

# Challenges and Progress on Extending DSM2 for Mercury and Sediment

DSM2 Session CWEMF  
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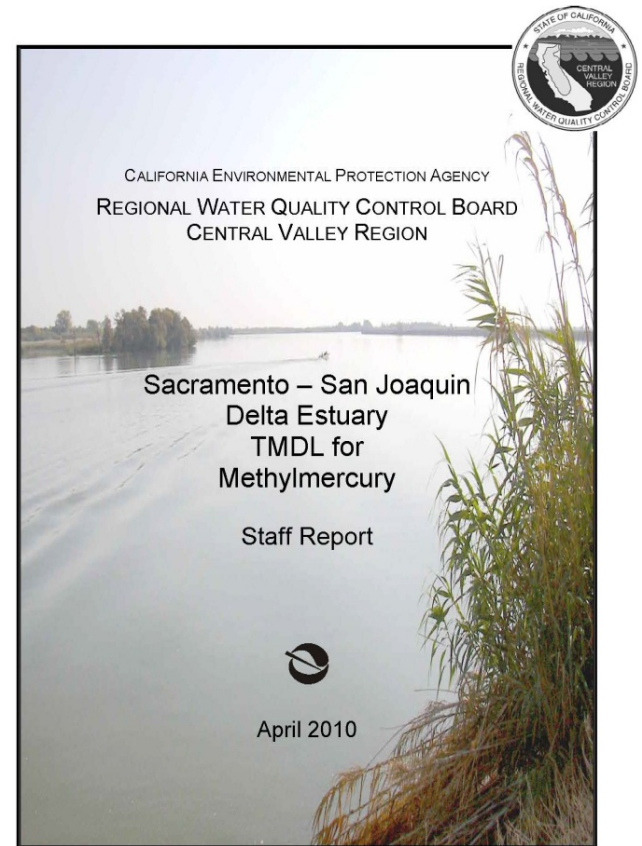


Department of Water Resources  
Modeling Support Branch  
Bay-Delta Office



# Why add Mercury and Sediment to DSM2?

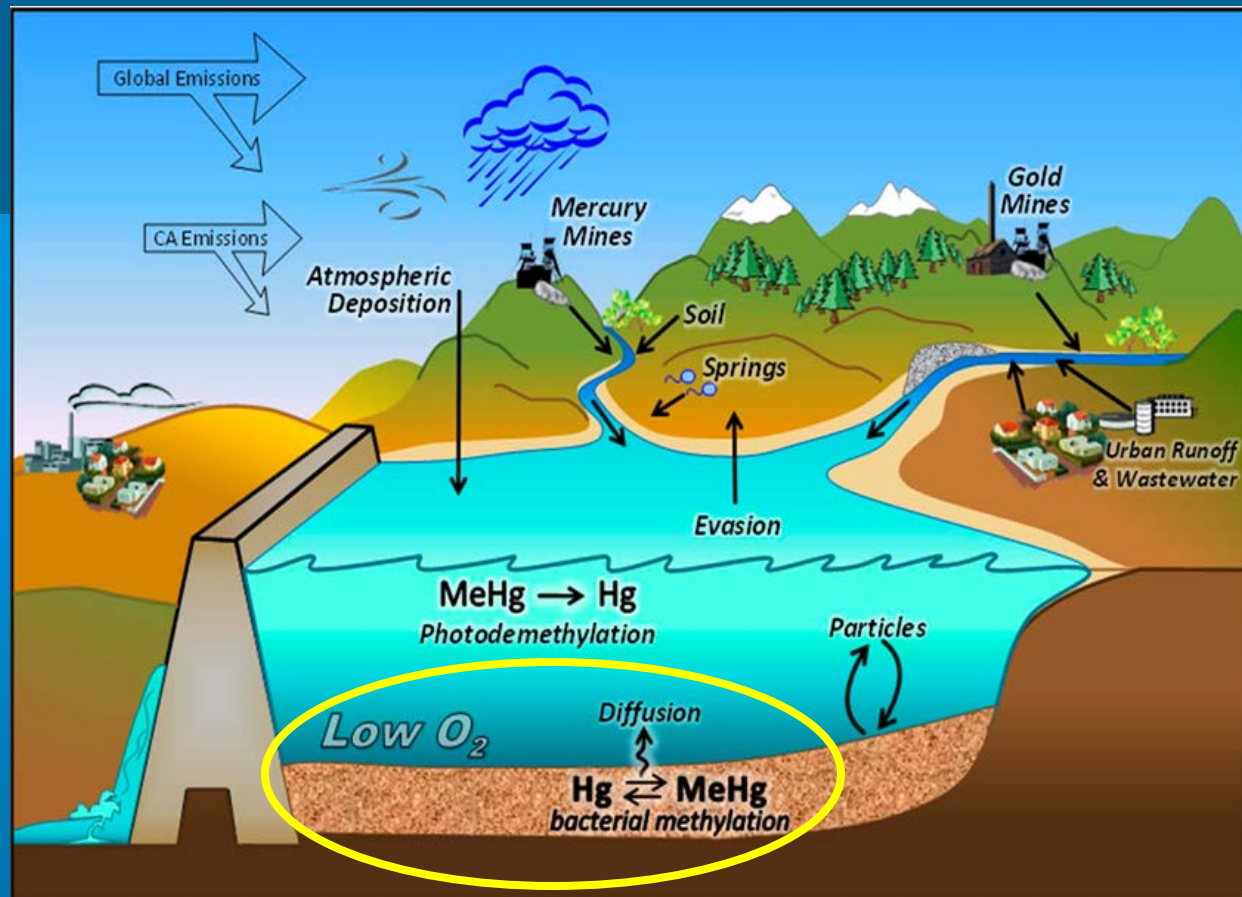
- Support the open water portion of the Delta Mercury Control Program
  - Established in 2010
  - US EPA approved TMDL in 2011
  - DWR must comply with the TMDL
- A Delta mercury model was desired to explore trends in MeHg production for changes in water project operations
- In order to add mercury to DSM2, we have to add sediment too



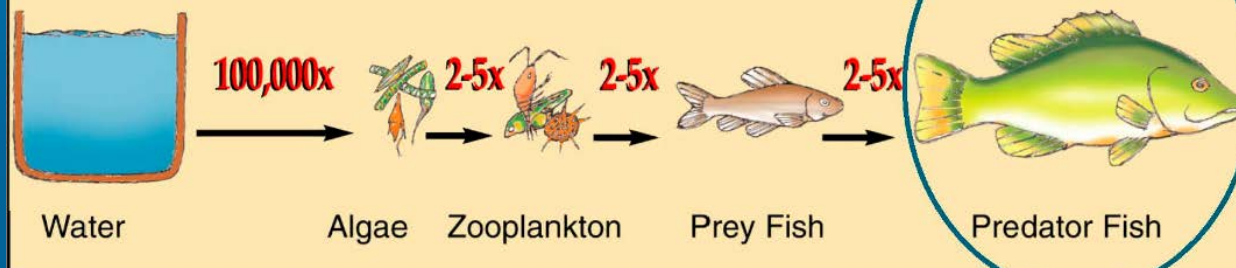
DSM2 = Delta Simulation Model 2  
TMDL=Total Maximum Daily Load  
MeHg = methylmercury

# What is Mercury Methylation?

- Anaerobic organisms convert inorganic Hg to organic methyl mercury (MeHg)
- Methyl mercury is consumed by organisms and remains in their tissues (**bioaccumulation**)
- A small amount of mercury in the water can lead to high concentrations of mercury in fish (**biomagnification**)



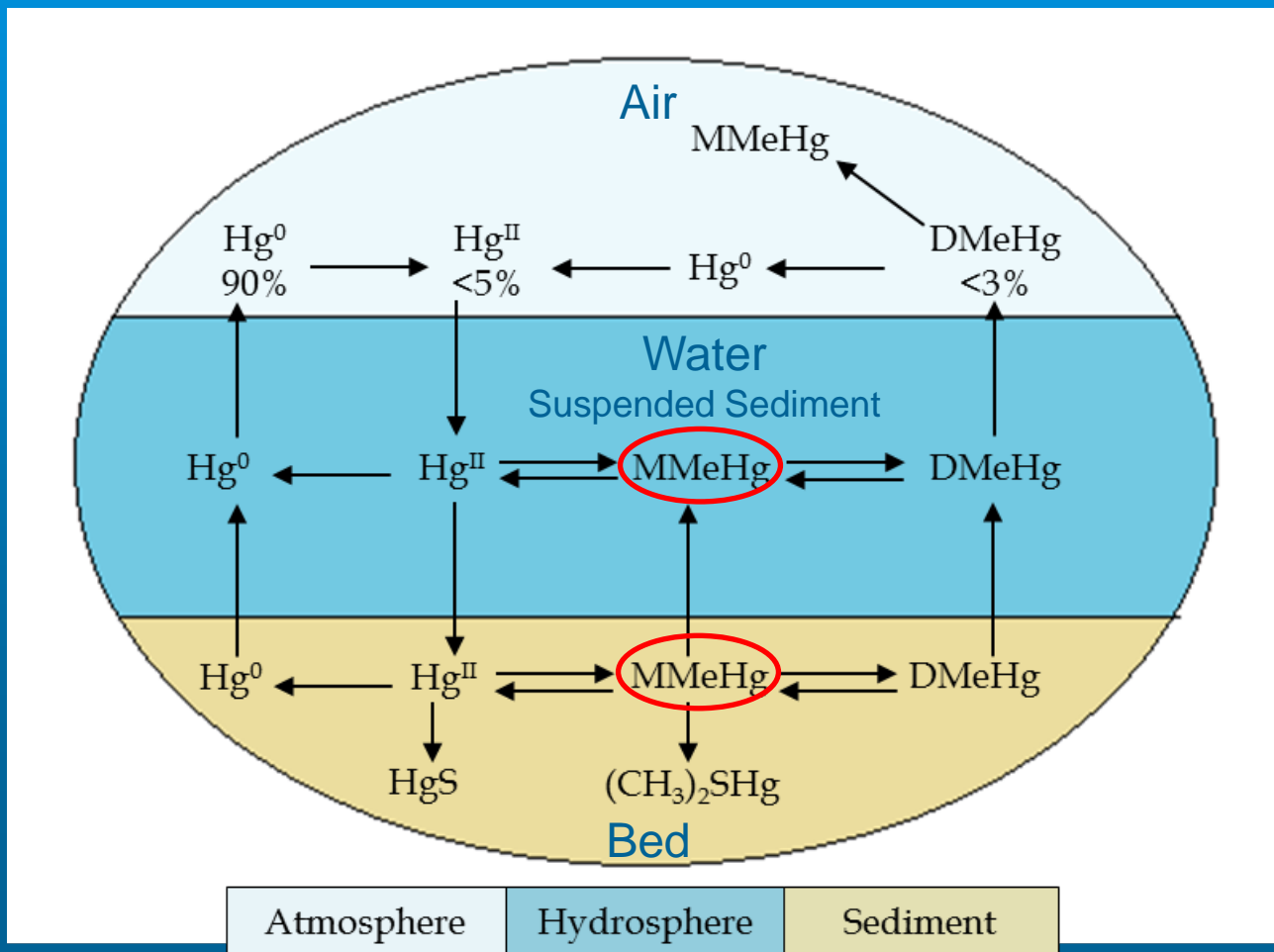
Example Magnification Per Step



# In order to model mercury, we need to model sediment too

Suspended sediments are important for mercury transport

Bed sediments are important for mercury cycling



# Where does Delta Mercury come from?

- Upstream sources
  - Historic mining
  - Natural deposits
- In-Delta production
- Atmospheric deposition
- Other
  - Storm water runoff
  - Wastewater discharge

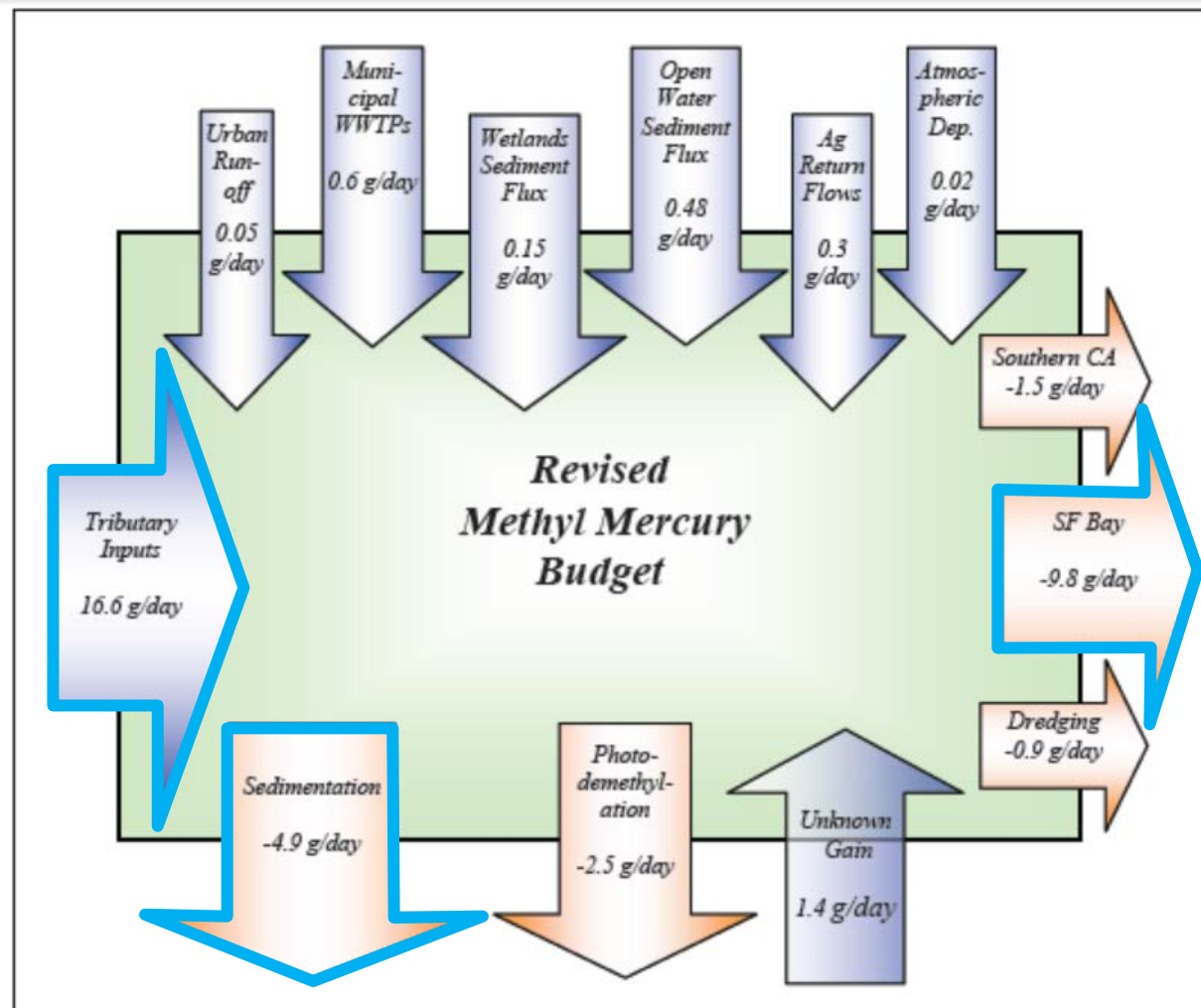


Figure 9. Revised methyl mercury mass balance model for the Delta. The revised model incorporates both some new rates for previously measured terms (tributary inputs and exports to southern California and San Francisco Bay) and rates for two previously unmeasured processes, (photo demethylation and sedimentation).

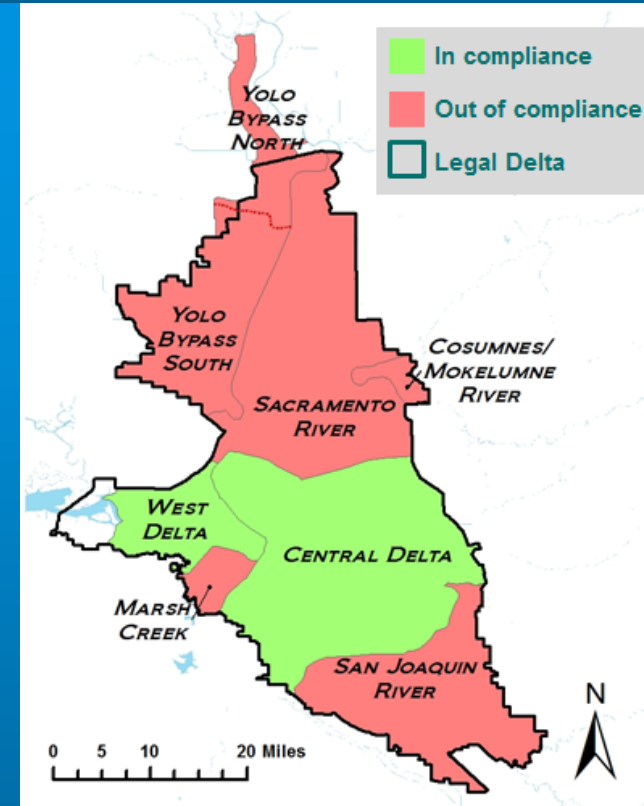
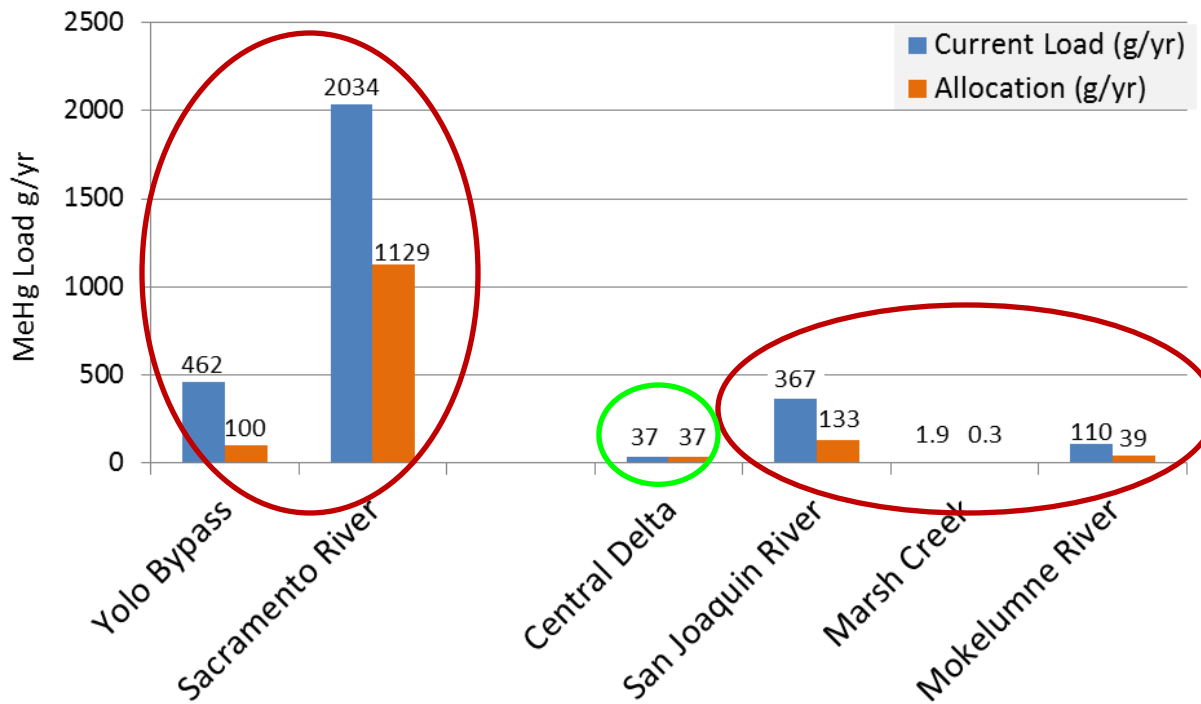
# Delta Mercury & Sediment

March 2003 to June 2006

- Sacramento River & Yolo Bypass are major sources
  - 84% of Delta mercury
  - 86% of Delta sediment
- Delta exports Hg & sediment to San Francisco Bay
  - Mercury: 198 kg/year (~440 lb/yr)
  - Suspended sediment: 801 Gg/year (~790,000 tons/yr)
- Delta is a Hg & sediment sink
  - Mercury: 200 kg/year (~440 lb/yr)
  - Sediment: 1497 Gg/year (1.5 million tons/yr)

# Tributary MeHg Loads & Allocations

Tributary MeHg Loads & Allocations from TMDL Table A

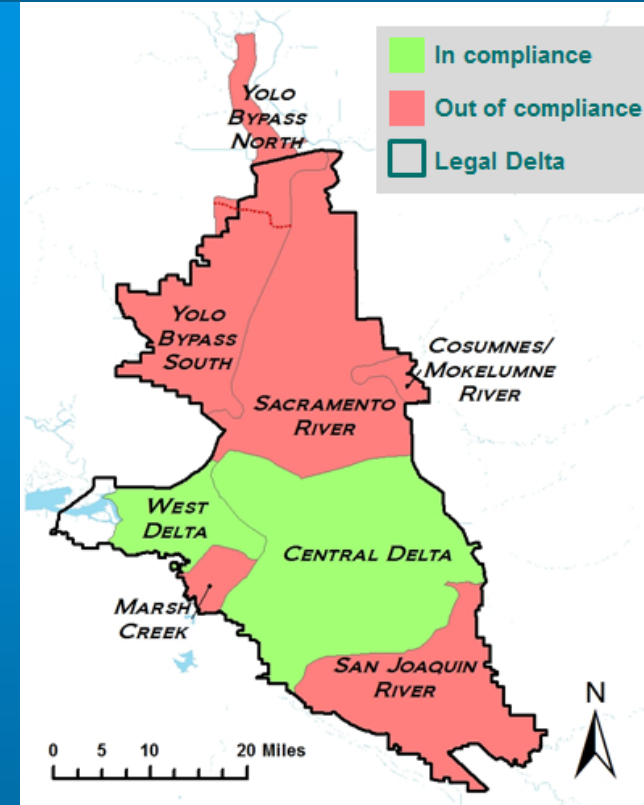
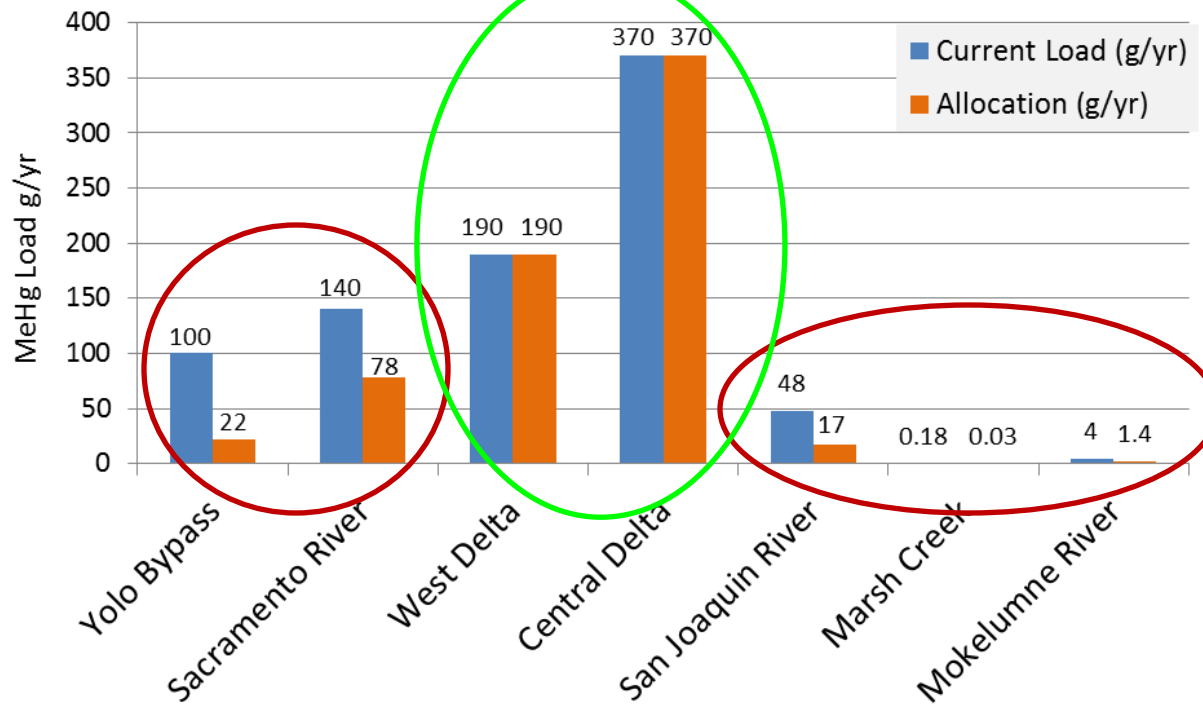


TMDL allocations are based on desired reduction in MeHg to bring fish tissue levels from that subarea to a level safe for a person to safely eat 8oz of fish per week

TMDL=Total Maximum Daily Load  
MeHg = methylmercury

# Open Water MeHg Loads & Allocations

Open Water MeHg Loads & Allocations from TMDL Table A



TMDL allocations are based on desired reduction in MeHg to bring fish tissue levels from that subarea to a level safe for a person to safely eat 8oz of fish per week

TMDL=Total Maximum Daily Load  
 MeHg = methylmercury





# Current DSM2 Modules

## **HYDRO**

Hydrodynamics Model  
1-D flow, velocity, & water levels

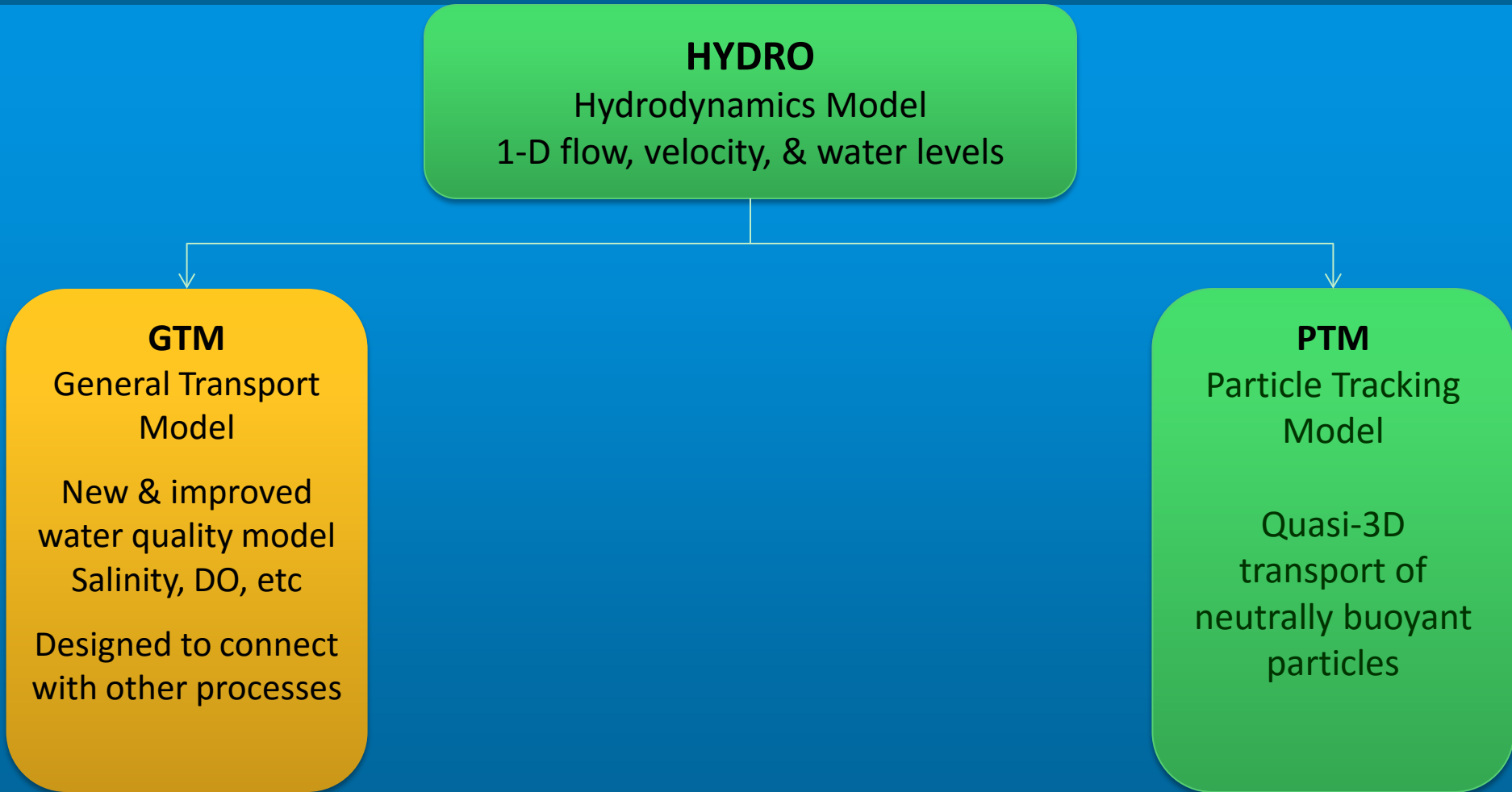
## **QUAL**

Water Quality Model  
Fate and transport of  
conservative and  
non-conservative  
constituents

## **PTM**

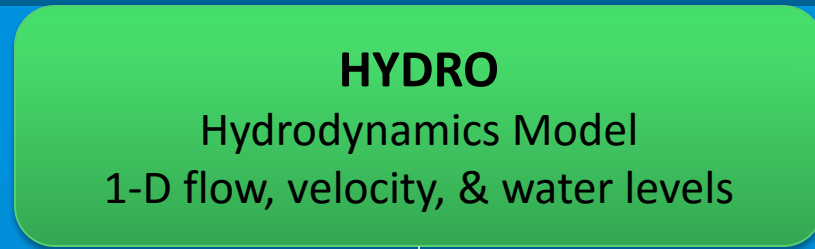
Particle Tracking  
Model  
  
Quasi-3D  
transport of  
neutrally buoyant  
particles

# DSM2 Modernization with GTM



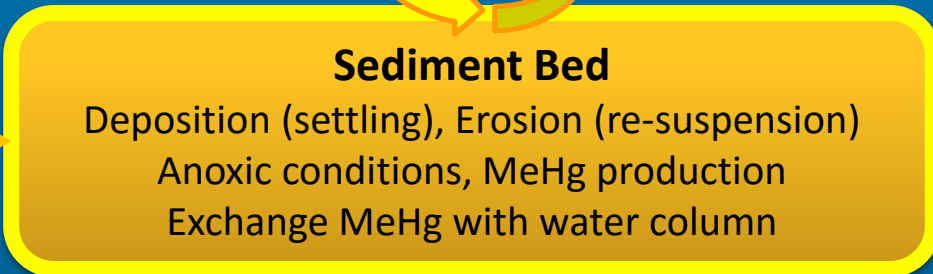
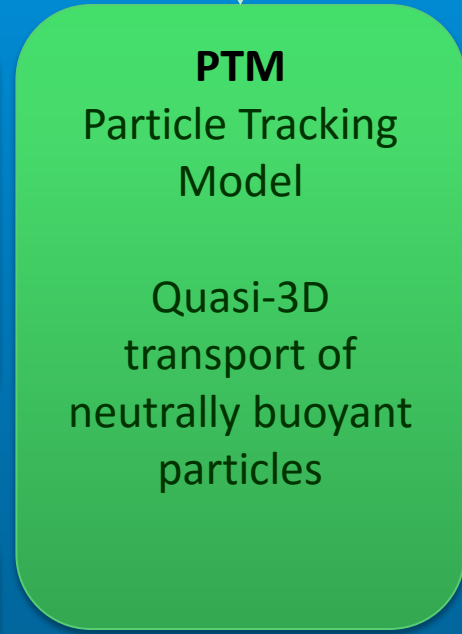
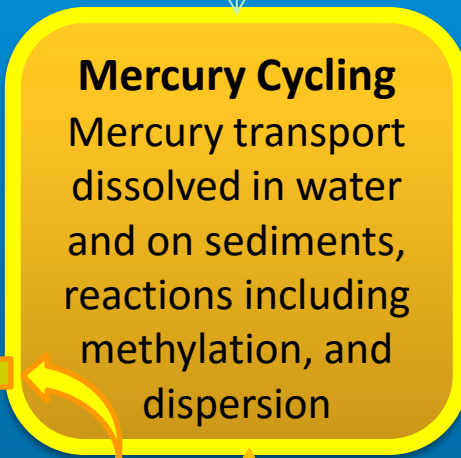
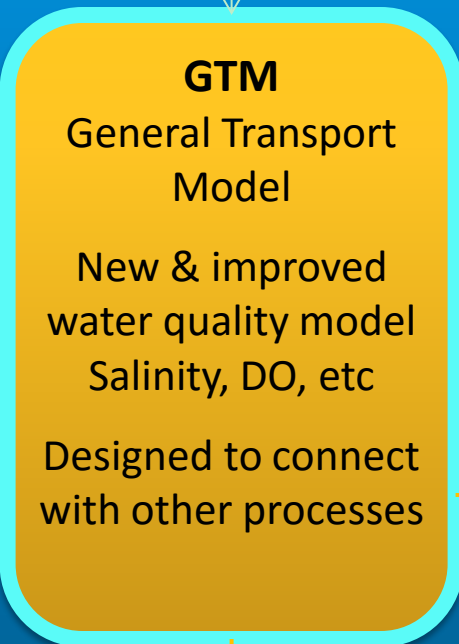
Modules to be added to DSM2

# DSM2 Extension for Mercury & Sediment



DWR Delta Modeling

Reed Harris Environmental



Modules to be added to DSM2

# Challenges



# Mercury is very complicated

Mercury modelers are part of the team

	Rxn No.	Conditions Favoring Reaction
$\text{Hg}^{2+} + 2\text{HS}^- \xrightarrow{\text{R}} \text{Hg}(\text{SH})_2$	(1)	Reducing Conditions/Low Sulfide (e.g., Anoxic Hypolimnion)
$\text{Hg}^{2+} + 2e^- \xrightarrow{\text{R}} \text{Hg}^0$	(2)	Mildly Reducing Conditions - Highly Volatile Product
$\text{Hg}^{2+} + \text{R} \rightleftharpoons \text{R}:\text{Hg}$	(3)	High DOC Waters (e.g., Bog Systems)
$\text{Hg}^{2+} + \text{R-SH} \rightleftharpoons \text{R-SH}:\text{Hg}$	(4)	Association with Biomass
$\text{Hg}^{2+} + \text{Mineral Colloid} \rightleftharpoons \text{Mineral Colloid}:\text{Hg}$	(5)	High Suspended Solids Circumneutral and Greater pH
$\text{Hg}^{2+} + \text{cell} \rightleftharpoons \text{cell}:\text{Hg}$	(6)	Association with Biomass
$\text{Hg}^{2+} + \text{Hg}^0 \xrightarrow{\text{R}} \text{Hg}_2^{2+}$	(7)	Presence of Elemental Hg
$\text{Hg}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Hg}(\text{OH})_2$	(8)	Circumneutral and Higher pH
$\text{Hg}^{2+} + x\text{Cl}^- \rightleftharpoons \text{HgCl}^{(2-x)}$	(9)	Lower pH and Even Small Amounts of $\text{Cl}^-$
$\text{Hg}^{2+} + 2\text{CH}_3^- \xrightarrow{\text{R}} \text{CH}_3\text{HgCH}_3$	(10)	Moderately Reducing Conditions, Higher pH (Ocean Waters) - Highly Volatile Product
$\text{Hg}^{2+} + \text{CH}_3^- \xrightarrow{\text{R}} \text{CH}_3\text{Hg}^+$	(11)	Moderately Reducing Conditions - Moderately Volatile Product

$\xrightarrow{\text{R}}$   
Rate-limited reaction

$\rightleftharpoons$   
Reaction which quickly comes to equilibrium

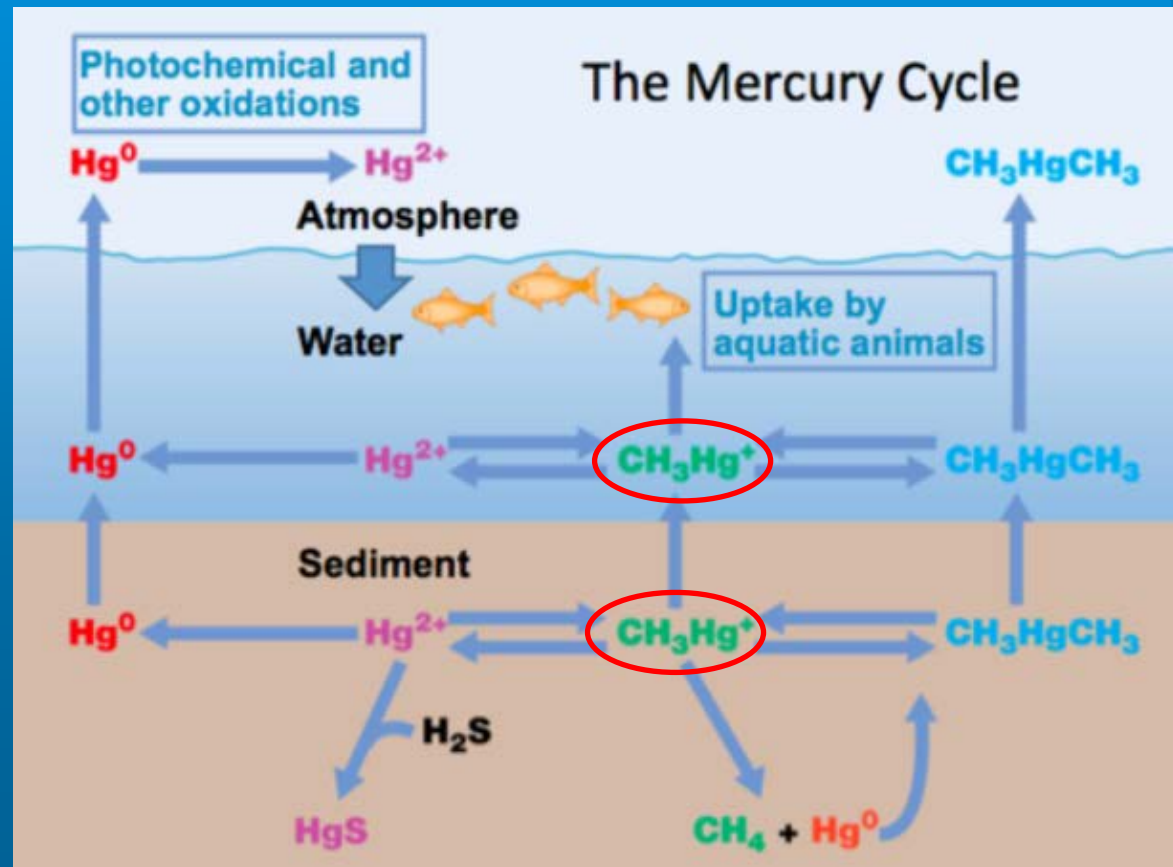


# Need suspended & bed sediment

From 2008 Delta mercury & suspended sediment study (Foe et al):

Mercury contamination in aquatic organisms is from **converting inorganic Hg to methylmercury** by sulfur reducing bacteria in surface sediments

- Suspended sediments transport mercury
- Inorganic mercury in bed sediments is a significant factor controlling methylmercury production and flux into the overlying water column

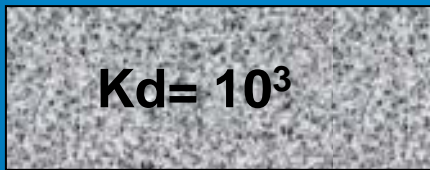




# Need organics and sediment

- Mercury binds to both dissolved organic carbon and suspended sediment
- For Delta mercury cycling we will start with 4 particle types

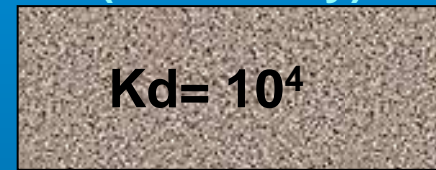
Coarse Inorganic  
(Sand)



$K_d = 10^3$

Does not decompose

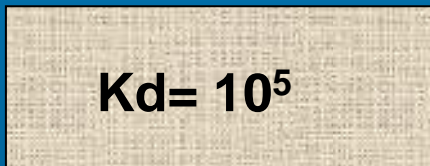
Fine Inorganic  
(Silt & Clay)



$K_d = 10^4$

Does not decompose

Labile Organic

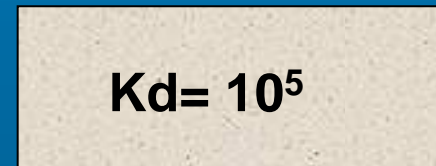


$K_d = 10^5$

Decomposes quickly

We need to add  
organics to our  
suspended  
sediment  
transport  
representation

Refractory Organic



$K_d = 10^5$

Decomposes  
very slowly

For Hg cycling,  
decomposition rates relate to microbe activity  
which is related to mercury methylation rates

$$K_d (L/Kg) = \frac{\text{Concentration of Hg on Solids}}{\text{Concentration of dissolved Hg}}$$





# Previously planned Sediment Transport Model does not cover all important processes for mercury

Add Organics

## Sediment Transport

- Advection (go with flow)
- Reaction
  - None for sands
  - Flocculation for clays
- Dispersion (mixing)
- Settling
- Resuspension
- Bed load

Sorption  
Desorption

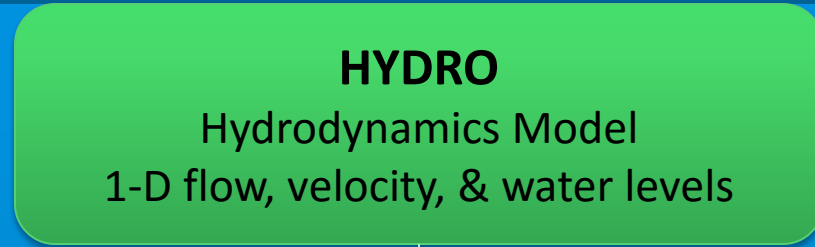
## Mercury Model

- Transport
  - Sorbed to sediment
  - Dissolved in water
- Reaction
  - Mercury cycle including methylation
- Dispersion (mixing)

## Bed Representation

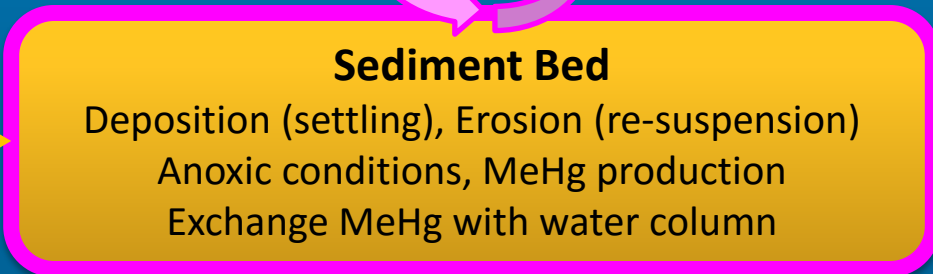
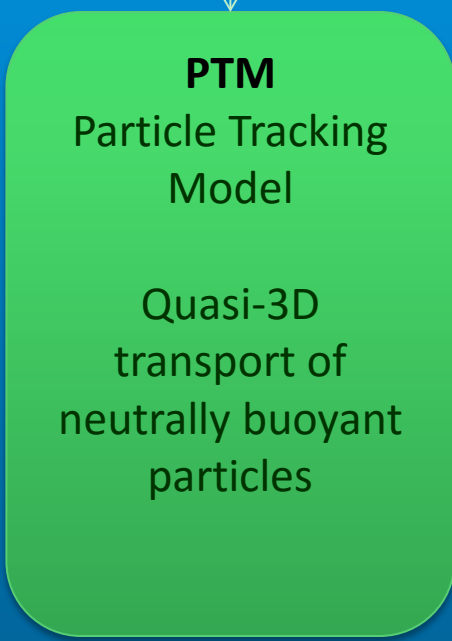
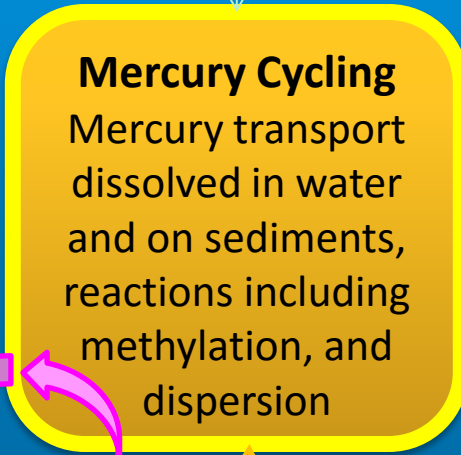
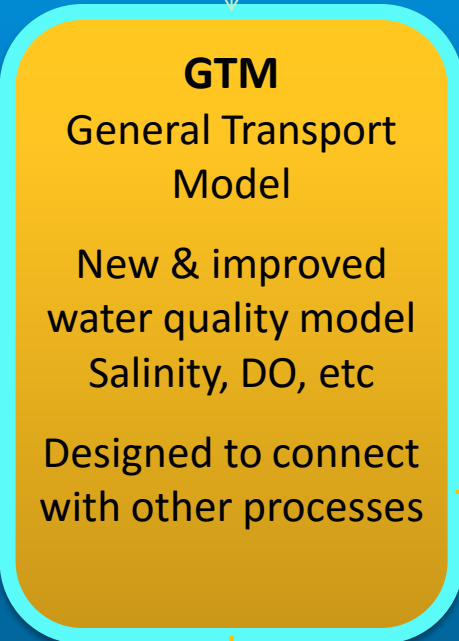
- Deposition/scour
- Anoxic conditions
- MeHg production
- Release of MeHg to water column

# DSM2 Extension for Mercury & Sediment



DWR Delta Modeling

Reed Harris Environmental



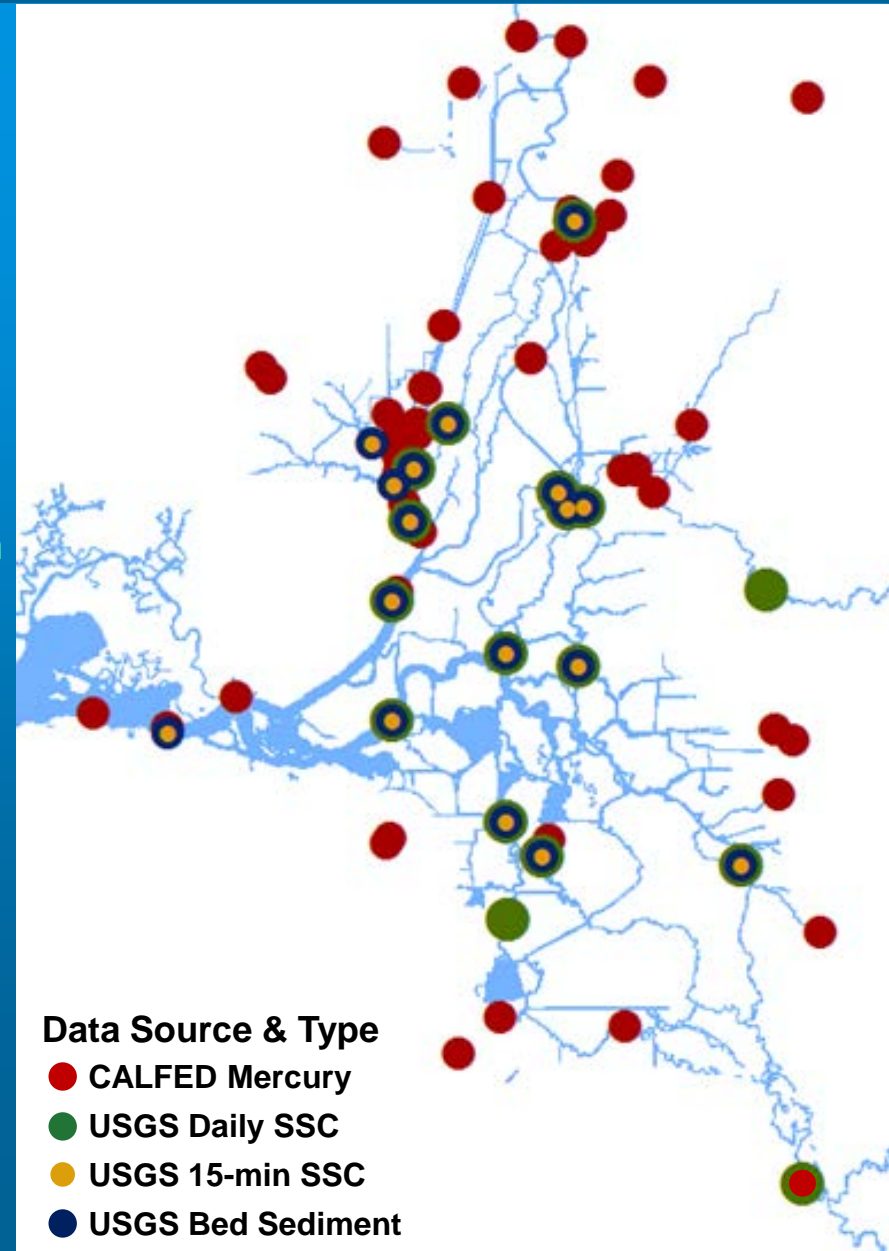
Modules to be added to DSM2



# Data don't line up in space & time

- Mercury Data
  - CALFED Mercury Program ~2000-2008
  - Mostly grab sample data (approximately monthly)
  - Coming soon 5 quarterly sites RMP
- Suspended Sediment Data
  - USGS Suspended Sediment Concentration 2012-present, Freeport & Vernalis 1956-present
  - Daily or 15-min data
- Bed Sediment Data
  - CALFED Mercury Program
  - USGS
  - Grab sample (intermittent)

Data gaps will be identified



# Progress to Date



- Monthly team meetings
- Progress report to State Water Resources Control Board submitted Oct 2015

[http://www.waterboards.ca.gov/centralvalley/water\\_issues/tmdl/central\\_valley\\_projects/delta\\_hg/control\\_studies/index.shtml](http://www.waterboards.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/delta_hg/control_studies/index.shtml)



Thank You!

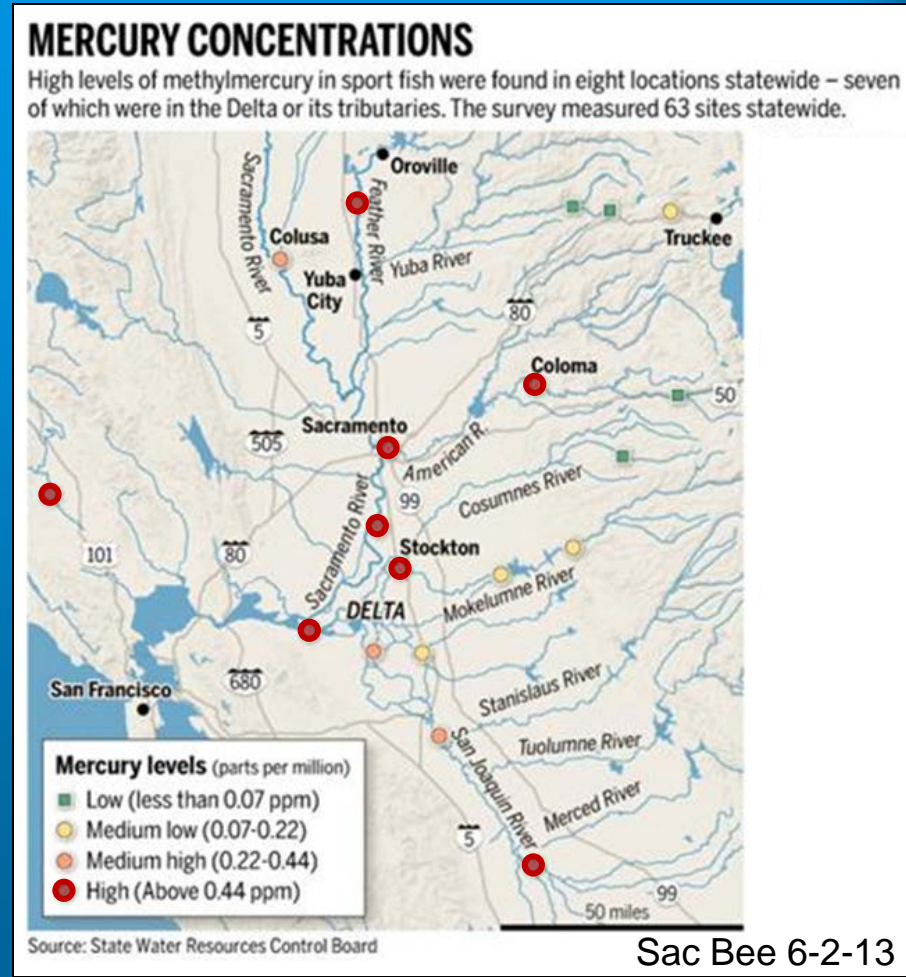
[jamiea@water.ca.gov](mailto:jamiea@water.ca.gov)

916-654-5455

Extra Slides

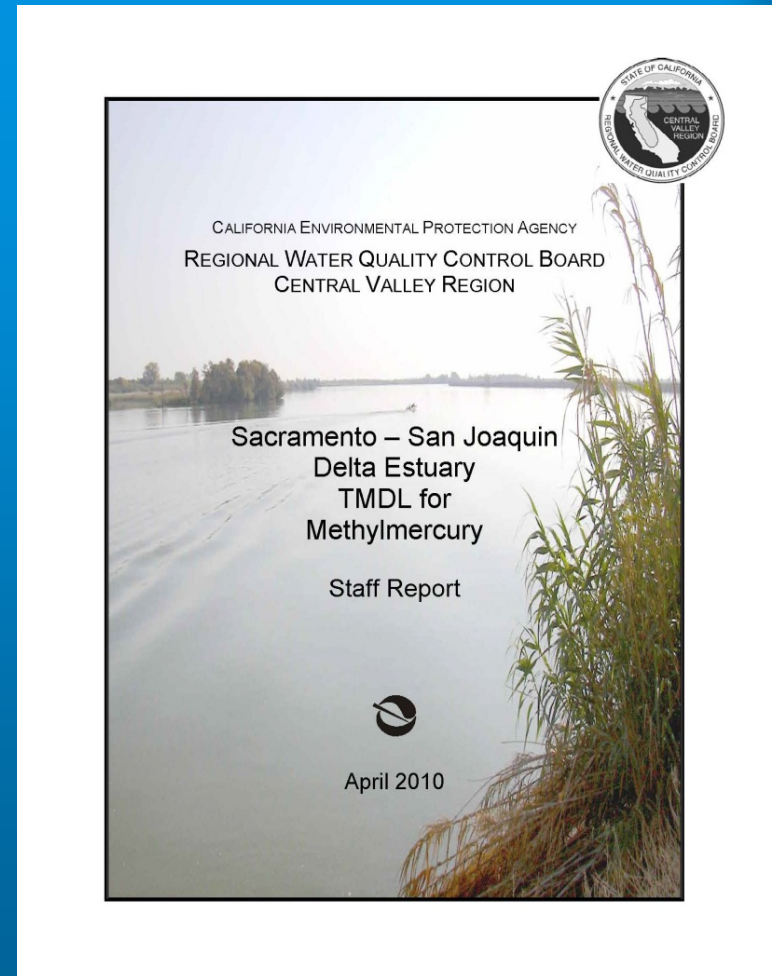
# Why is Mercury an Issue in the Delta?

- Mercury bioaccumulates in the food chain
  - mercury concentrations in fish can be a million fold increase over water concentrations
- Delta sports fish have high mercury levels
- Eating fish with high mercury concentrations
  - Can harm nervous system, brain, heart, kidneys, lungs, etc
  - Pregnant woman, infants and children are the most vulnerable



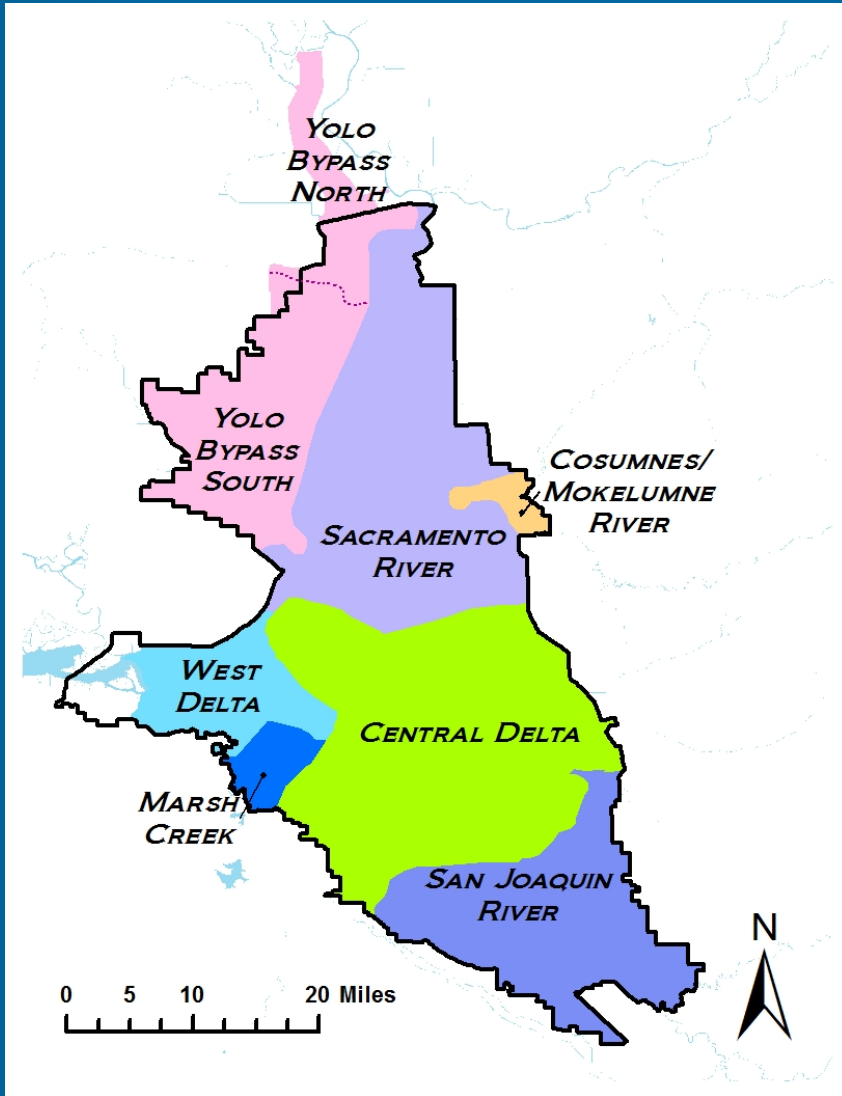
# Delta Mercury Total Maximum Daily Load (TMDL)

- **1990** Sacramento-SJ Delta listed as impaired for fish consumption due to mercury [Clean Water Act 303 (d) list]
- **2010** Regional Water Quality Control Board adopted amendments to the Sacramento River and San Joaquin River Basin Plan to establish the **Delta Mercury Control Program** which establish Total Maximum Daily Loads (TMDL) for mercury in the Delta
- **2011** US EPA approved the TMDL and DWR is required to comply with the TMDL

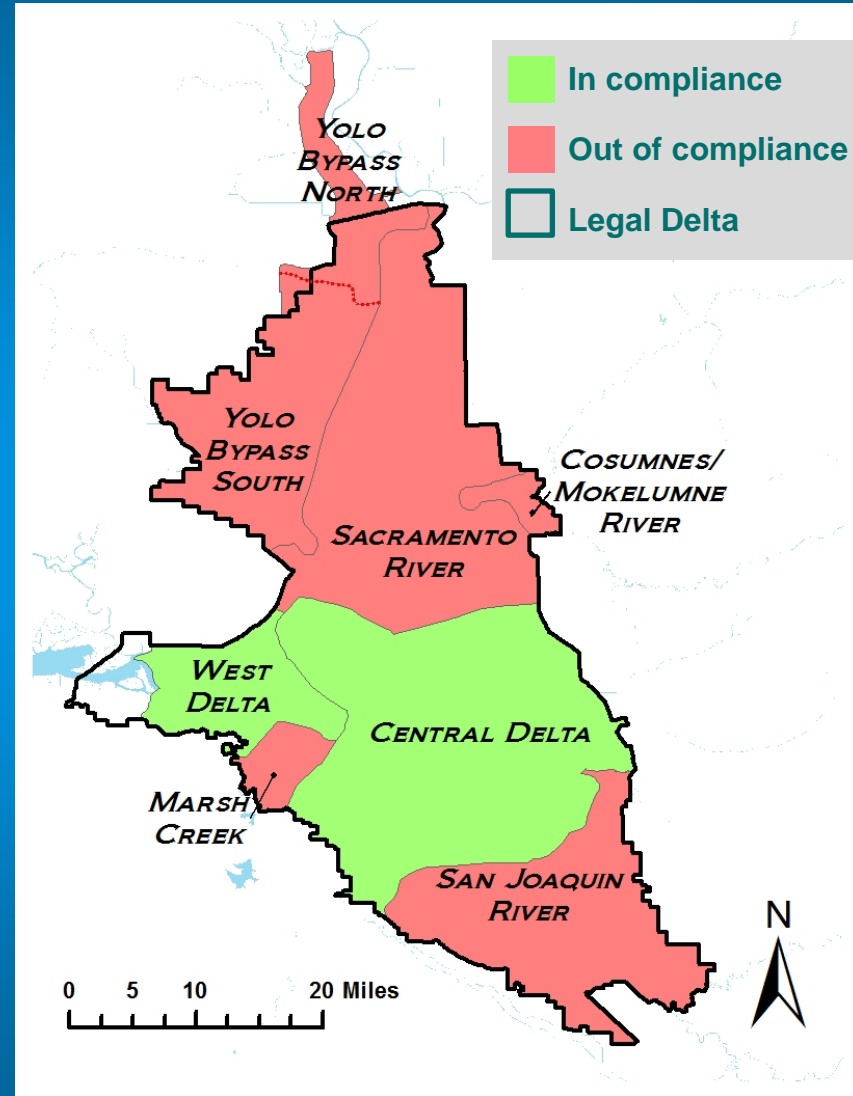




# What areas are affected by the TMDL?



# What areas require load reductions?



TMDL=Total Maximum Daily Load

Adapted from DiGiorgio, DWR

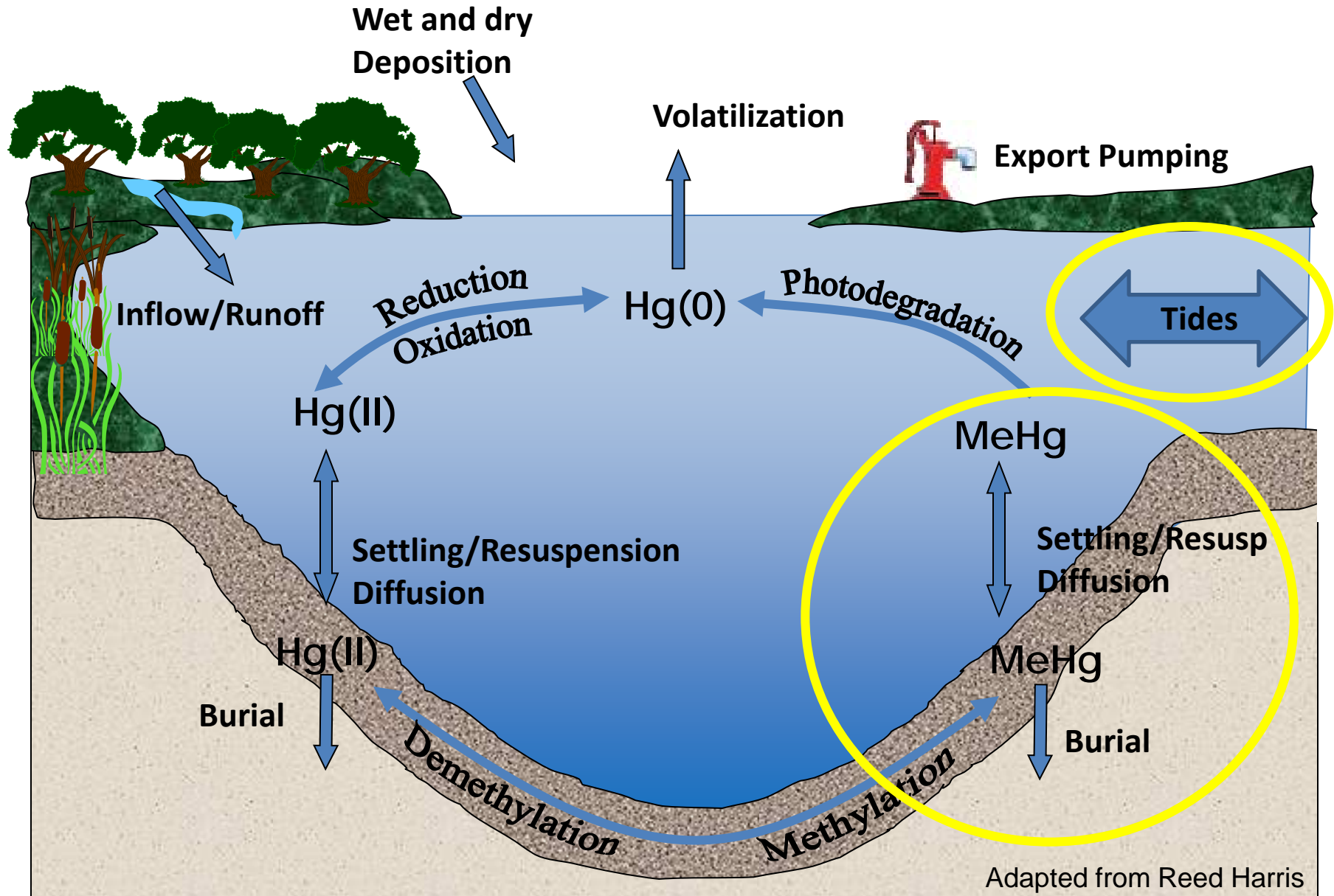
# Load Reductions Required for:

**TABLE A**  
**METHYLMERCURY LOAD AND WASTE LOAD ALLOCATIONS FOR EACH DELTA SUBAREA BY SOURCE CATEGORY**

Source Type	DELTA SUBAREA													
	Central Delta		Marsh Creek		Mokelumne River		Sacramento River		San Joaquin River		West Delta		Yolo Bypass	
	Current Load (g/yr)	Allocation (g/yr)	Current Load (g/yr)	Allocation (g/yr)	Current Load (g/yr)	Allocation (g/yr)	Current Load (g/yr)	Allocation (g/yr)	Current Load (g/yr)	Allocation (g/yr)	Current Load (g/yr)	Allocation (g/yr)	Current Load (g/yr)	Allocation (g/yr)
<b>Methylmercury Load Allocations</b>														
Agricultural drainage <sup>(d)</sup>	37	37	2.2	0.40	1.6	0.57	36	20	23	8.3	4.1	4.1	19	4.1
Atmospheric wet deposition	7.3	7.3	0.23	0.23	0.29	0.29	5.6	5.6	2.7	2.7	2.4	2.4	4.2	4.2
Open water	370	370	0.18	0.032	4.0	1.4	140	78	48	17	190	190	100	22
Tributary Inputs <sup>(a)</sup>	37	37	1.9	0.34	110	39	2,034	1,129	367	133			462	100
Inputs from Upstream Subareas	(b)	(b)	---	---	---	---	---	---	---	---	(b)	(b)	---	---
Urban (nonpoint source)	0.14	0.14	---	---	0.018	0.018	0.62	0.62	0.0022	0.0022	0.066	0.066	---	---
Wetlands <sup>(d)</sup>	210	210	0.34	0.061	30	11	94	52	43	16	130	130	480	103
<b>Methylmercury Waste Load Allocations</b>														
NPDES facilities <sup>(a)</sup>	1.3	1.3	0.086	0.086	0	0	162	90	40	15	0.0019	0.0019	1.0	0.42
NPDES facilities future growth <sup>(a)</sup>	---	0.32 <sup>(b)</sup>	---	0.21	---	0	---	8.6	---	2.1	---	0.25 <sup>(b)</sup>	---	0.60
NPDES MS4 <sup>(a)</sup>	5.4	5.4	1.2	0.30	0.045	0.016	2.8	1.6	4.8	1.7	3.2	3.2	1.5	0.38
<b>Total Loads<sup>(c)</sup> (g/yr)</b>	<b>668</b>	<b>668</b>	<b>6.14</b>	<b>1.66</b>	<b>146</b>	<b>52.6</b>	<b>2,475</b>	<b>1,385</b>	<b>528</b>	<b>195</b>	<b>330</b>	<b>330</b>	<b>1,068</b>	<b>235</b>

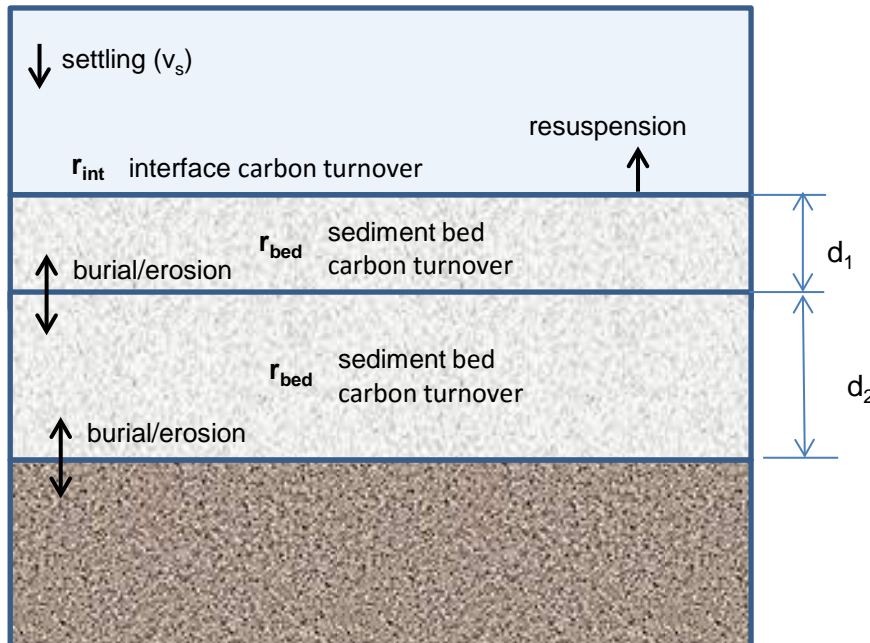


# Mercury Cycling in Water and Sediments



## D-MCM v4

- Up to four particle types (labile organic, refractory organic, silt, sand).
- Variable number of sediment layers with one underlying deep bed which acts as a Hg boundary condition. Hg and particles mass balance is done for Hg and particulates in the deep bed (used when overlying layer is eroding and burying).
- Sediment layer has constant thickness/volume, variable mass and porosity.
- Mass balance on all four sediment types for each layer.
- Decomposition/mineralization is a first order temperature dependent reaction.
- Fraction of settling solids that decomposes before incorporation into sediments is assigned.
- Particulate mass balance for sediment layer but none for water column.
- Different settling and resuspension rates for different particle types.
- Different turnover rates for labile and refractory organic particles.



sediment bed properties:

- $\rho$  - particle density ( $\text{g/m}^3$ )
- $P$  - porosity (calculated)
- $d$  - bed depth (m)
- $A$  - area ( $\text{m}^2$ )