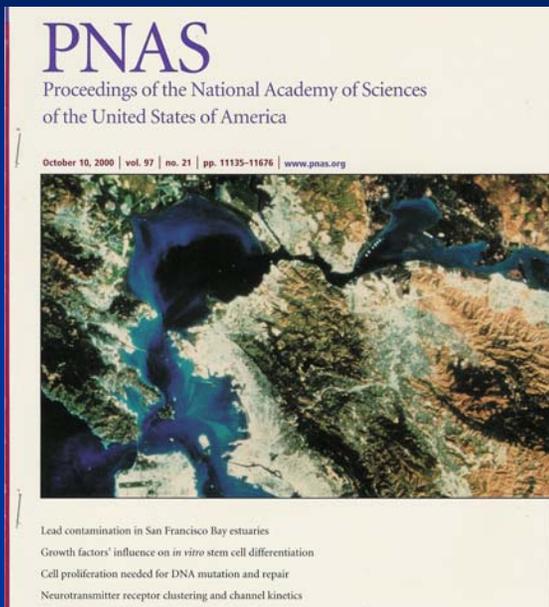
You get what you pay for:
GIGO (garbage in = garbage out)
good data stands up in court



In the long term , everyone benefits from
long-term, systematic measurements of
the highest quality – which is groovy.



WHO CARES ?



Students & Postdocs

Theses ~ 14

Pubs ~ 40

Jobs

UC Toxics Program

Regulators

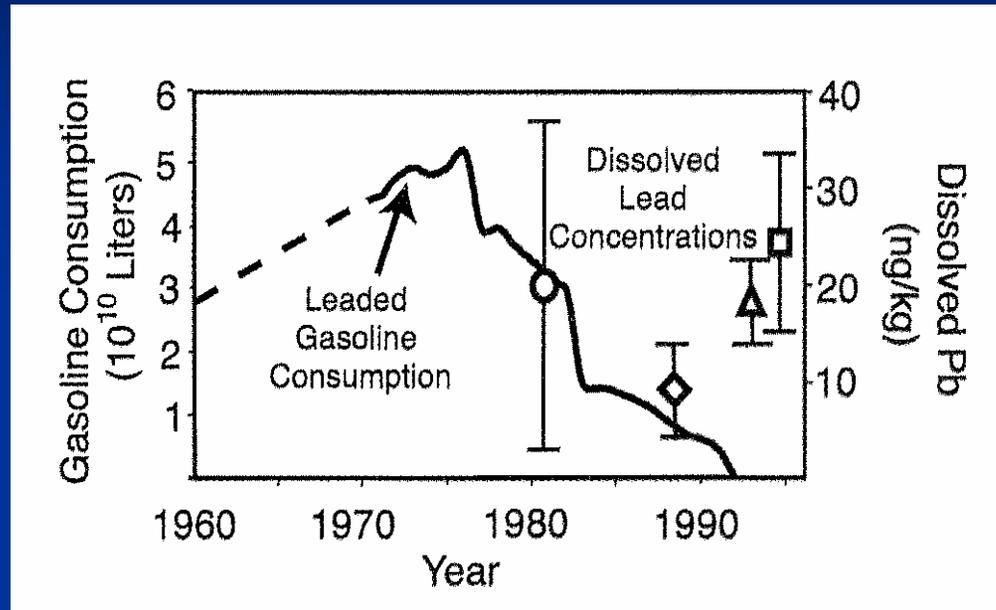
Dischargers

Engineers

Environmentalists

Taxpayers

Billions have been spent to remove billionths of pollutants in US waters



But it is difficult, if not impossible, to quantify any benefits from reductions in metal contaminants in most US waters because there are insufficient accurate measurements of that contamination.

Sanudo-Wilhelmy et al., 2004. ES&T

SF Bay Regional Monitoring Program

Initial collections 1989

Extended over a decade

26 locations

Seasonal samplings

Trace metal clean protocols

Rigorous QA/QC

Analytical precision $\leq 10\%$

SRM recoveries $\pm 25\%$

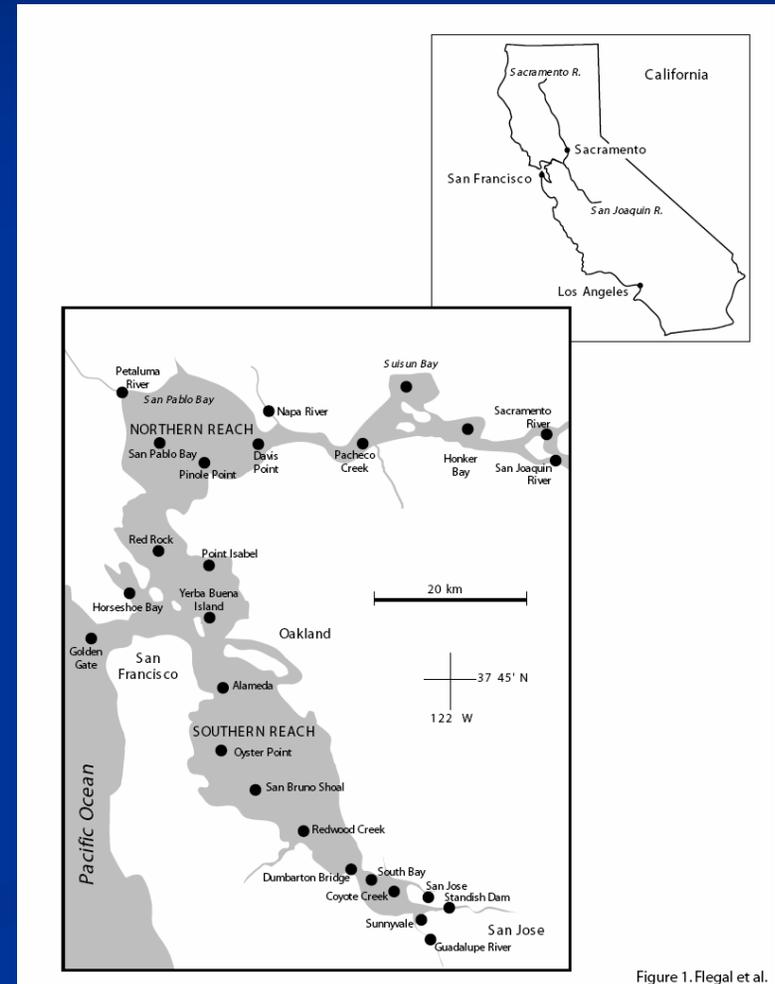


Figure 1. Flegal et al.