

Mercury in Fish Tissue Across the Western United States and Implications of Selenium Interactions with Mercury

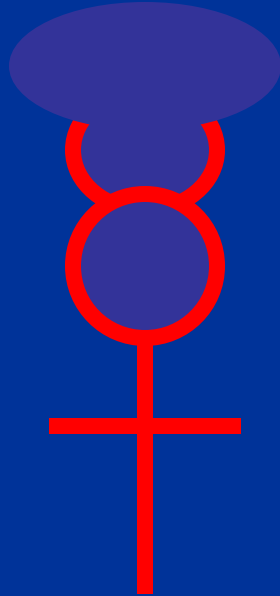
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Mercury



Statement

- Living organisms have no known requirements for Hg in their physiological functioning, and it is known to be toxic to them at various concentrations.
- A primary source of Hg to humans and wildlife is through consumption of fish.

Questions

- What is the extent of Hg contamination in fish tissue across all Western U.S. streams and rivers?
- What are the factors related to mercury levels in fish?



EMAP-West Survey

- Sample sites were selected using the systematic, randomized EMAP sampling design from all perennial western U.S. streams/rivers
 - Additional hand-picked sites selected to characterize best sites
- Site selections from the digitized version of the 1:100,000 scale USGS maps
- Inferences to the entire stream network can be made from probability survey data using site inclusion probabilities

Field Methods

- Fish sampled by electrofishing
- Streams: backpack shocker on 40 channel width long sample reaches
- Rivers: raft mounted shocker on 100 channel width reaches
- Associated measurements of water chemistry, physical habitat, and watershed characteristics



Tissue Samples

- Collect large and small fish sample at each site if sufficient numbers of fish were available
- Large Fish: Adults \geq 120 mm total length
- Small Fish: Adults $<$ 120 mm
- Samples kept on ice, shipped overnight to laboratory and then frozen until analysis.

Most Common Species Analyzed

- Large Fish
(2,707 fish, 626 sites)
- Non-Piscivores (85%)
 - Rainbow, Brown, Brook, Cutthroat Trout
 - White, largescale Sucker
 - Mountain Whitefish, Carp
- Piscivores (15%)
 - Smallmouth Bass
 - Northern Pikeminnow
 - Walleye, Northern Pike
- Small Fish
(386 samples)
 - Mottled Sculpin
 - Common Shiner
 - Redside Shiner
 - Fathead Minnow
 - Creek Chub
 - Speckled Dace
 - Longnose Dace

Hg Laboratory Analysis

- Whole body analysis ($\mu\text{g Hg/g}$ wet weight)
 - Fish ground up in blender (homogenized)
 - Sub-sampled and frozen until analysis
 - Thawed, re-homogenized and analyzed without further sample preparation

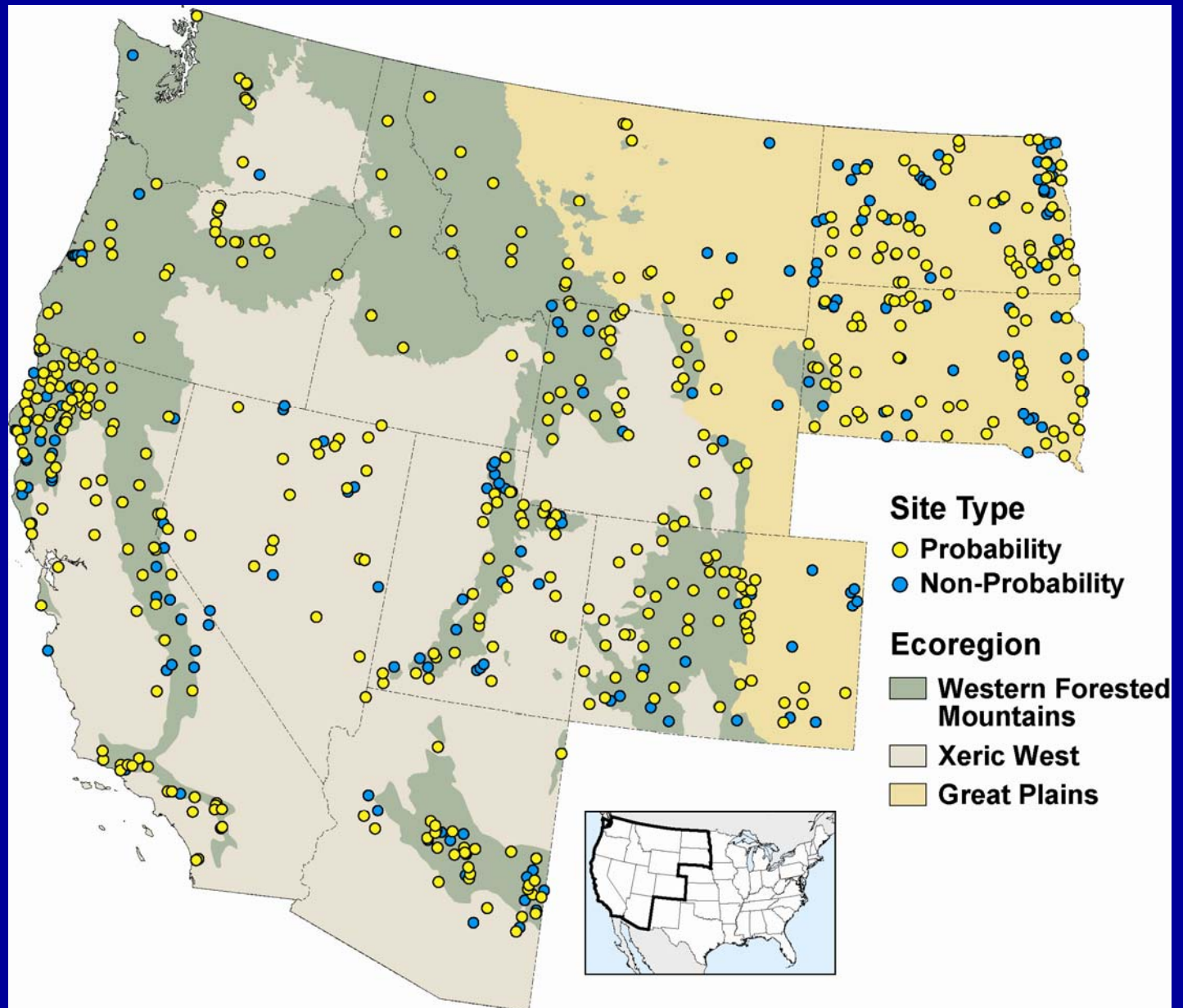
Analyzed by Combustion Atomic Absorption Spectrometry (CAAS)



QA and Detection Limits

- Samples run in duplicate and repeated if more than 10% variation between duplicates
- Method Detection Limit (MDL):
= 0.002 μg Hg/g wet wt.

EMAP
West
Fish
Tissue
Sample
Sites
n=625



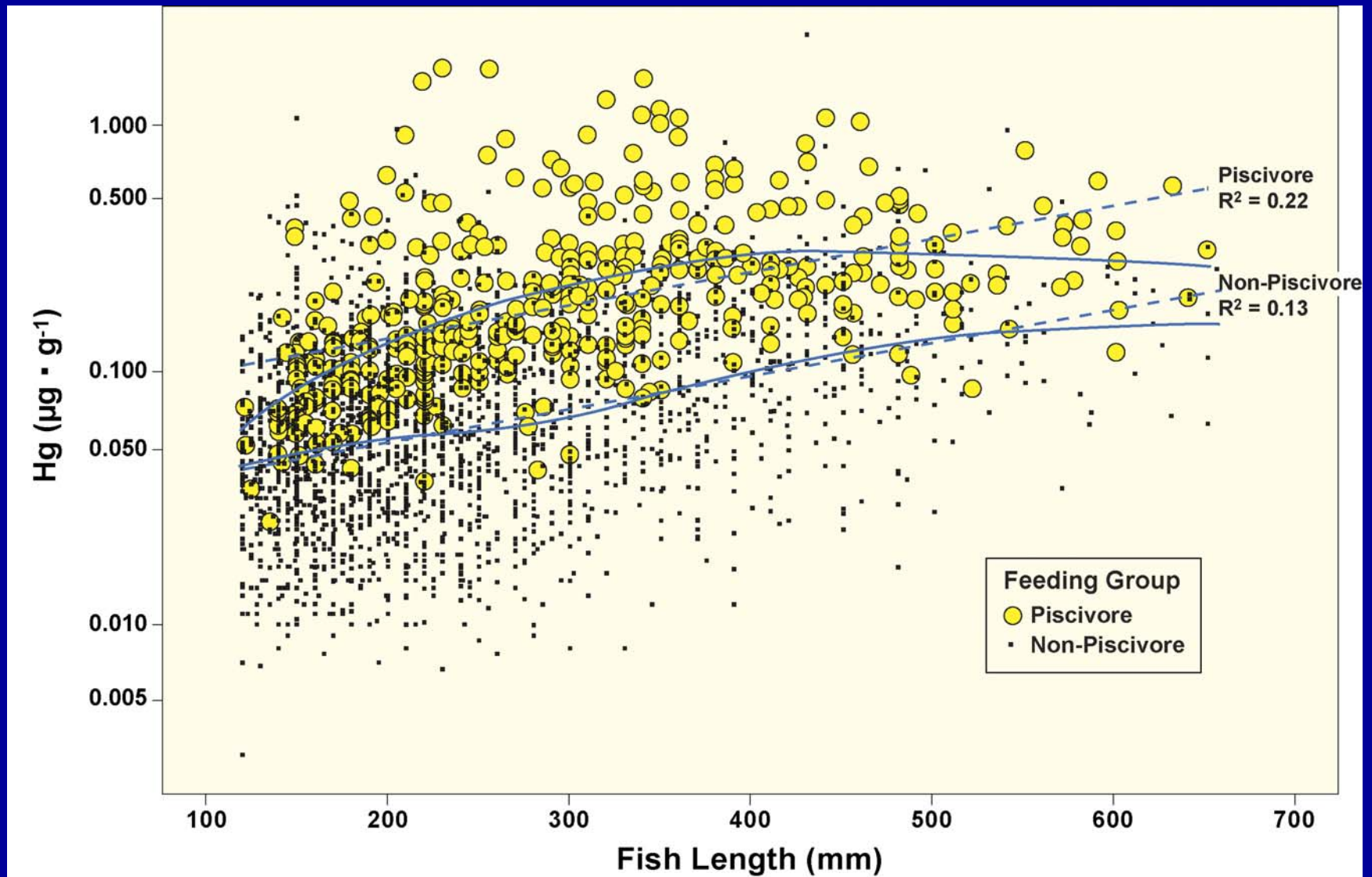
Factors Considered

- Fish Size (Total length)
- Fish Classification
 - Species (genus)
 - Family
 - Trophic Class (piscivore, non-piscivore)
- Site Disturbance Class (Low, Moderate, High)
 - Based on:
 - Physical Habitat
 - Water Quality
 - Air Photo Analysis

Analysis Types

- Linear and Local Regression (LOESS)
- ANCOVA - Site Condition Effects Tested w/Fish Length as Covariate
- Partial Correlation Analysis to Assess Environmental Variable Influences
- Population Estimates (Stream Length)

Mercury – Fish Length Relationship for Individual Large Fish



ANCOVA RESULTS

Fish Group	Length Effect		Site Effect	
	(Partial F) ^a	(df)	(Partial F) ^b	(df)
Cutt/Rain Trout	135	1, 275	0.34	2, 206
Brown Trout	73.8	1, 157	0.22	2, 102
Mt. Whitefish	117	1, 83	0.56	2, 36
Suckers	137	1, 259	0.29	2, 179
Bullheads	19.2	1, 67	0.41	2, 49
Bass	170	1, 70	0.74	2, 36

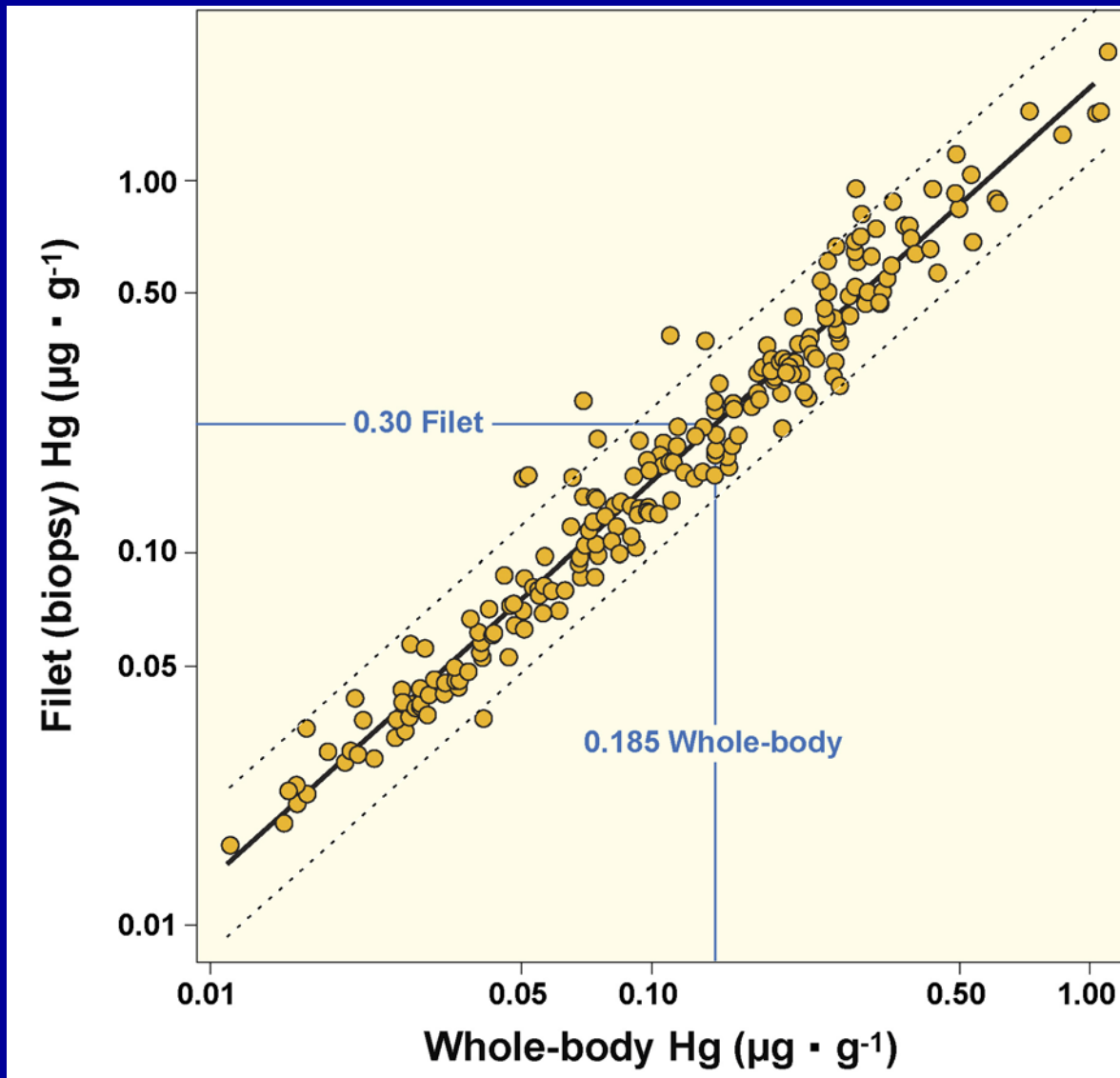
Correlation between Hg and environmental variables after partialing out fish length

Fish Group	r_{length}	No. Fish	Top Environmental Correlates
Bass	0.72	110	Ann. Runoff (0.37), WS slope (0.37), Longitude (0.35)
Pikeminnow	0.52	100	pH (-0.60), WS area (-0.37), ANC (-0.56)
Suckers	0.48	442	None > 0.3
Br. Trout	0.33	120	None > 0.3
Cutt/RB Trout	0.20	485	None > 0.3
Brook Trout	0.17	159	DOC (0.47), WS slope (-0.36)

Various Fish Tissue Mercury Criteria Values

- Human Health
 - 0.35 $\mu\text{g/g}$ (Oregon Health Div., 1997)
 - 0.30 $\mu\text{g/g}$ (EPA, 2001)
 - 0.10 $\mu\text{g/g}$ (Faroe Island Study, 1998)
- Wildlife protection values - Lazorchak et al. 2003
 - 0.10 $\mu\text{g/g}$ (Otter)
 - 0.07 $\mu\text{g/g}$ (Mink)
 - 0.03 $\mu\text{g/g}$ (Kingfisher)

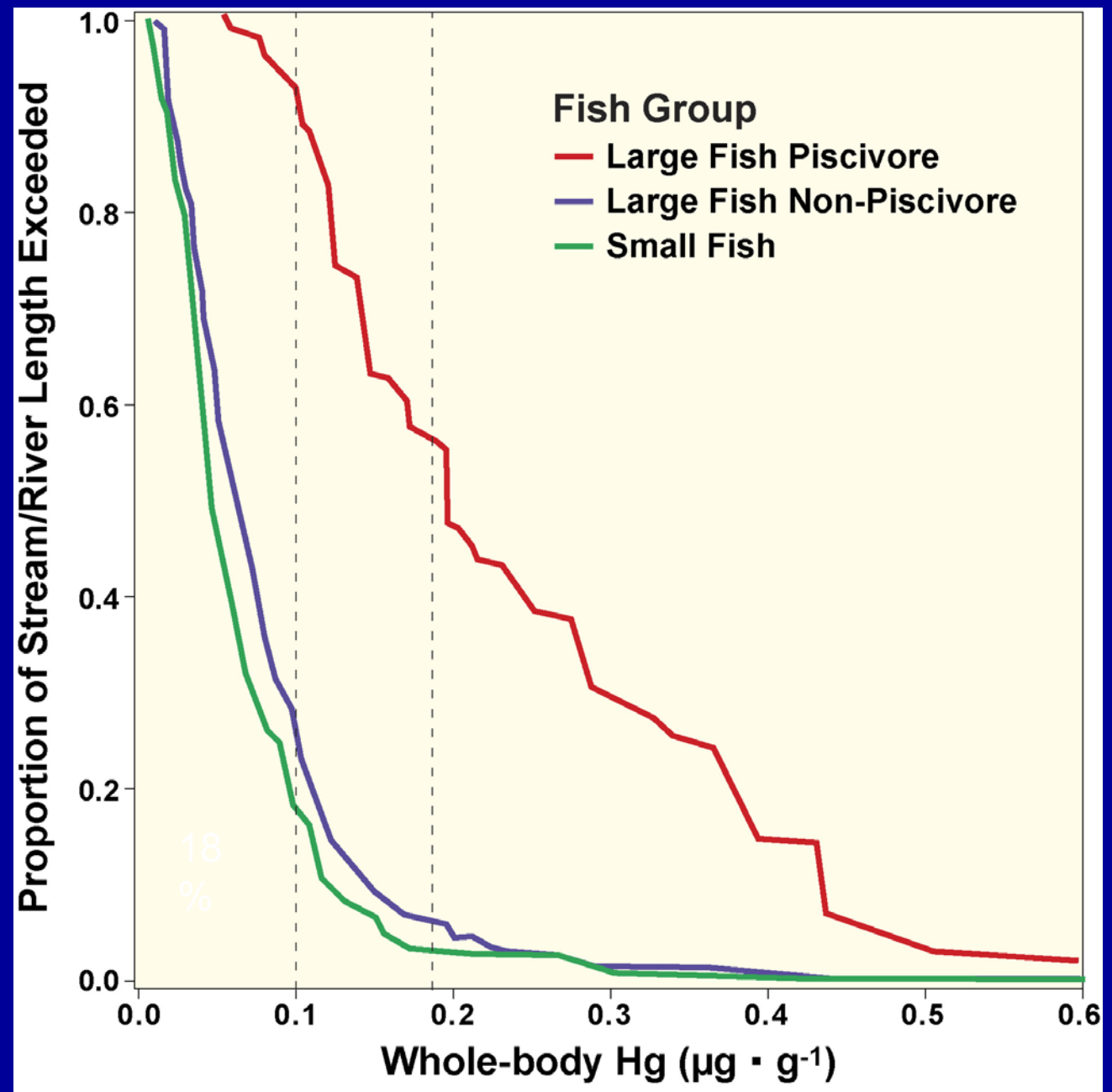
Relationship Between Fish Whole Body and Filet Hg Conc.



$n = 210, r^2 = 0.96$

**Whole fish Hg
conc. $\geq 0.185 \mu\text{g Hg/g}$
exceeds the USEPA
tissue based water
quality criterion of $0.3 \mu\text{g Hg/g}$
in filets**

Cumulative Distribution Frequency (CDF) for Site Mean Mercury in Fish Tissue



Summary

- Fish tissue mercury concentrations were most strongly related to trophic group and fish length
- Site disturbance effect was non-existent
- Other environmental factors influence Hg in fish to different degrees and with no consistent pattern
- **0.185 $\mu\text{g Hg/g}$ whole fish = 0.3 $\mu\text{g Hg/g}$ filet**
- In terms of % Stream Length exceeding criteria
- Piscivores
 - 57% > 0.185 $\mu\text{g Hg/g}$
 - 93% > 0.1 $\mu\text{g Hg/g}$
- Non-piscivores
 - 6% > 0.185 $\mu\text{g Hg/g}$
 - 26% > 0.1 $\mu\text{g Hg/g}$

Summary (con't)

- Fish tissue mercury concentrations in Western U.S. streams and rivers were found in a fairly narrow range (90% = 0.02 to 0.2 $\mu\text{g/g}$) and all fish above the detection limit (0.002 $\mu\text{g Hg/g}$)
- High concentration “hot spots” ($\text{Hg} > 0.5 \mu\text{g/g}$) were rare (< 2% of stream resource)
- The above (plus Jaffy et al., 1999; Hope, 2006) strongly suggests a broad diffuse source of mercury from atmospheric deposition.

Summary (con't)

Consumption of large game fish from extensive lengths of western streams/rivers presents a potential risk to sensitive consumers relative to the current fish tissue based water quality criterion

- Both wildlife and human (particularly females of offspring bearing age).

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JANUARY 24, 2007

The Oregonian

SUN
EDIT

PORTLAND, OREGON

VOICE OF THE NORTHWEST SINCE 1850

Mercury found in all fish tested in the West

Dietary limits | The extent of the neurotoxin surprises Oregon scientists, who suspect the air is the source

By **RICHARD L. HILL**
THE OREGONIAN

A sweeping study by Oregon scientists has found mercury-contaminated fish throughout the West.

In the most widespread survey of mercury in the nation's streams, four Corvallis researchers with the U.S. Environmental Protection Agency and Oregon State University sampled more than 2,700 fish in Oregon, Washington and 10 other Western states. They found detectable — and in some

G.I. Joe's will sell controlling interest

Northwest icon | A San Francisco firm will buy a major stake for an undisclosed sum

By **LAURA GUNDERSON**
THE OREGONIAN

G.I. Joe's Inc., one of the Northwest's biggest and best-known retailers, has agreed to sell a controlling interest to a San Francisco investment firm for an undisclosed sum.

Norm Daniels, chief executive of the 55-year-old sporting and outdoor goods chain, would not release terms of the deal in an in-

terview late Tuesday, but said he expects it to close this month following federal and shareholder approval. Daniels said he and other managers will remain in place, ready to launch an expansion — sped up by the sale — adding 15 stores in two new states over the next three years.

A spokeswoman for Gryphon Investors declined to comment. The company's Web site said it typically invests between \$25 million and \$50 million in its acquired companies — a range Daniels said is reflective of Gryphon's investment in G.I. Joe's.

This year, G.I. Joe's sales are expected to

exceed \$240 million, Daniels said, perhaps making them one of the larger acquisitions at Gryphon, which typically invests in companies posting sales of \$25 million to \$150 million, according to its Web site.

Daniels said G.I. Joe's is Gryphon's only retail holding and that he expects the firm to fill three to four seats on the retailer's six-member board.

For G.I. Joe's, the sale provides the "financial support to compete with anybody who would come to town, plus grow at the rate we'd plan to grow," Daniels said. "This gives

Please see **G.I. JOE'S**, Page A4



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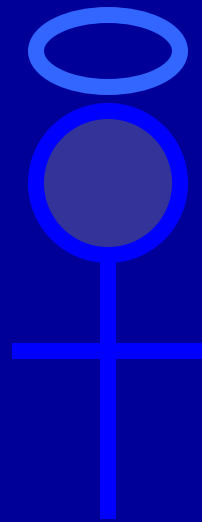
2007 | STATE OF THE UNION

Bush works to salvage Iraq

Bush's proposa
with these work

And Now: The Rest of the
Story!

Selenium



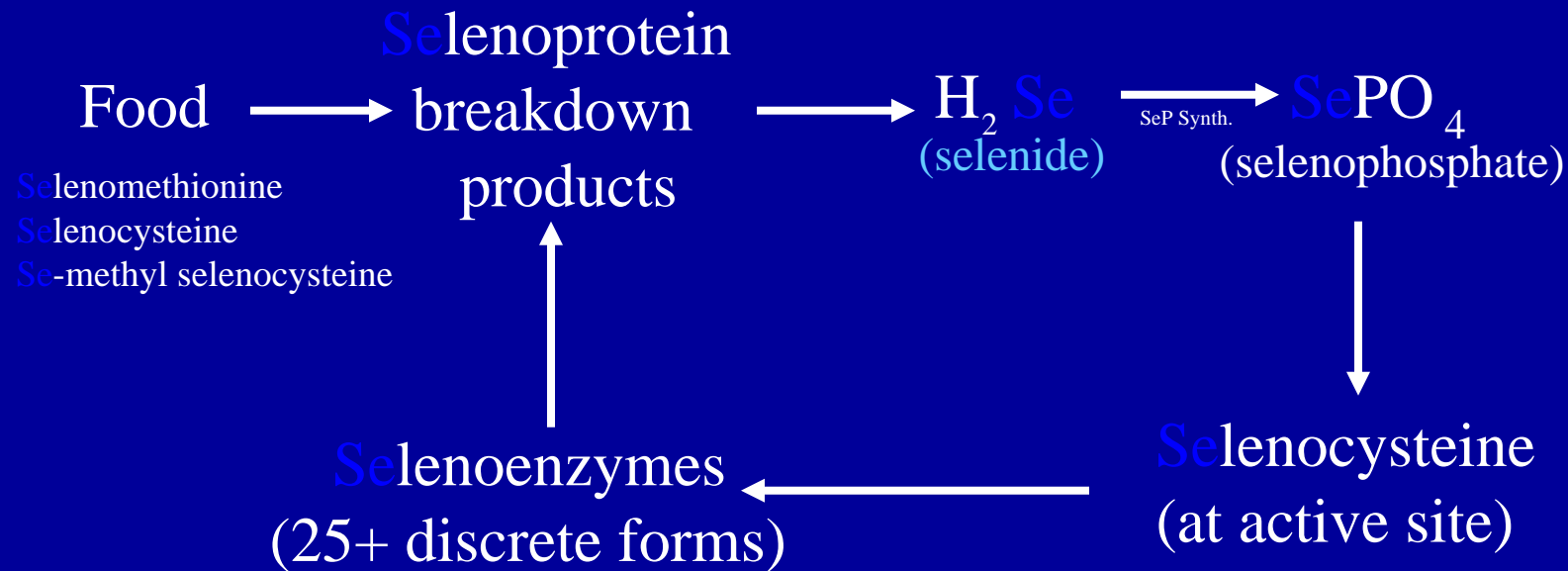
Selenium

- Toxic to fish at $\geq 0.8 \mu\text{g/g}$ wet wt. and to piscivorous wildlife when fish tissue concentration $\geq 0.6 \mu\text{g/g}$ wet wt. (Lemly, 1996)
- However: Se is also essential for normal selenoenzyme functions in all animal cells
- Se is the functional component of the 21st amino acid, **selenocystine**

Se-Physiology Background

- **Selenocystine** is formed de novo during each cycle of protein synthesis and is incorporated at active selenoenzyme sites
- **Selenocysteine** synthesis involves formation of selenide
- Mercury binds preferentially to selenide over any other partner
- **Mercury** toxicity impairs cellular selenoenzyme activities

Normal Selenoprotein Synthesis

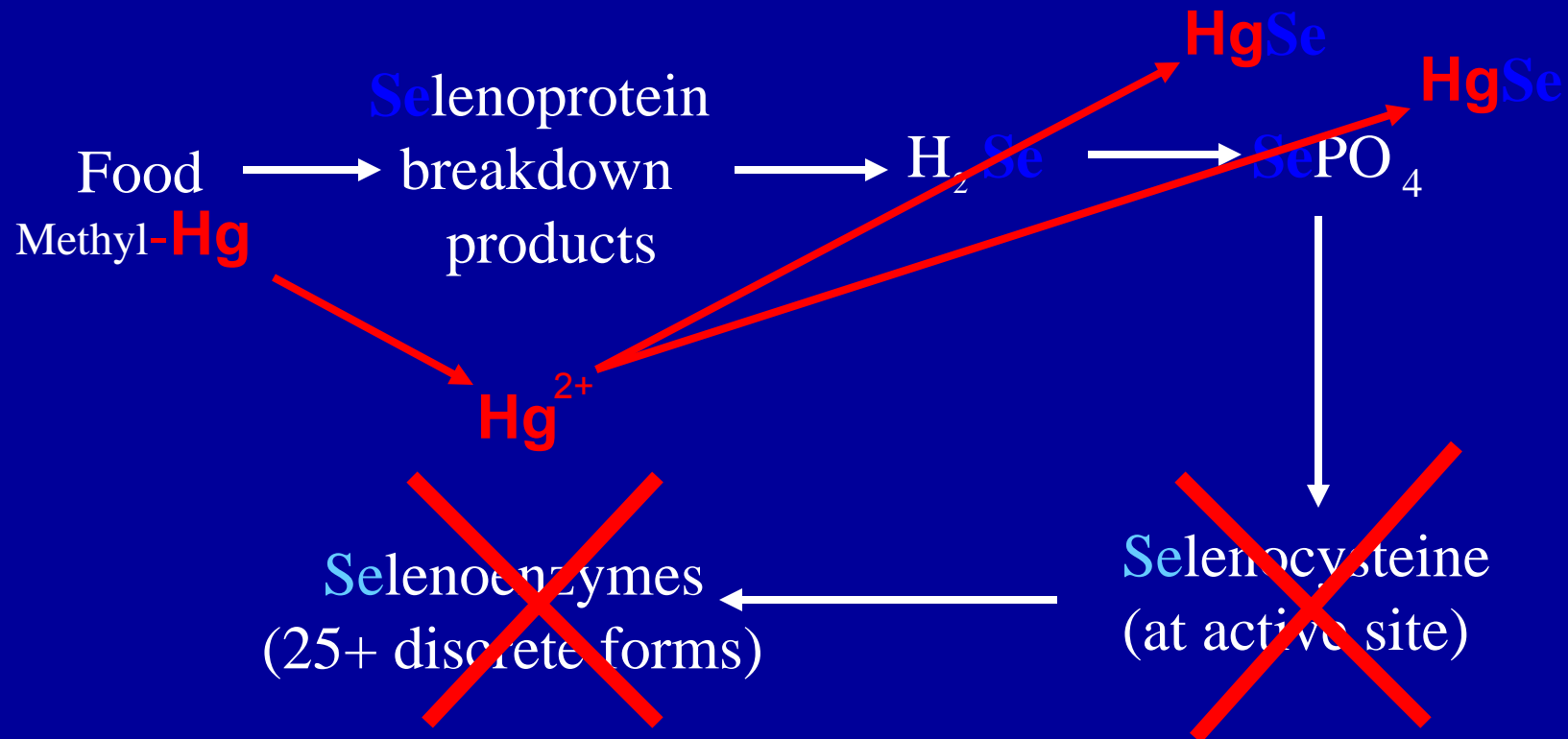


Selenocysteine is the only amino acid that must be recreated for each cycle of protein synthesis

Methylmercury Toxicity

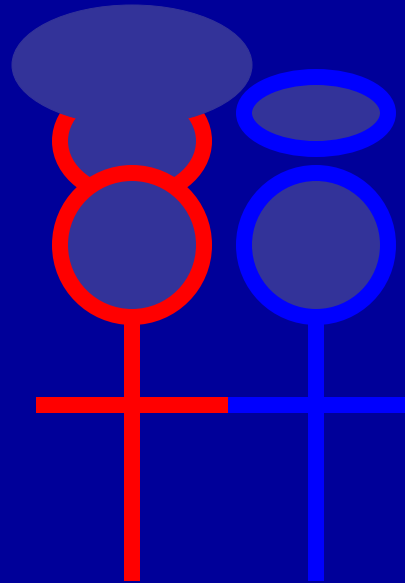
- Neurotoxic effects of MeHg exposures are well documented in humans and animals
- Developing nervous systems are particularly sensitive to MeHg: fetal & young animal brains
- MeHg impacts phospholipid glutathione peroxidase and selenoprotein W in the brain

Se-Physiology Under the Influence of MeHg



Loss of free selenium disables enzymes that normally detoxify free radicals, activate thyroid hormones, and support normal brain functions.

Mercury selenide



Also known as Tiemannite,
stability coefficient = 10^{45}

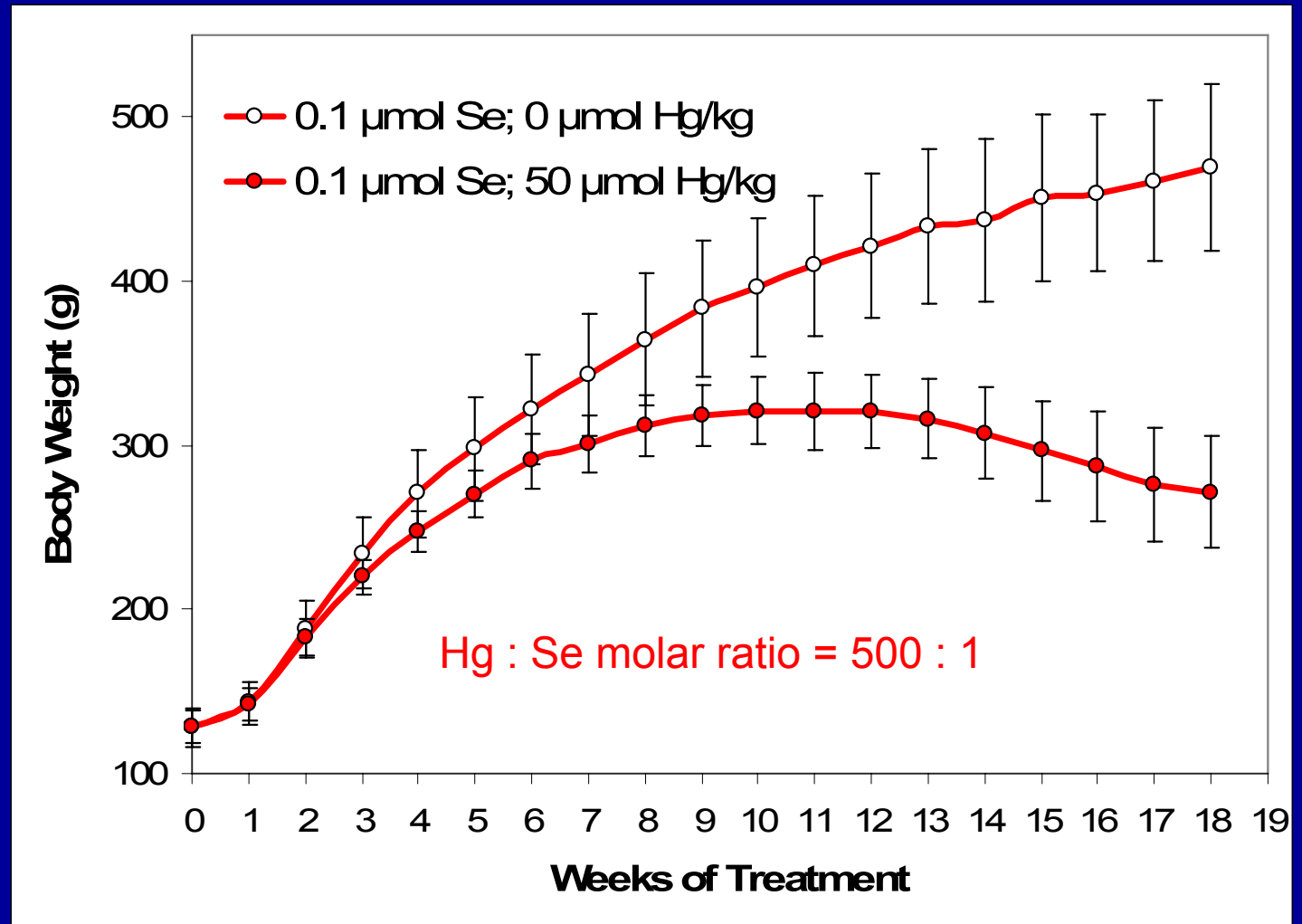
So, What Effect Does this Hg/Se
Association Have on Higher Organisms

And

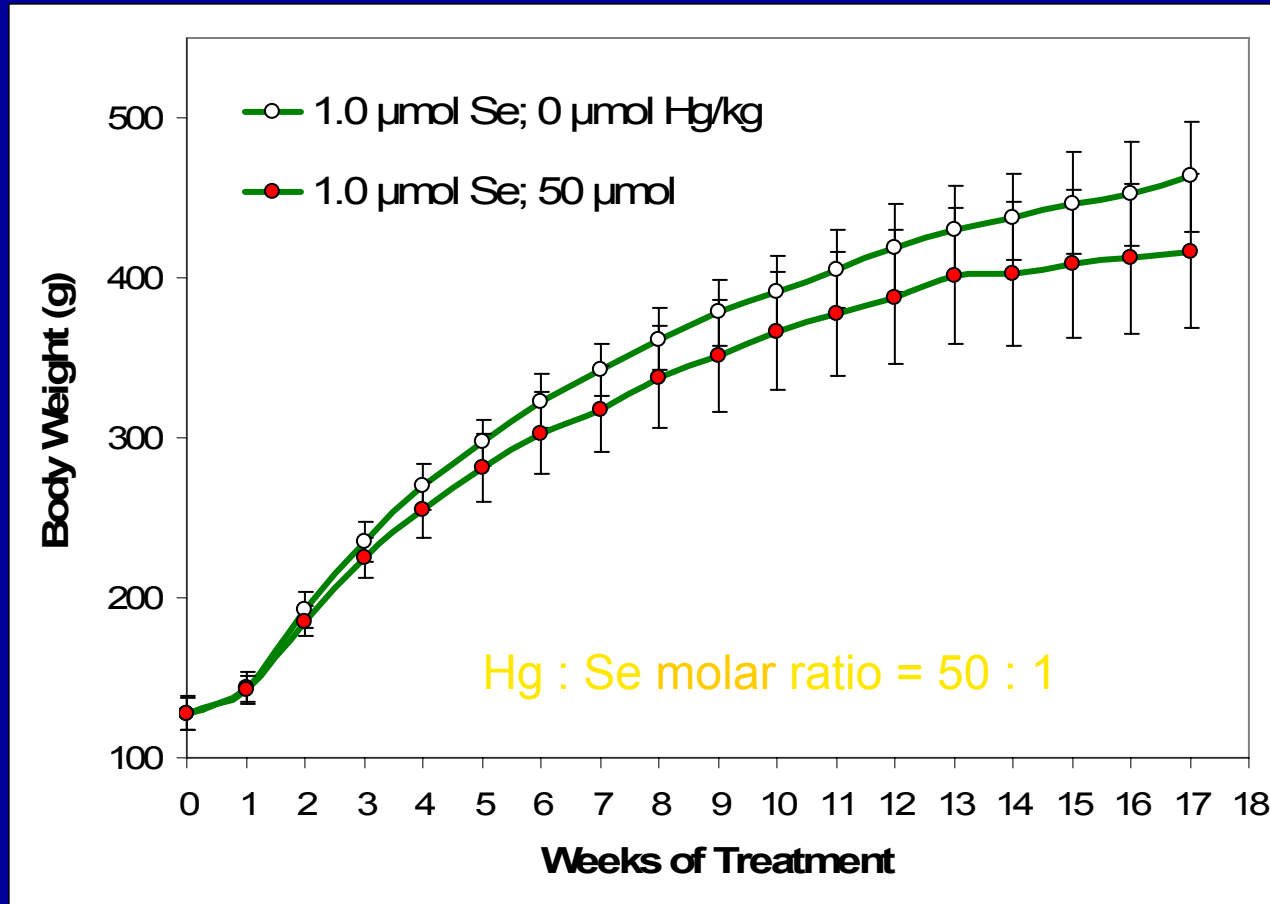
What Does that Have to Do With the EMAP
Derived Fish Tissue Mercury
Concentrations Across the
Western United States?

Effect of Hg:Se Ratio on Growth

- 1) Control
Outgrows Hg fed
group
- 2) Latent effects
are short –
diverge at day 3
when MeHg
accrual is
calculated to be
~1:1 for Hg:Se
- 3) Hg toxicity
symptoms arise
when Hg-
dependent Se-
sequestration
impairs Se
availability in the
brain and
neuroendocrine
tissues



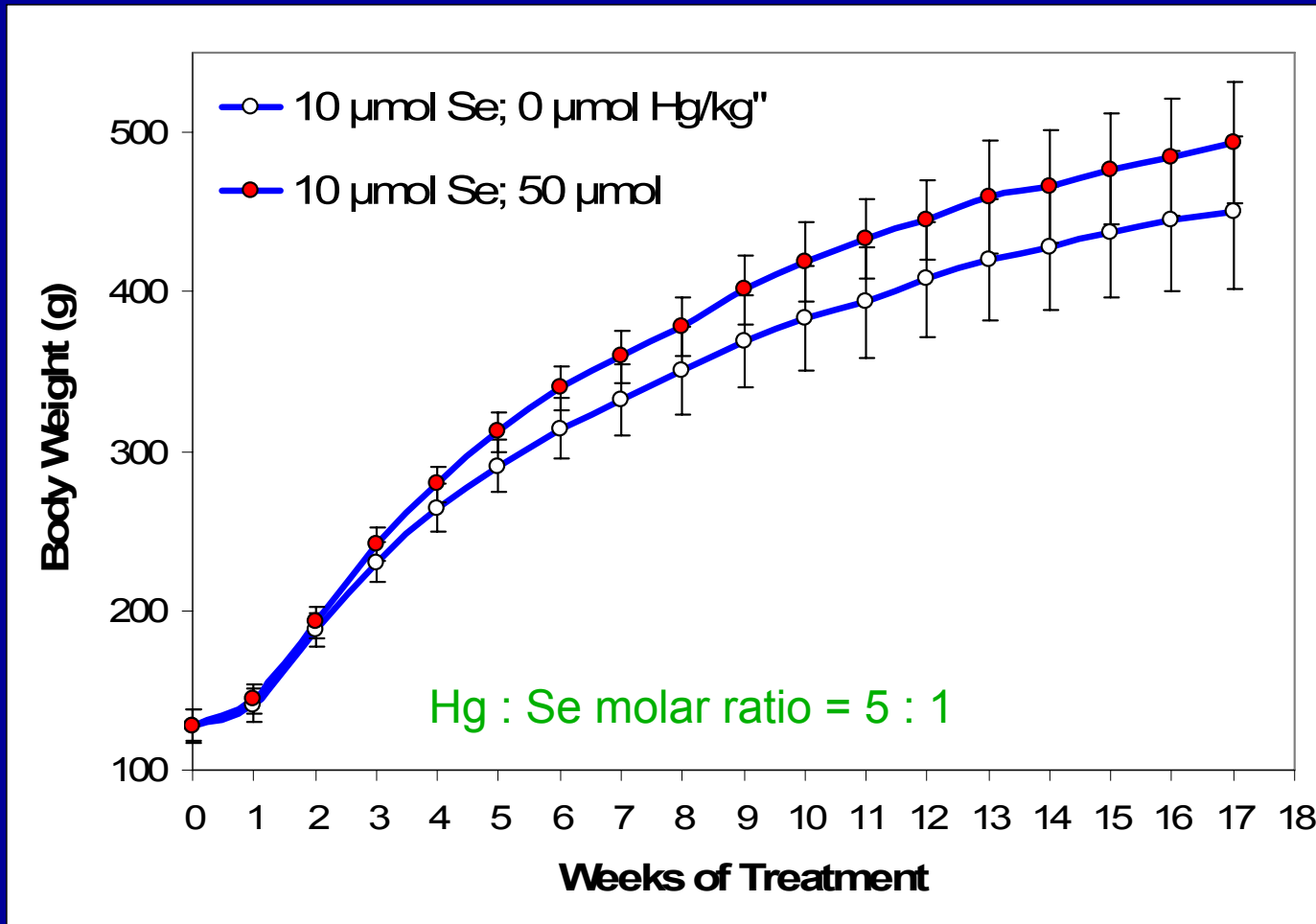
Effect of Hg:Se Ratio on Health



Control rat group at top (moderate Se; no Hg grow better than:

Treatment group (Hg : Se molar ratio of 50 : 1) being fed a moderate amount of Hg

Effect of Hg:Se Ratio on Health



All rats fed rich Se diet

The MeHg treated group actually grew more rapidly than the control – so **there is no MeHg dependent growth impairment**

Se in this test is slightly less than the average Se Conc. in marine fish

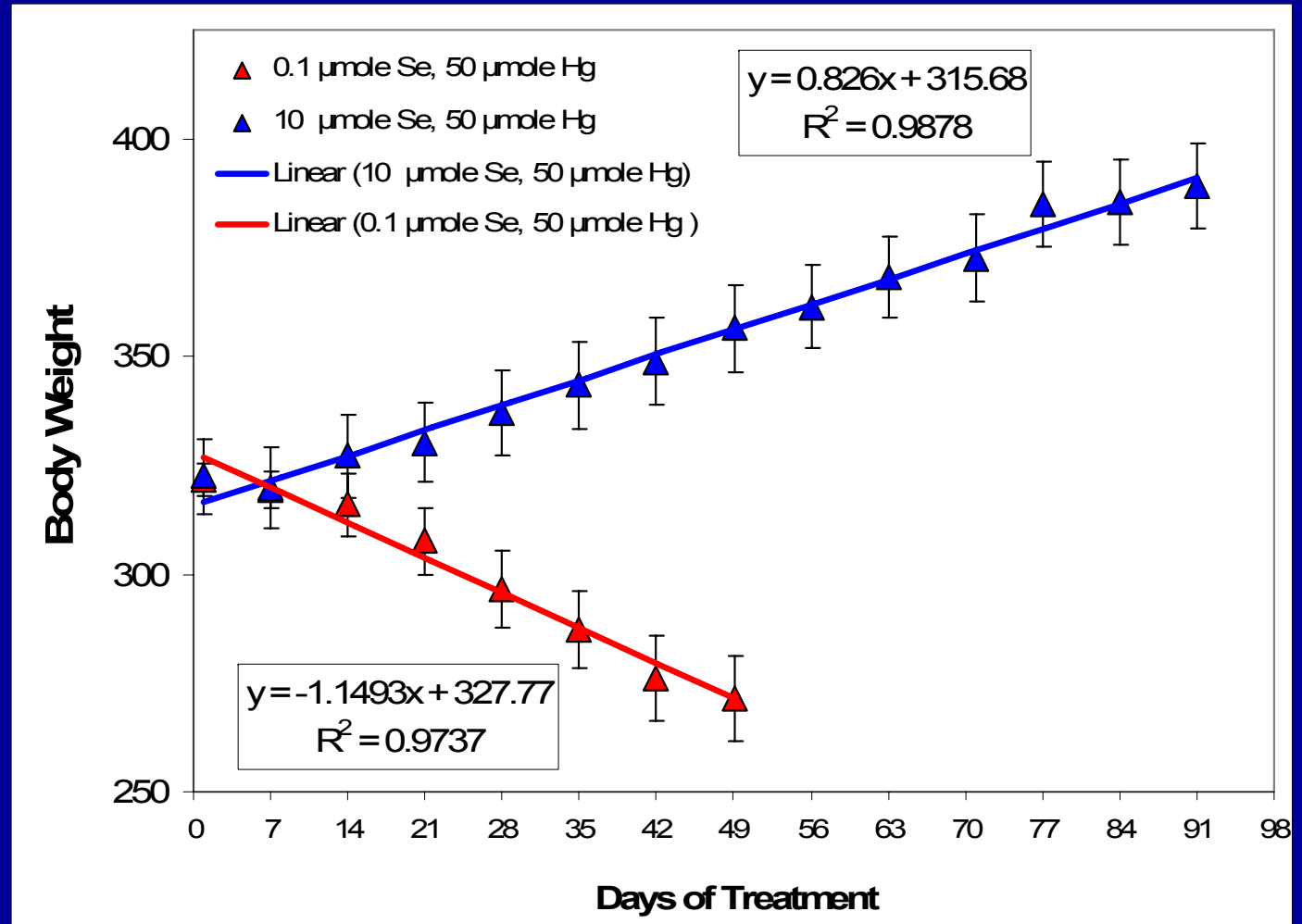
Therapeutic Effects of Se - Recovery

Day 1 here started day 77 of a previous feeding study when rats started losing weight

The day 77 rats were split into two groups

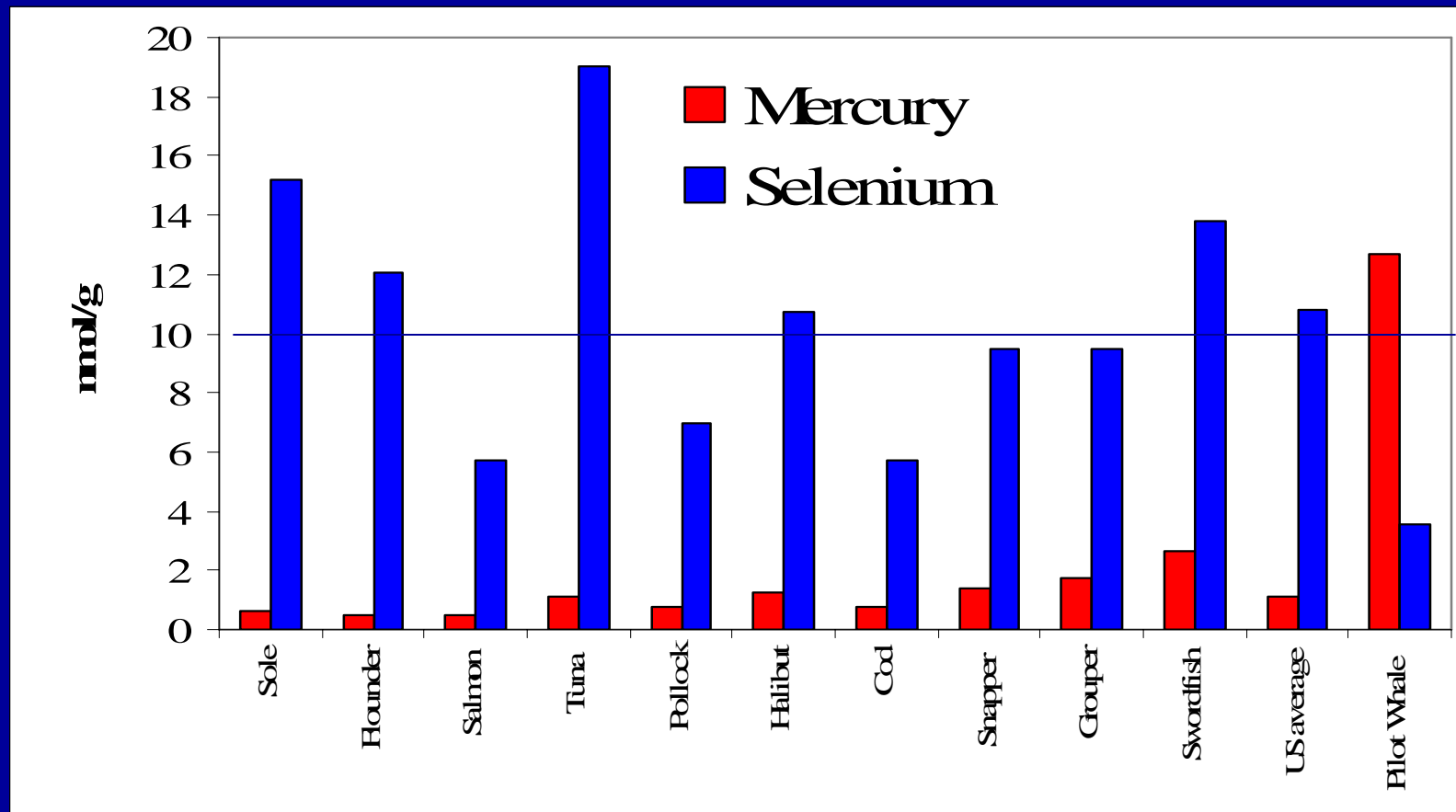
Both groups got 50µmole Hg in feed

One group got only 0.1µmole Se: the other got enriched 10µmole Se along with the Hg



The low Se group was terminated early due to several rat deaths, while the high Se group started to gain wt. immediately & overall health appeared to be restored

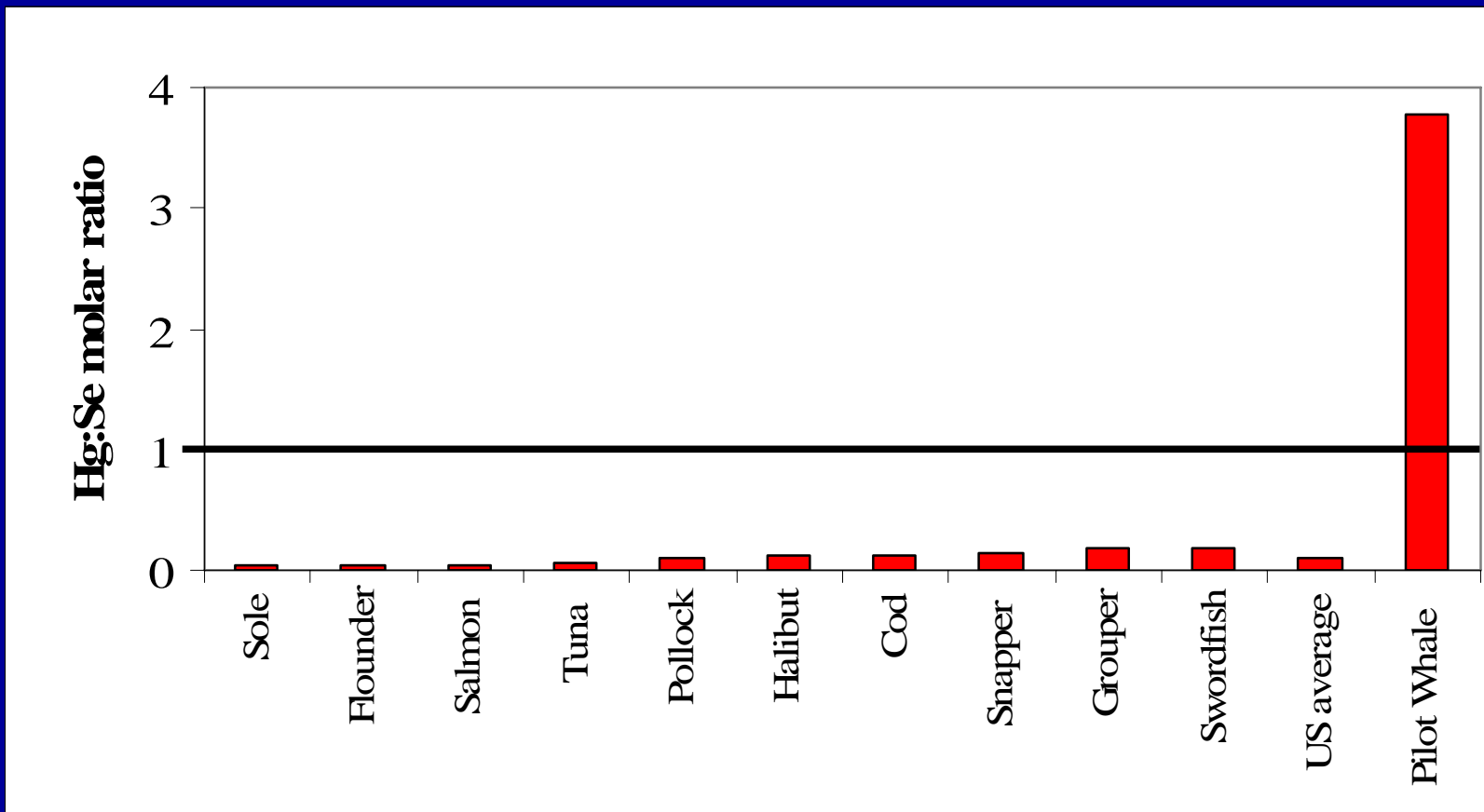
Hg & Se Concentrations in Marine Organisms



Line at 10 nmole/g is the Se concentration used in previous rat studies

Se exceeds Hg by a large margin in all marine fish

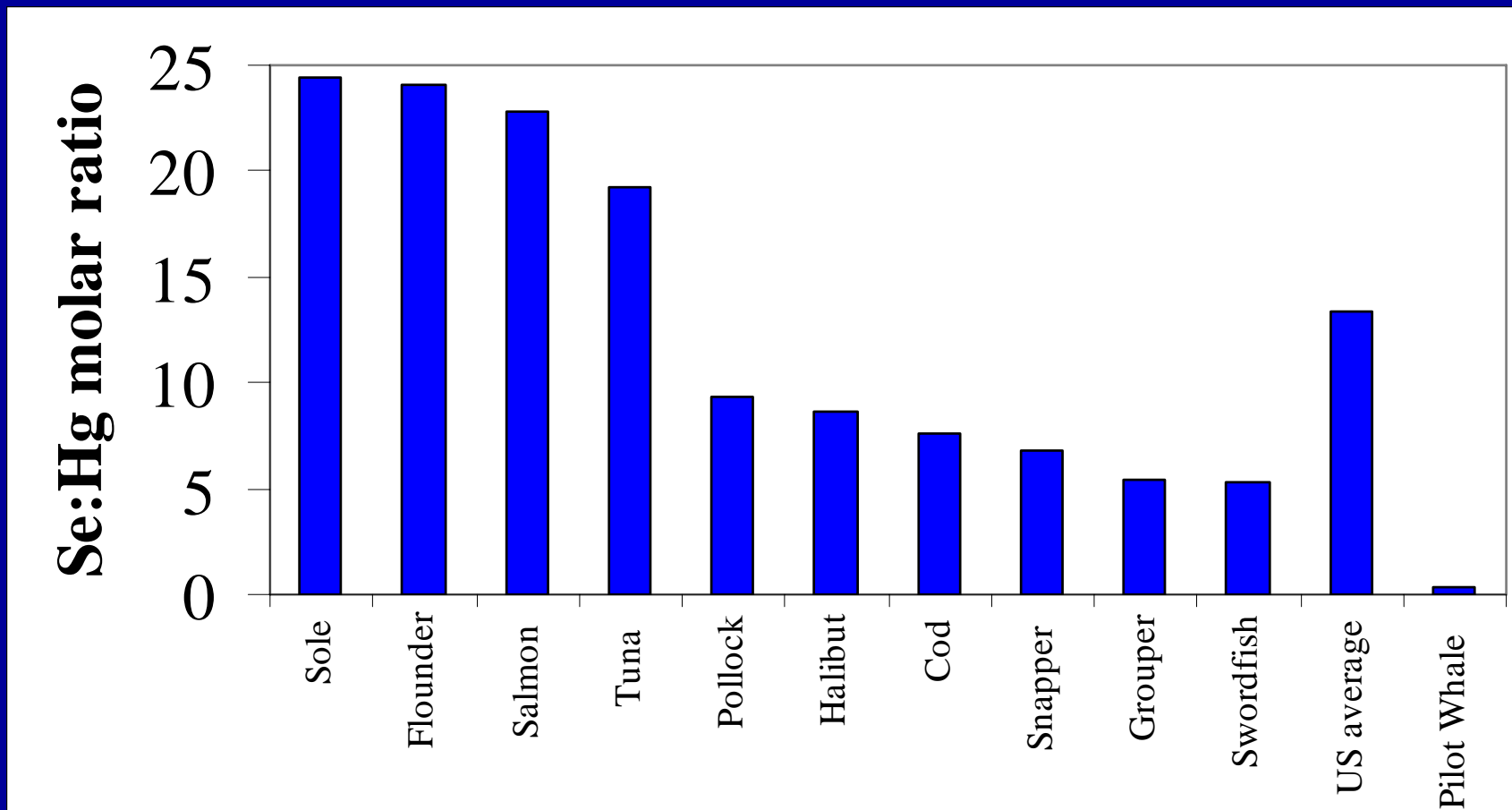
MOLAR RATIOS OF Hg : Se



.The line designates the Hg:Se 1:1 molar ratio.

The molar ratio doesn't even come close to the 1:1 level for marine fish. The ratio of Hg to Se in pilot whale is ~4, and begins to approach the dangerous levels (10 – 40) calculated for fish from Minamata Bay.

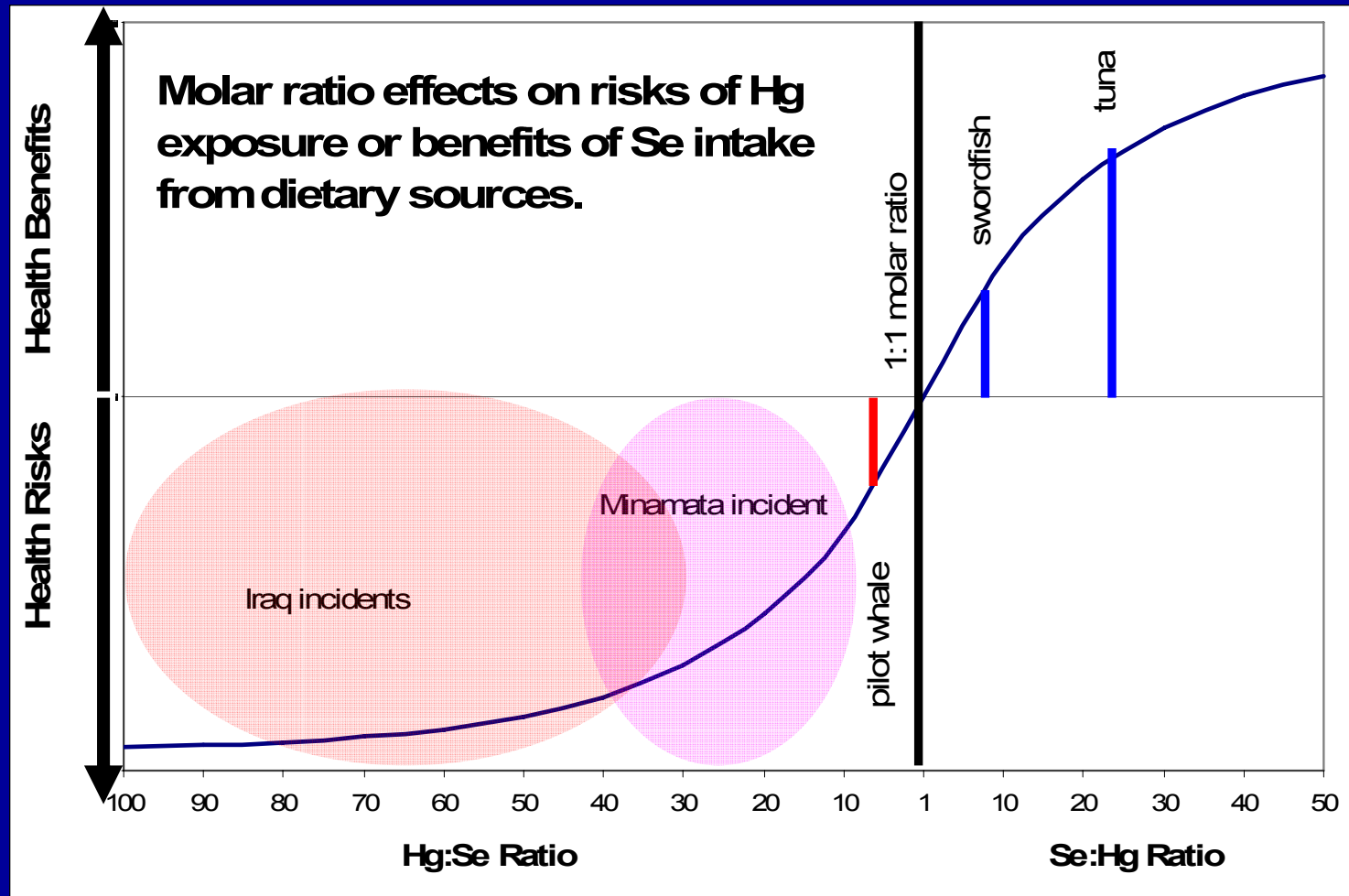
MOLAR RATIOS OF Se : Hg



This reflects moles of Se relative to moles of Hg, and is the inverse of previous slide

All fish show strong exceedance of Se over Hg.

Hg : Se Ratio and Health Effects



This displays health effects of food consumption relative to its Hg:Se molar ratio.

Marine fish fare well in this assessment.

Whale meat does poorly and approaches molar ratios associated with fish from Minamata Bay.

Summarizing Seleniums Role in the Mercury Issue

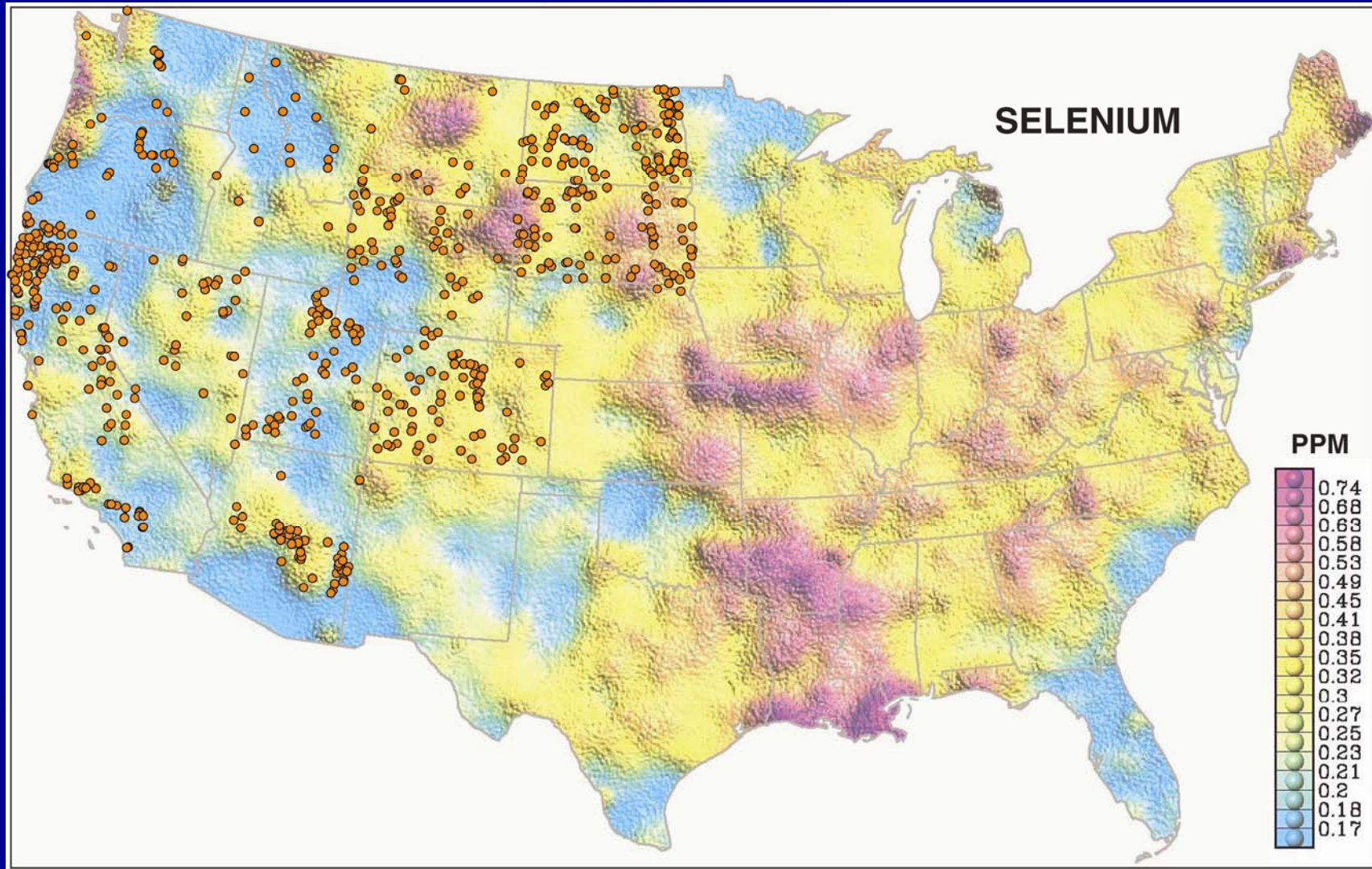
- Dietary selenium provides highly effective protection against mercury toxicity.
- Dietary selenium is an effective treatment of mercury toxicity and rapidly restores health while preventing progression of mercury toxicity, but Hg brain damage is irreversable.
- The biochemical mechanism of mercury toxicity involves loss of selenium-dependent enzyme activities due to mercury sequestering selenium.

Effects of Selenium From Fish

- Ocean fish are rich sources of selenium
- The average selenium contents of ocean fish are equal to the levels demonstrated to provide protection against and treatment of mercury toxicity
- Protective and therapeutic effects of selenium will be tested using freeze dried ocean fish (tuna and or swordfish) as the selenium feeding source for rats

So What Does All of This Have to
Do With the EMAP West
Fish Tissue Hg
Assessment?

Se in U.S. Soils & Fish Sample Sites



Se concentration in soils of the U.S. are likely far more heterogeneous than this low resolution map depicts

Soil/water chemistry has been used to predict toxicity problem areas

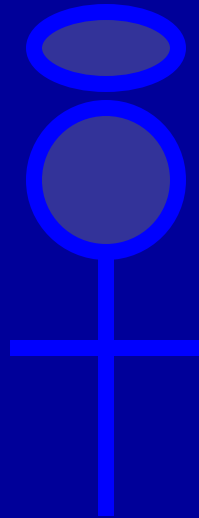
Opportunity to Expand the Value of Existing EMAP Data

- Concern is for the effect of Hg on fish and fish consumers
- Soil/water based chemistry toxicity predictions are generally correct, but incomplete and inaccurate because they do not account for several environmental variables that influence Hg toxicity
- pH, redox and Se presence all affect Hg bioavailability
- We are developing Se concentrations for all archived fish tissue samples that we have already analyzed for Hg

We plan to develop Hg : Se molar ratios
for all fish tissue samples
from the EMAP western
stream survey
(2000 – 2004)

Our purpose is to identify those areas
where Hg toxicity potentials are
highest according to the
Se protection
paradigm

SELENIUM



Se is a required micronutrient and is protective against Hg toxicity when Hg : Se molar ratios are in close proximity

The alchemy symbolized arch-angel of Se is not perfect, she is often misunderstood, but she is generally beneficial relative to Hg toxicity

We are doing a direct fish tissue based assessment to determine where angelic Se likely is, and is not, doing her job best in the western USA