

Application of Multiple Approaches for Stressor Identification in Southern California Sediments

Steve Bay

*Southern California Coastal Water
Research Project*



Sediment Quality Management

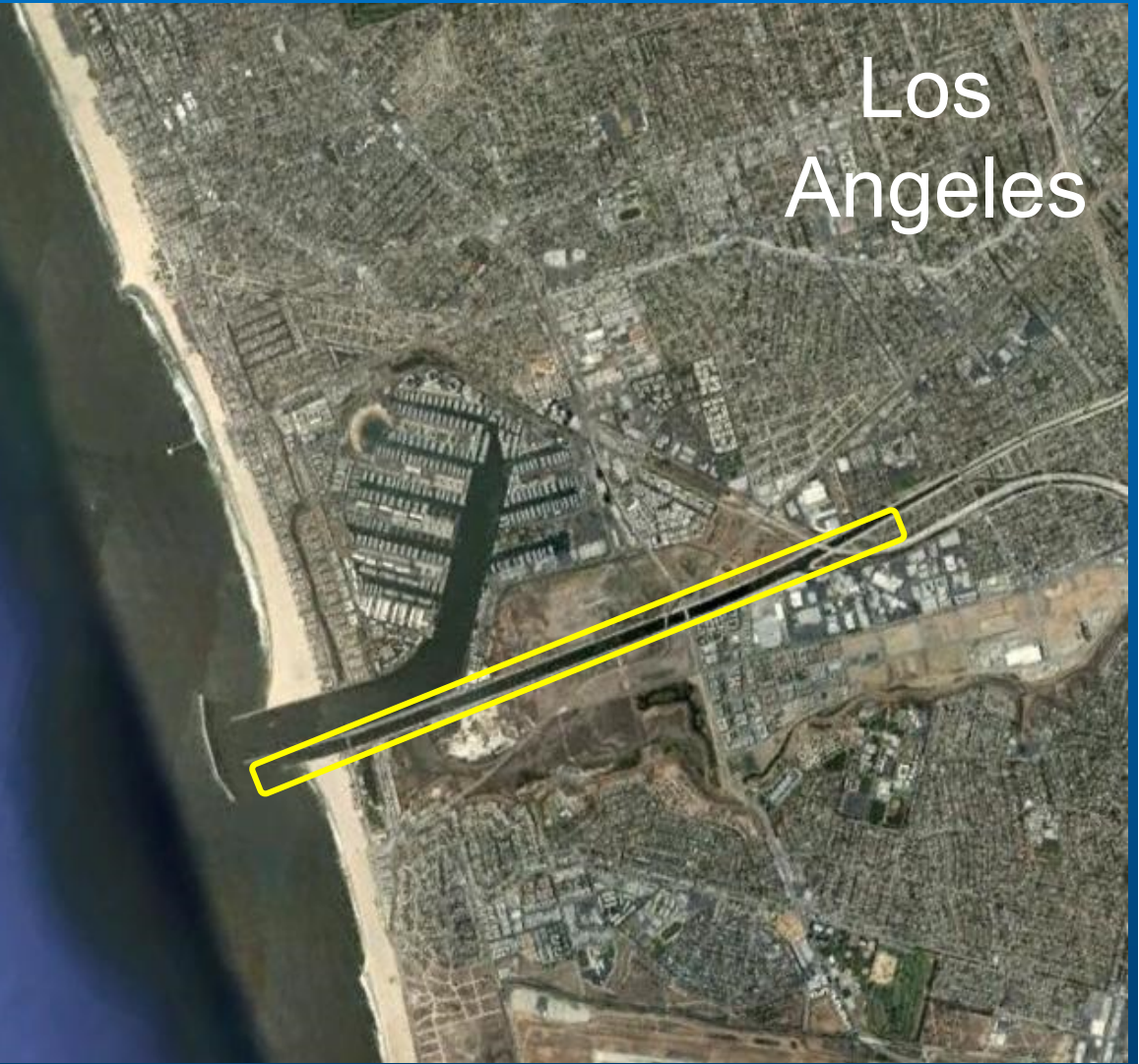
- **Sediment quality assessment is not the only information needed to manage sediments**
 - Doesn't determine the cause of poor sediment quality
- **Cause of the impacts (stressor) must be determined to guide management**
 - Identify sources
 - Establish contaminant concentration and loads to protect sediment quality (TMDLs)
- **Stressor identification studies can improve process**
 - Often not used or incomplete
 - Ballona Creek Estuary example

Ballona Creek Estuary

- Ballona Creek Estuary listed as impaired for multiple sediment contaminants

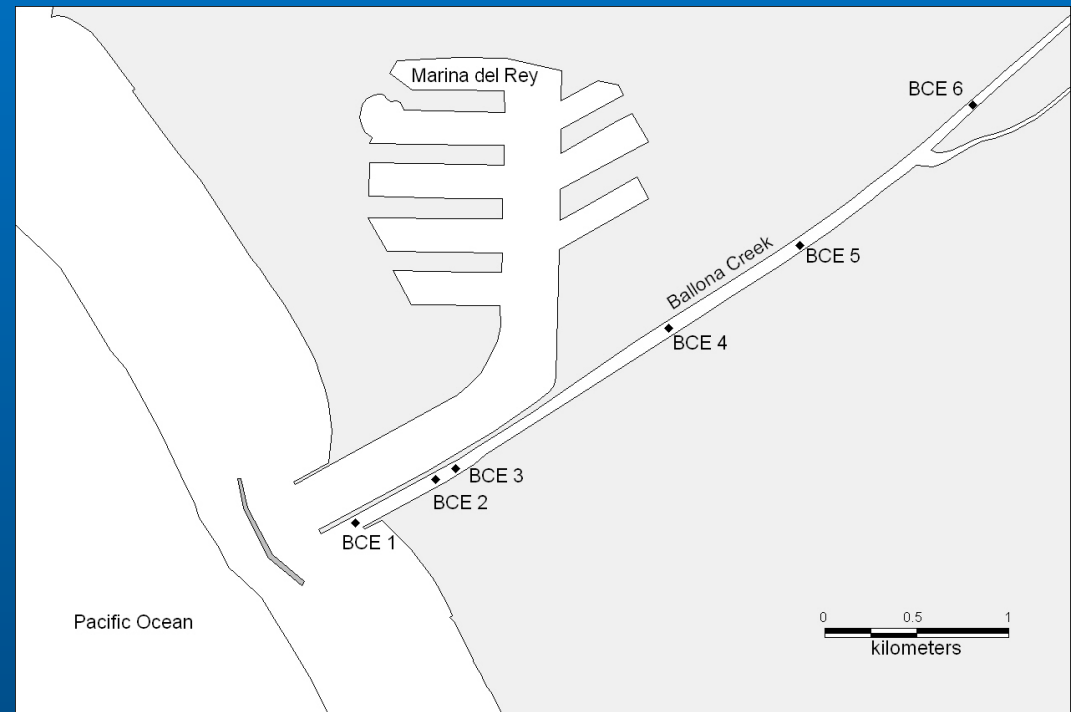
- Metals: cadmium, copper, silver, lead, zinc
- Organics: DDTs, PCBs, chlordane, PAHs

Los Angeles



Ballona Creek Estuary Special Study

- **Sediment contaminant limits may not be accurate**
 - Based on Sediment Quality Guidelines
 - Current use pesticides not evaluated
- **Special study designed to address data gaps**
 - Collaboration with City of LA Watershed Protection Div. and EMD
 - SCCWRP Toxicology and Chemistry Departments



Study Design

- **Update and expand sediment quality assessment**
 - Spatial and temporal patterns in chemistry & toxicity
 - Investigate current use pesticides
- **Identify cause of sediment toxicity**
 - Laboratory Toxicity Identification Evaluation (TIE)
- **Confirm Toxicity Identification**
 - Chemistry:toxicity relationships
- **Evaluation of TMDL targets (concentrations)**
 - Toxicity thresholds for sediment contaminants

Identification Methods

- **Comparison of sediment chemistry to effect thresholds**
 - Easy, but frequently misinterpreted
 - Might miss important contaminants that are not monitored
- **Toxicity Identification Evaluation (TIE)**
 - Direct evidence using established methods
 - Can exclude contaminants
- **Chemical bioavailability analysis**
 - Technically difficult but good scientific foundation
- **Statistical correspondence**
 - May not be conclusive

2007 Chemistry and Toxicity

Parameter	Target	BCE1	BCE2	BCE3	BCE4	BCE5	BCE6
Amphipod %Surv.		89	3	0	16	18	8
Cadmium (mg/kg)	1.2	0.5	1.6	1.8	0.5	0.4	0.3
Copper (mg/kg)	34	18	55	117	14	16	13
Lead (mg/kg)	46.7	30.3	52.1	66.7	11.3	15.2	4.9
Silver (mg/kg)	1.0	0.6	1.4	1.6	0.2	0.3	nd
Zinc (mg/kg)	150	89	228	430	103	107	58
DDTs (ug/kg)	1.6	5.3	5.8	5.3	1.1	1.2	nd
Chlordane (ug/kg)	0.5	5.1	5.1	6	nd	nd	nd
PCBs (ug/kg)	22.7	nd	43	39	nd	82	nd
PAHs (ug/kg)	4022	nd	nd	nd	nd	nd	nd

Sediment toxicity widespread and of high magnitude

TMDL target exceedances show little relationship to toxicity

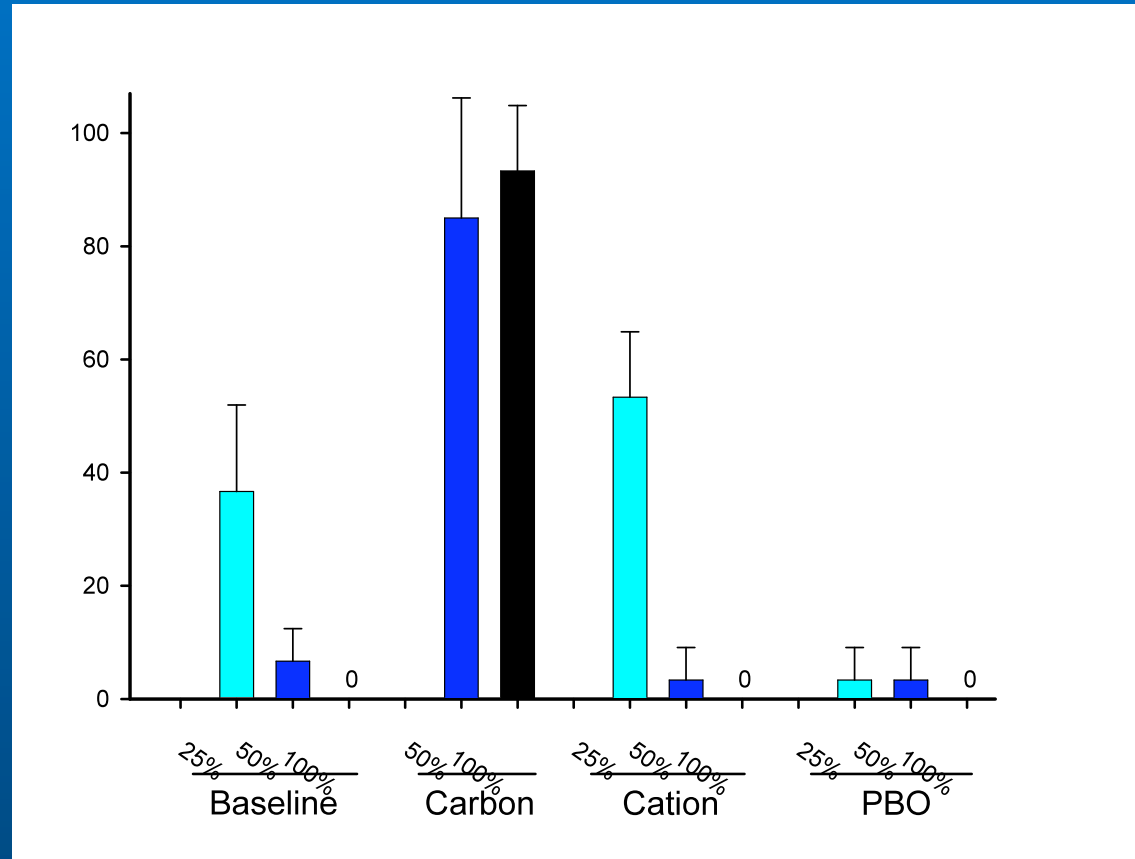
 **TIE Site**

TIE Treatments

Treatment	Matrix	Purpose
EDTA	Water	Chelation of cationic metals (e.g. Zn, Cu)
Sodium thiosulfate (STS)	Water	Reducing agent for oxidizers (e.g. chlorine); reduces toxicity of some metals
C-18 column extraction	Water	Removal of non-polar organics
Cation exchange column extraction	Water	Removal of cationic metals
Coconut carbon	Sediment	Binding of organic contaminants
Cation exchange resin	Sediment	Binding of cationic metals
Piperonyl butoxide (PBO)	Water/ Sediment	Inhibits pesticide metabolism. Renders organophosphorus pesticides non-toxic; increases toxicity of pyrethroid pesticides
Carboxylesterase	Water/ Sediment	Degrades op/pyrethroid pesticides
Temperature Reduction	Water/ Sediment	Enhances mechanism of action

2007 Station 2: Sediment TIE

Amphipod Survival



Reduction of toxicity with carbon suggests organics
Increase of toxicity with PBO suggests pyrethroids

TIE Summary: 2007/08

Amphipod Survival: Sediment

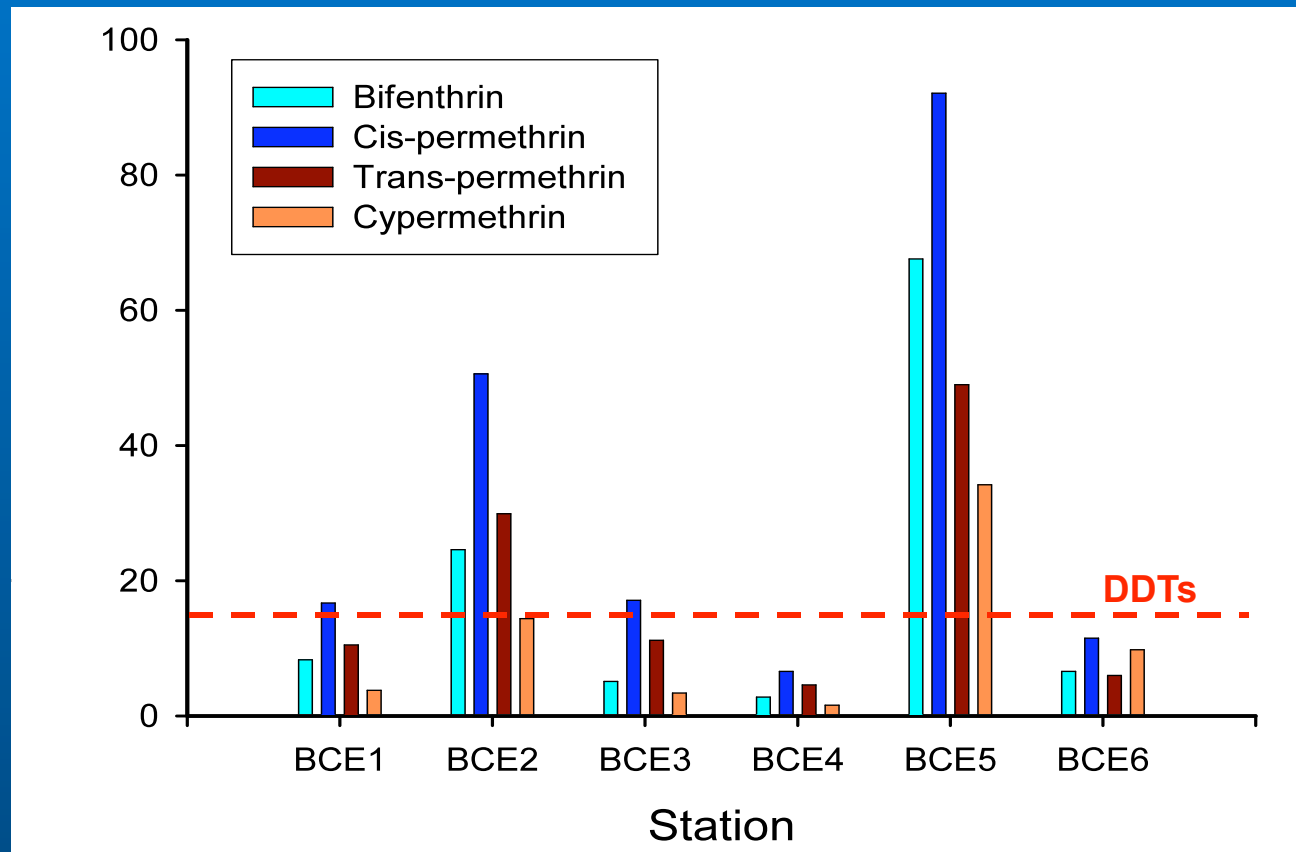
Treatment	BCE2		BCE4	BCE5
	2007	2008	2007	2008
Piperonyl Butoxide Addition	Reduced Survival	Reduced Survival	Reduced Survival	Reduced Survival
Cation Exchange Resin	Slight Increase	No Effect	Slight Increase	No Data
Coconut Carbon	Increased Survival	No Effect	No Data	No Data

PBO response pattern consistent with pyrethroids for all samples
Inconsistent effects of carboxylesterase and temperature reduction
Role of metals and other organics is uncertain
Results are often not definitive

Chemistry Confirmation

- **Do sediment chemistry results support toxicant identification?**
 - Sediment concentrations of pyrethroids and other contaminants
 - Estimate toxic units
- **Are the contaminants bioavailable?**
 - Pore water analysis using passive samplers
 - Compare to water effect thresholds

Pyrethroid Pesticides June 2008



Multiple pyrethroids detected at every station

Relatively high concentrations

Fipronil also detected

Toxic Units

- Toxic units (TUs) estimate potential for toxicity from specific chemicals
 - Strong toxicity expected when $TU \geq 1$

$$TU = \frac{\text{Sediment concentration } (\mu\text{g/g oc})}{E. \text{ estuarius } LC_{50} (\mu\text{g/g oc})}$$

Pyrethroid	<i>E. estuarius</i> LC ₅₀ (μg/g OC)
Bifenthrin	1.03
Cypermethrin	1.41
Permethrin	17.9

	BCE1	BCE 2	BCE 3	BCE 4	BCE 5	BCE 6
June 2008						
Bifenthrin	1.8	2.0	0.9	0.9	3.8	1.9
Cypermethrin	0.6	0.9	0.4	0.4	1.4	2.1
Permethrin	0.4	0.4	0.3	0.2	0.4	0.3

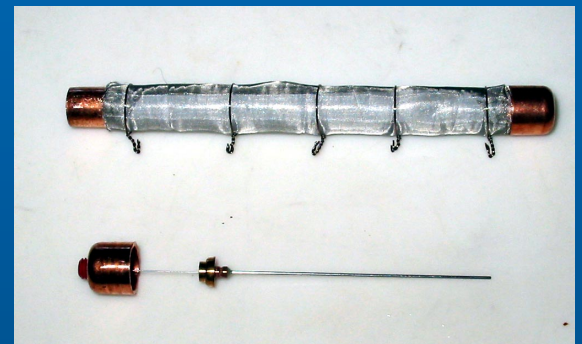
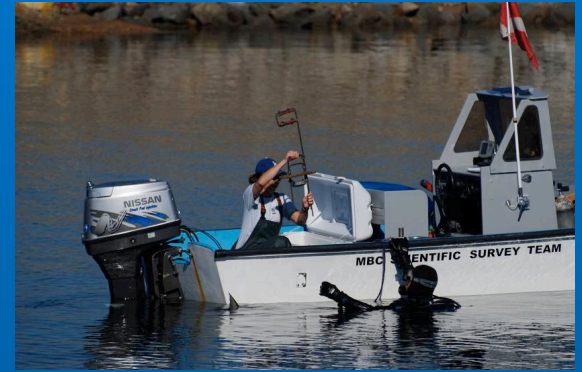
Pyrethroid concentrations sufficient to cause toxicity at every station
***E. estuarius* thresholds not available for other pyrethroids**

Unresolved Issues

- **How much data is needed to reach a conclusion?**
 - # samples, seasonality
 - Multiple species?
- **What are data requirements to remove a potential stressor from the list?**
 - Use of low-range SQGs often result in a long list
 - Anti-backsliding concern

Quantifying Bioavailable Contaminants

- **Pore water contaminants**
 - Field and laboratory
 - Organics: SPME
 - Metals: peepers
 - Compare to water effect thresholds or WQ criteria
- **AVS-SEM**
 - Field samples
 - Excess AVS indicates low metals bioavailability



Metals Bioavailability

Parameter	Units	Target	BCE1	BCE2	BCE3	BCE4	BCE5	BCE6
Amphipod	%		55	40	14	43	0	28
Gravel	%		0	0	0	34.4	49.5	85.5
AVS-SEM								
AVS	µmol/dry g		10.42994	8.549179	7.279746	5.64539	0.053023	8.018949
SEM	µmol/dry g		0.244	0.6721	0.782	0.4019	0.3471	0.3324
SEM/AVS	µmol/dry g		0.023394	0.078616	0.107421	0.071191	6.546216	0.041452
SEM-AVS	µmol/dry g		-10.18594	-7.877079	-6.497746	-5.24349	0.294077	-7.686549
PW Dissolved Metals CTR								
Arsenic (As)	µg/L	36	12.77	2.82	3.41	4.66	4.77	3.92
Cadmium (Cd)	µg/L	9.3	0.047	0.093	0.05	0.069	0.106	0.07
Copper (Cu)	µg/L	3.1	0.13	0.61	0.84	5.81	24.53	7.09
Lead (Pb)	µg/L	8.1	0.61	0.431	0.588	2.717	0.984	1.665
Nickel (Ni)	µg/L	8.2	2.18	1.514	2.619	6.972	15.277	2.51
Selenium (Se)	µg/L	71	1.19	0.4	0.68	0.85	2.07	0.5
Silver (Ag)	µg/L	1.9	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Zinc (Zn)	µg/L	81	28.085	28.165	31.405	26.405	51.065	58.375

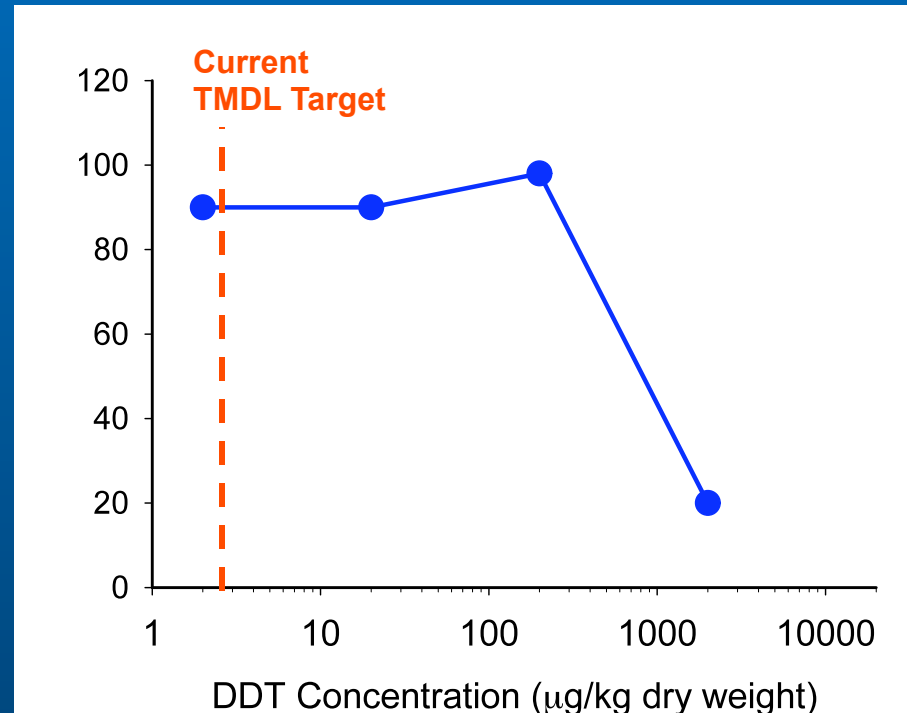
Most stations/metals below criteria

Applicability for coarse sediments?

Which criteria to use for comparison: LC50s or CTR?

TMDL Target Evaluation

- **What concentrations of sediment contaminants are toxic to amphipods?**
 - Spiked sediment studies using Santa Monica Bay sediment
 - Provides confirmation of TIE results by TU calculation
 - Can be used to refine TMDL targets
 - Sufficient evidence to exclude contaminants?



Summary

- **Stressor identification is a critical component of sediment quality assessment**
 - Provides essential information for management decisions
- **Multiple approaches are needed**
 - TIE treatments
 - Advanced chemical analysis
 - Dose-response relationships
- **Additional resources needed to support wider use in management programs**
 - Study design guidance and standardized methods
 - Interpretation guidance