Deposition & Cycling of Sulfur Control Mercury Accumulation in Isle Royale Fish

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Funding

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SETAC
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Data Sharing

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Logistical Support

National Park Service

Laboratory Assistance

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Field Assistance

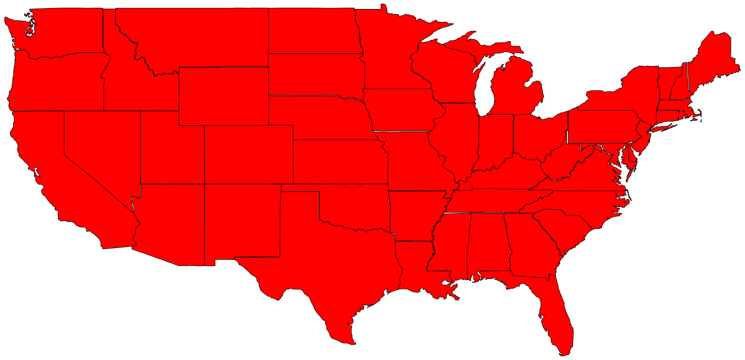
Many volunteers

Hg is toxic to and through fish

Hg is ubiquitous in the environment, but is mostly of concern as CH_3Hg in fish

CH_3Hg is toxic to fish and wildlife/human consumers

Fish consumption advisories for CH_3Hg are common



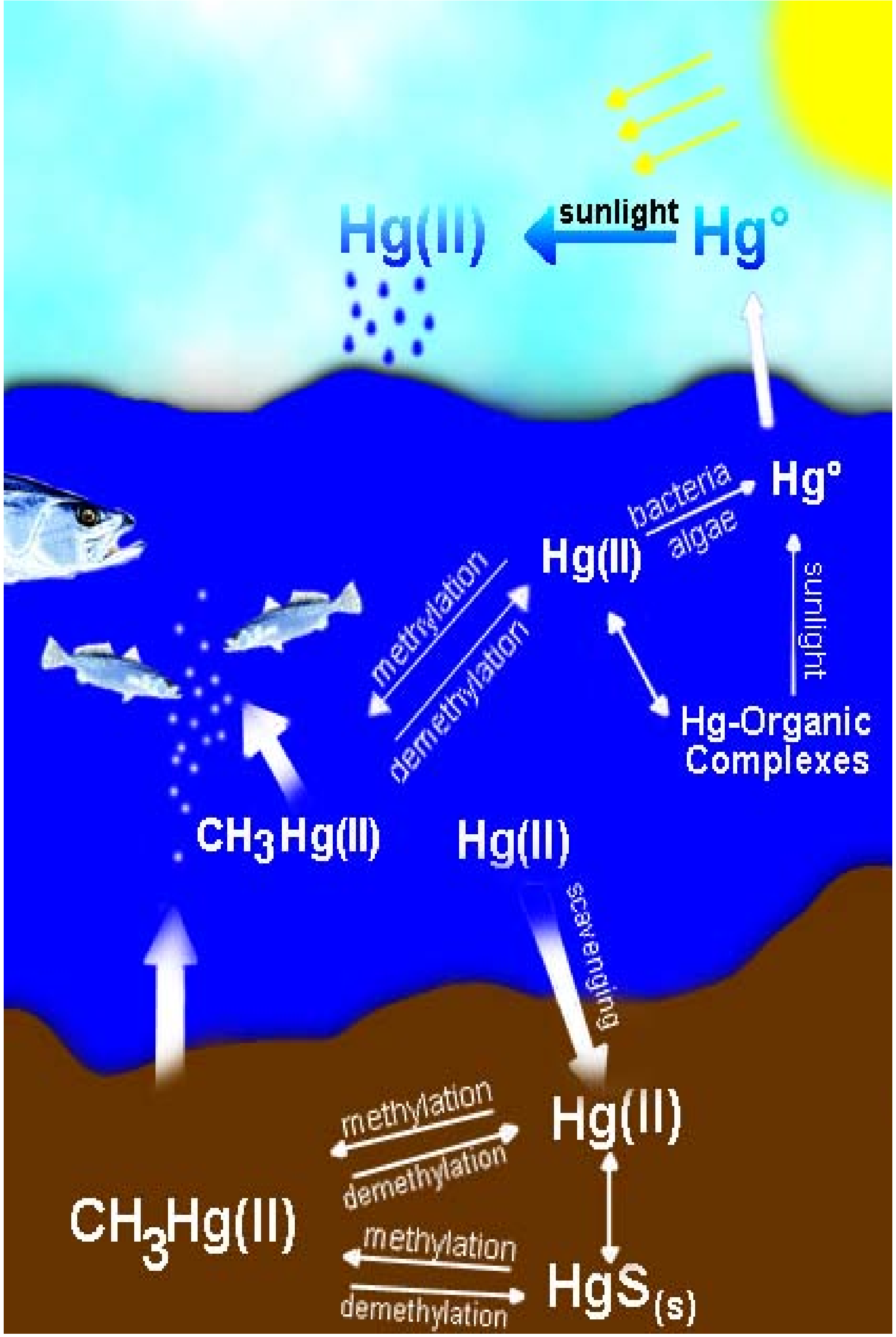
Hg in lakes

Methylation of Hg

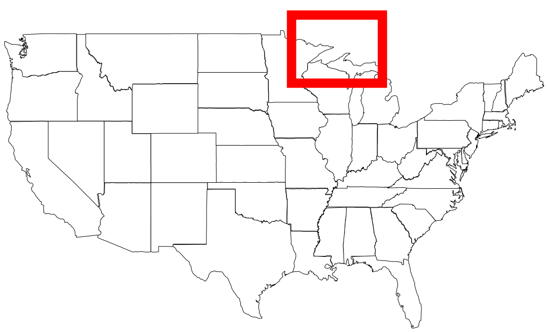
Biomagnification of CH_3Hg

High Hg_T concentrations in fish

Source: loer.tamug.tamu.edu



Isle Royale National Park

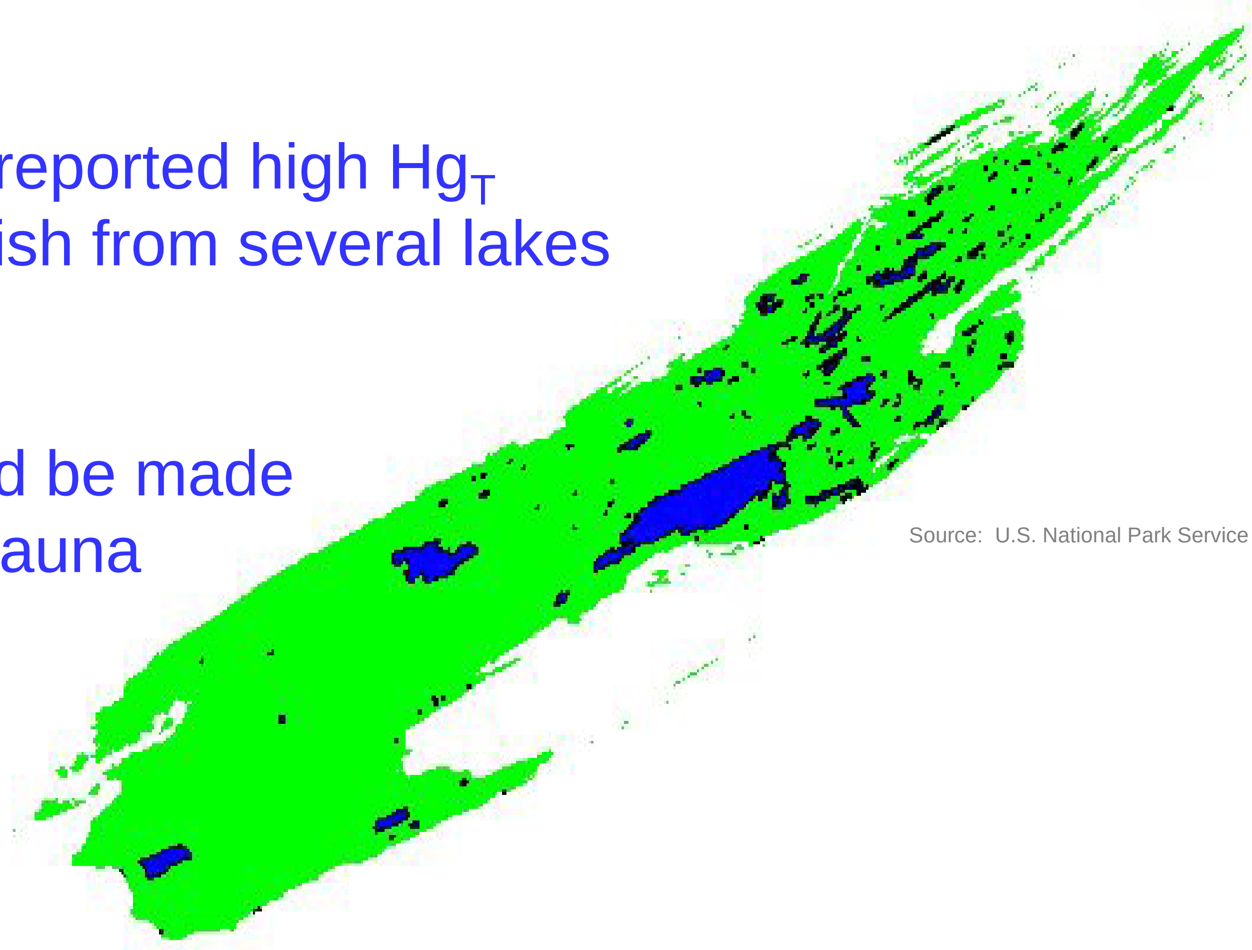


Isle Royale's inland lakes

>40 lakes are renowned as pristine aquatic ecosystems

Kallemeyn (2000) reported high Hg_T concentrations in fish from several lakes

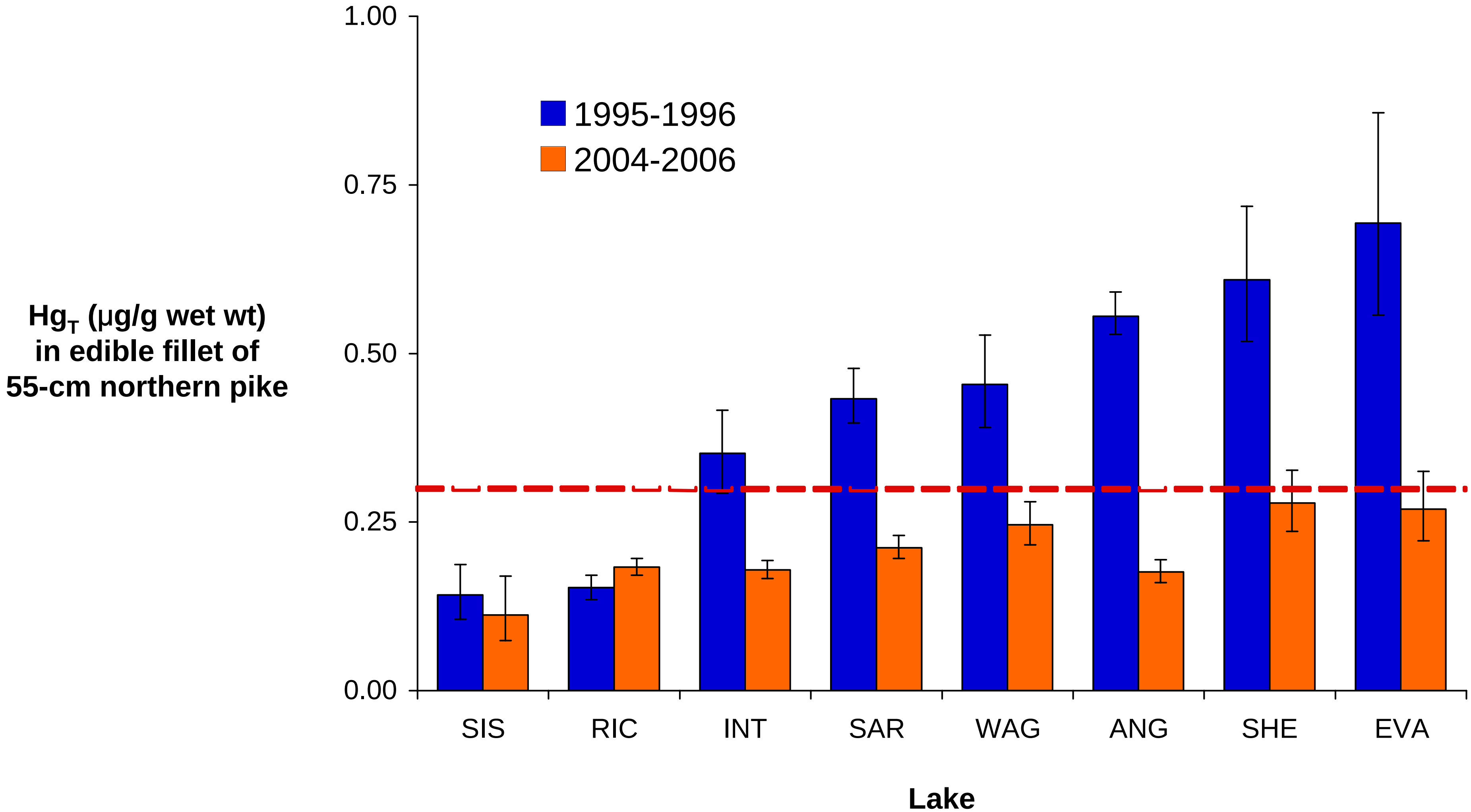
"Every effort should be made to protect the fish fauna of Isle Royale"



Source: U.S. National Park Service

Objective 1

Determine the toxicological effects of CH_3Hg on fishes in inland lakes of Isle Royale National Park



1995-1996
2004-2006
HgT (µg/g wet wt) in edible fillet of 55-cm northern pike
1.00
0.75
0.50
0.25
0.00
SIS
RIC
INT
SAR
WAG
ANG
SHE
EVA
Lake

Objective 1

Determine the toxicological effects of CH_3Hg on fishes in inland lakes of Isle Royale National Park

Objective 2

Determine cause for CH_3Hg decline in northern pike

Hypothesis 1

Atmospheric Hg deposition has declined, reducing the amount of Hg available for methylation

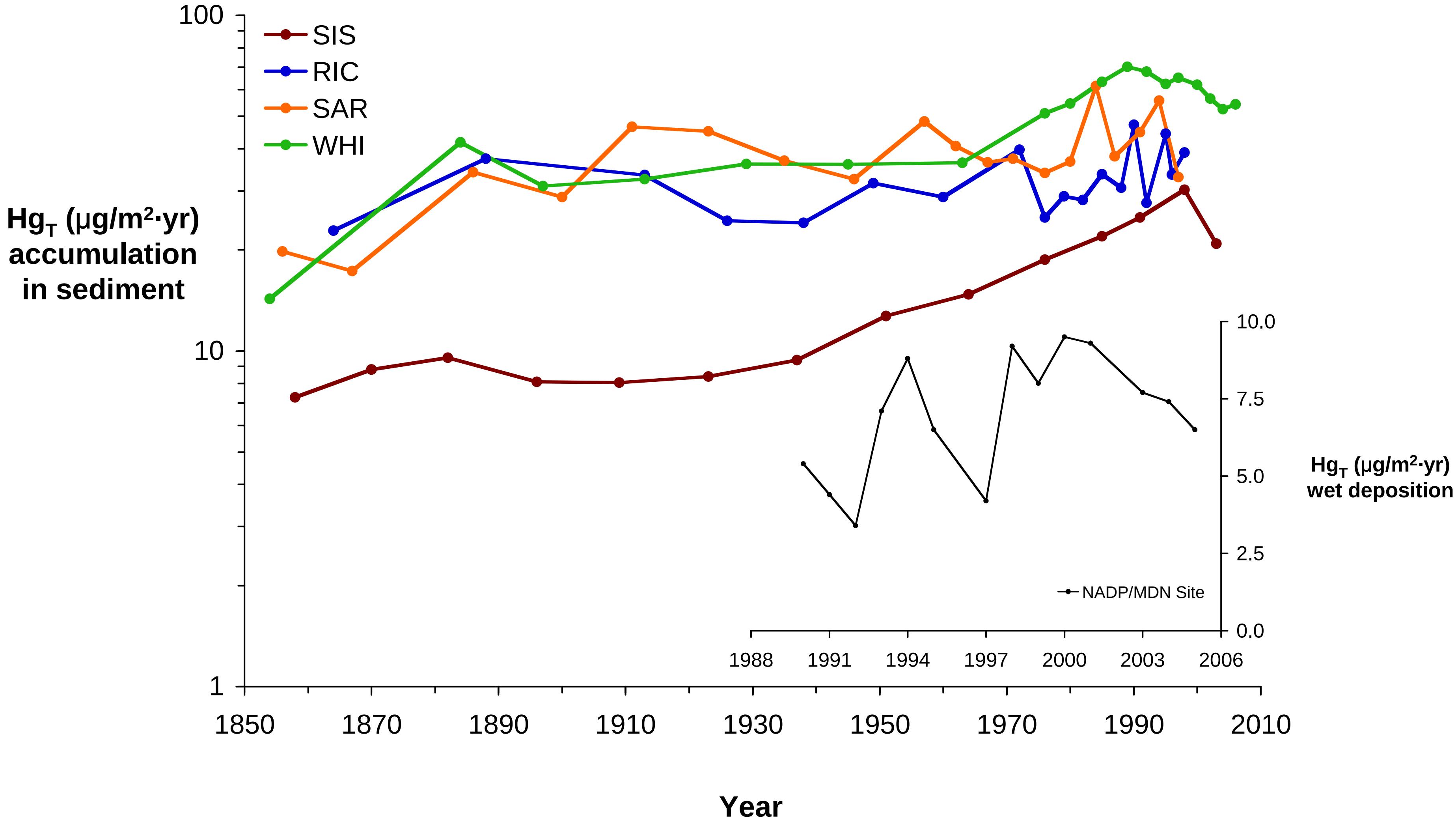
Hypothesis 2

Changes in the ecology of northern pike and/or its underlying food web have occurred, reducing the bioaccumulation and/or biomagnification of methylmercury

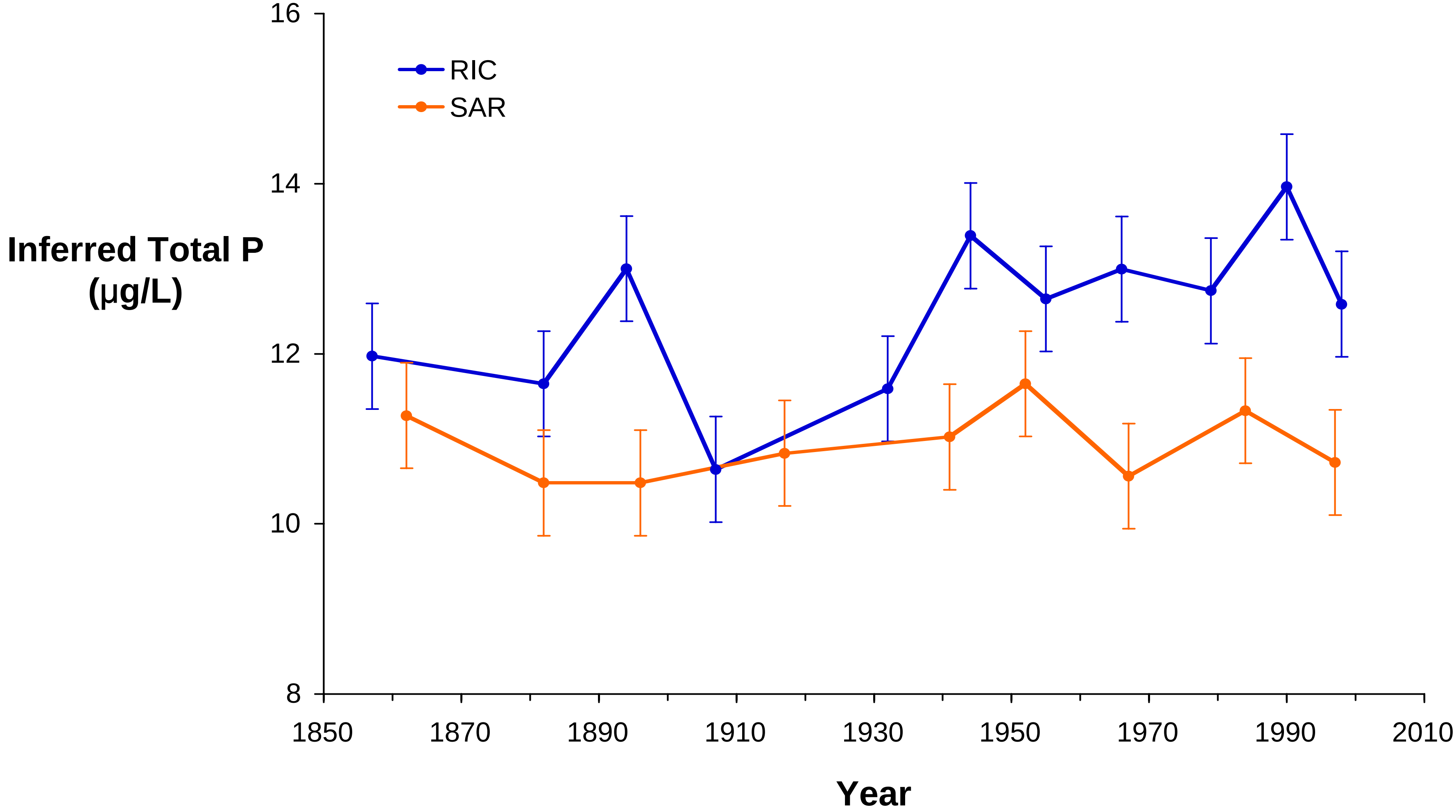
Hypothesis 3

Environmental factors that stimulate net methylation have lessened, reducing the amount of CH_3Hg for bioaccumulation

Atmospheric Hg deposition has not declined



Changes in the ecology of northern pike have not occurred



Changes in the ecology of northern pike have not occurred

Mean (1 SE) stable carbon (δ13C) and nitrogen (δ15N) isotope compositions in edible fillets of northern pike in lakes of Isle Royale

	1905			1929			1998-1999			2004-2006		
Lake	*n*	δ^{13}C (ä)	δ^{15}N (ä)	*n*	δ^{13}C (ä)	δ^{15}N (ä)	*n*	δ^{13}C (ä)	δ^{15}N (ä)	*n*	δ^{13}C (ä)	δ^{15}N (ä)
ANG	.	.	.	3	-25.27 (0.10)	8.47 (0.20)	.	.	.	12	-28.20 (0.22)	9.10 (0.15)
EVA	.	.	.	3	-28.51 (0.51)	9.76 (0.30)	.	.	.	12	-29.59 (0.27)	9.73 (0.11)
INT	.	.	.	3	-24.44 (0.77)	8.84 (0.11)	.	.	.	20	-27.13 (0.12)	10.21 (0.12)
RIC	.	.	.	2	-25.99 (0.36)	9.98 (0.19)	11	-26.06 (0.34)	9.99 (0.14)	16	-26.50 (0.25)	9.70 (0.28)
SAR	1	-24.39 (na)	9.49 (na)	3	-25.97 (0.35)	9.80 (0.32)	14	-27.90 (0.17)	10.29 (0.14)	20	-26.95 (0.14)	10.58 (0.16)
SHE	.	.	.	3	-28.79 (0.16)	8.17 (0.48)	.	.	.	14	-30.92 (0.11)	9.57 (0.08)
SIS	.	.	.	1	-22.02 (na)	8.39 (na)	.	.	.	11	-23.18 (0.50)	8.48 (0.17)
WAG	.	.	.	5	-26.61 (0.29)	8.28 (0.13)	.	.	.	19	-28.63 (0.40)	8.47 (0.12)

Changes in the ecology of northern pike have not occurred

Mean back-calculated total length (cm) of northern pike in lakes of Isle Royale

Kallemeyn (*12*); 1995-1996

			Age (Years)											total length = a + b Ln(age)		
Lake	Sex	*n*	1	2	3	4	5	6	7	8	9	10	11	a	b	r^2
ANG	F	16	18.1	36.4	48.4	53.1	56.9	60.2	65.3	.	.	.	.	19.606	23.595	0.991
	M	11	17.5	34.6	46.9	52.4	55.4	56.9	.	.	.	.	.	18.925	22.822	0.981
EVA	F	5	20.1	31.1	43.0	50.3	52.6	.	.	.	.	.	.	18.995	21.332	0.984
	M	2	18.2	32.4	42.4	47.9	.	.	.	.	.	.	.	18.007	21.671	0.998
INT	F	24	19.9	35.9	46.4	52.2	54.8	55.3	.	.	.	.	.	21.373	20.711	0.977
	M	21	21.0	36.6	46.3	50.0	52.4	53.5	54.7	.	.	.	.	23.651	17.471	0.960
RIC	F	39	20.8	34.5	42.9	51.1	56.1	64.7	.	.	.	.	.	19.083	23.650	0.983
	M	23	19.4	32.2	42.8	50.5	52.7	.	.	.	.	.	.	18.797	21.643	0.991
SAR	F	50	20.9	38.9	49.4	53.7	56.5	58.2	59.8	.	.	.	.	23.813	20.024	0.967
	M	27	19.6	36.3	46.5	51.5	53.7	55.7	54.5	54.2	.	.	.	23.722	17.184	0.919
SHE	F	2	17.8	30.3	42.2	49.3	52.4	53.4	.	.	.	.	.	17.610	21.240	0.984
	M	3	14.2	27.2	38.4	47.1	51.5	53.7	.	.	.	.	.	13.246	23.198	0.991
SIS	F	3	22.0	41.4	53.0	65.6	73.0	74.6	79.9	82.9	93.7	95.9	98.3	19.997	32.015	0.990
	M	2	22.0	37.9	58.7	63.9	68.6	.	.	.	.	.	.	20.987	30.531	0.975
WAG	F	10	18.5	32.8	42.8	47.0	48.6	50.2	50.1	.	.	.	.	20.921	16.839	0.954
	M	7	16.3	32.1	41.5	44.6	46.5	46.3	47.2	48.2	.	.	.	20.519	14.951	0.913

Drevnick et al.; 2004-2006

			Age (Years)											total length = a + b Ln(age)		
Lake	Sex	*n*	1	2	3	4	5	6	7	8	9	10	11	a	b	r^2
ANG	F	7	19.4	34.3	42.7	51.9	56.3	60.4	63.7	67.9	.	.	.	18.627	23.356	0.997
	M	5	18.4	32.3	41.7	51.3	57.2	59.7	61.6	62.9	.	.	.	18.052	22.685	0.988
EVA	F	8	21.5	32.3	40.4	46.5	51.5	54.3	58.7	.	.	.	.	19.142	20.302	0.995
	M	4	21.0	31.1	37.4	43.5	50.5	54.0	.	.	.	.	.	19.270	18.523	0.980
INT	F	13	20.9	35.8	43.3	49.4	52.9	55.2	57.3	59.3	62.3	.	.	22.413	18.329	0.993
	M	7	21.0	36.1	43.2	47.8	51.6	54.6	57.2	63.6	65.0	66.0	66.5	21.581	19.145	0.993
RIC	F	13	19.7	34.5	44.0	49.9	54.9	59.5	64.9	.	.	.	.	19.068	22.756	0.997
	M	3	19.1	34.1	42.2	47.6	.	.	.	.	.	.	.	19.364	20.615	0.999
SAR	F	13	22.4	38.2	45.4	49.3	53.3	56.5	59.1	61.3	63.5	.	.	24.105	18.118	0.994
	M	6	21.0	34.7	43.6	46.9	52.0	53.7	55.8	.	.	.	.	21.988	18.031	0.992
SHE	F	10	19.2	32.5	42.3	48.7	53.3	55.8	.	.	.	.	.	18.880	21.040	0.998
	M	4	16.6	30.3	41.5	46.4	50.5	52.9	.	.	.	.	.	16.801	20.991	0.994
SIS	F	9	23.0	40.1	52.8	63.7	69.4	74.2	80.7	83.4	.	.	.	21.371	29.824	0.996
	M	2	23.2	38.3	48.2	56.3	.	.	.	.	.	.	.	22.712	23.664	0.997
WAG	F	11	19.5	33.5	43.3	49.3	53.4	58.3	59.5	.	.	.	.	19.505	21.140	0.998
	M	5	19.6	31.4	40.1	46.6	51.5	54.6	59.0	.	.	.	.	18.528	20.311	0.997

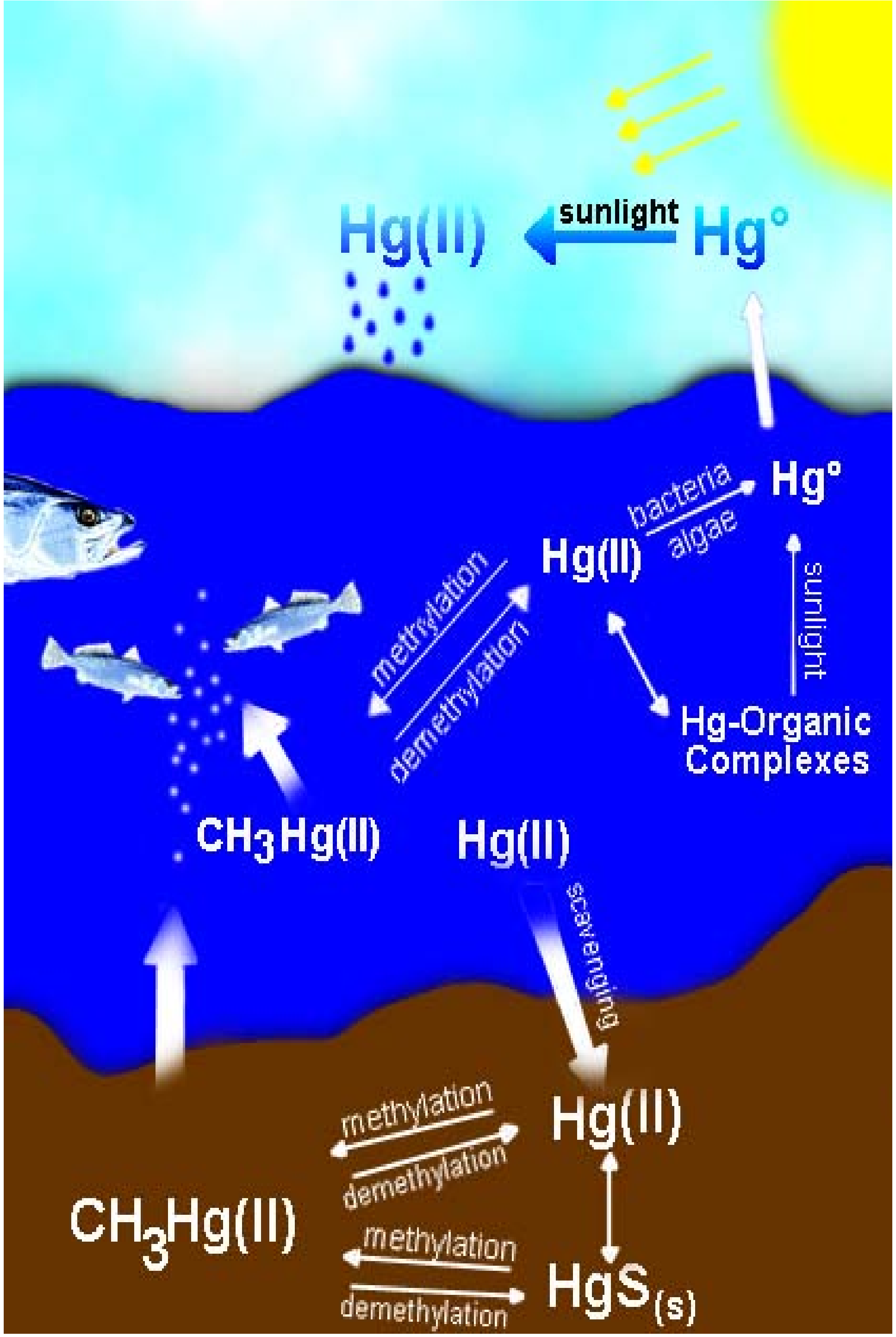
Environmental factors: SO_4

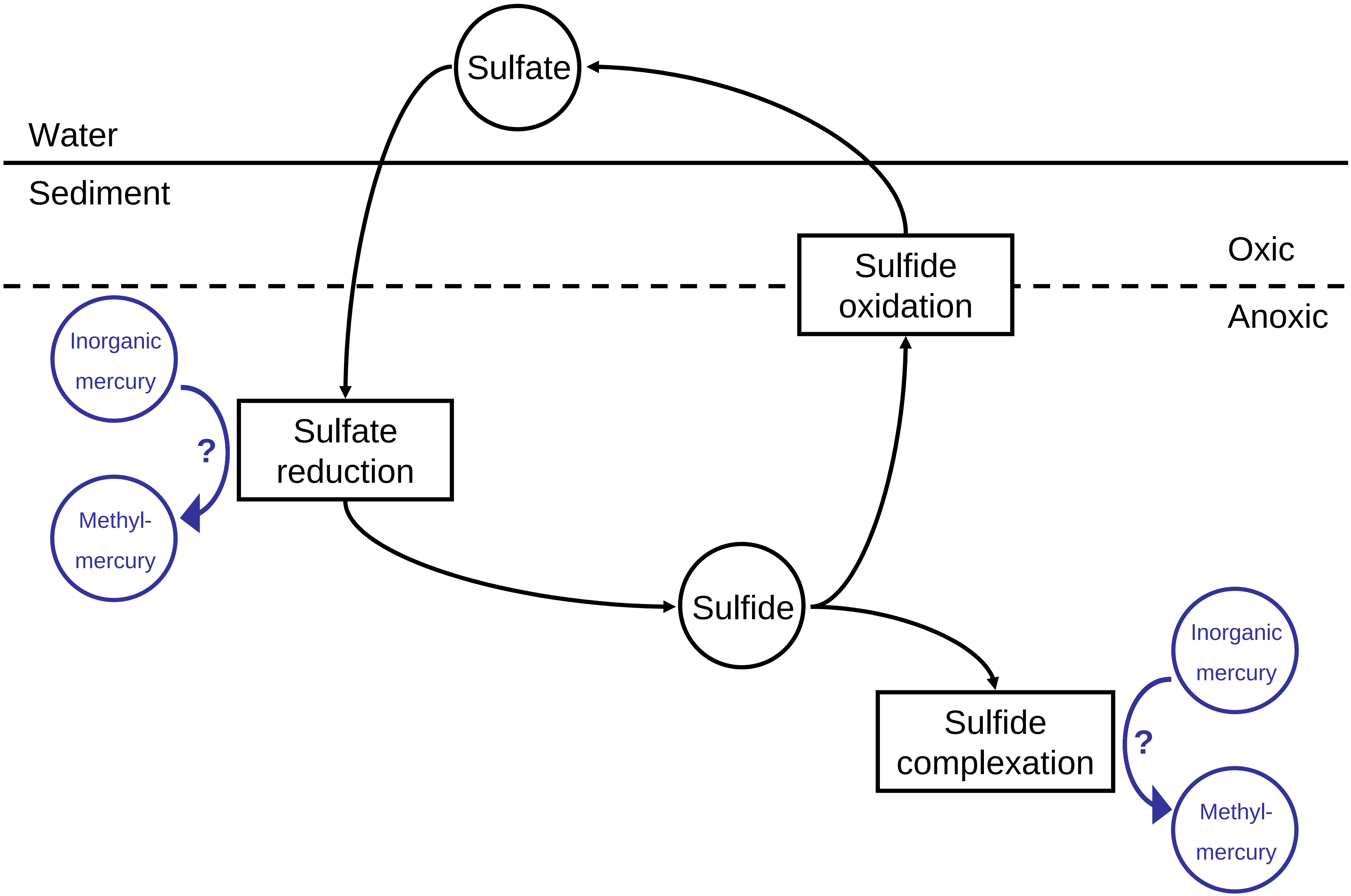
Methylation of Hg is dependent on $[SO_4]$

SO_4 addition experiments:

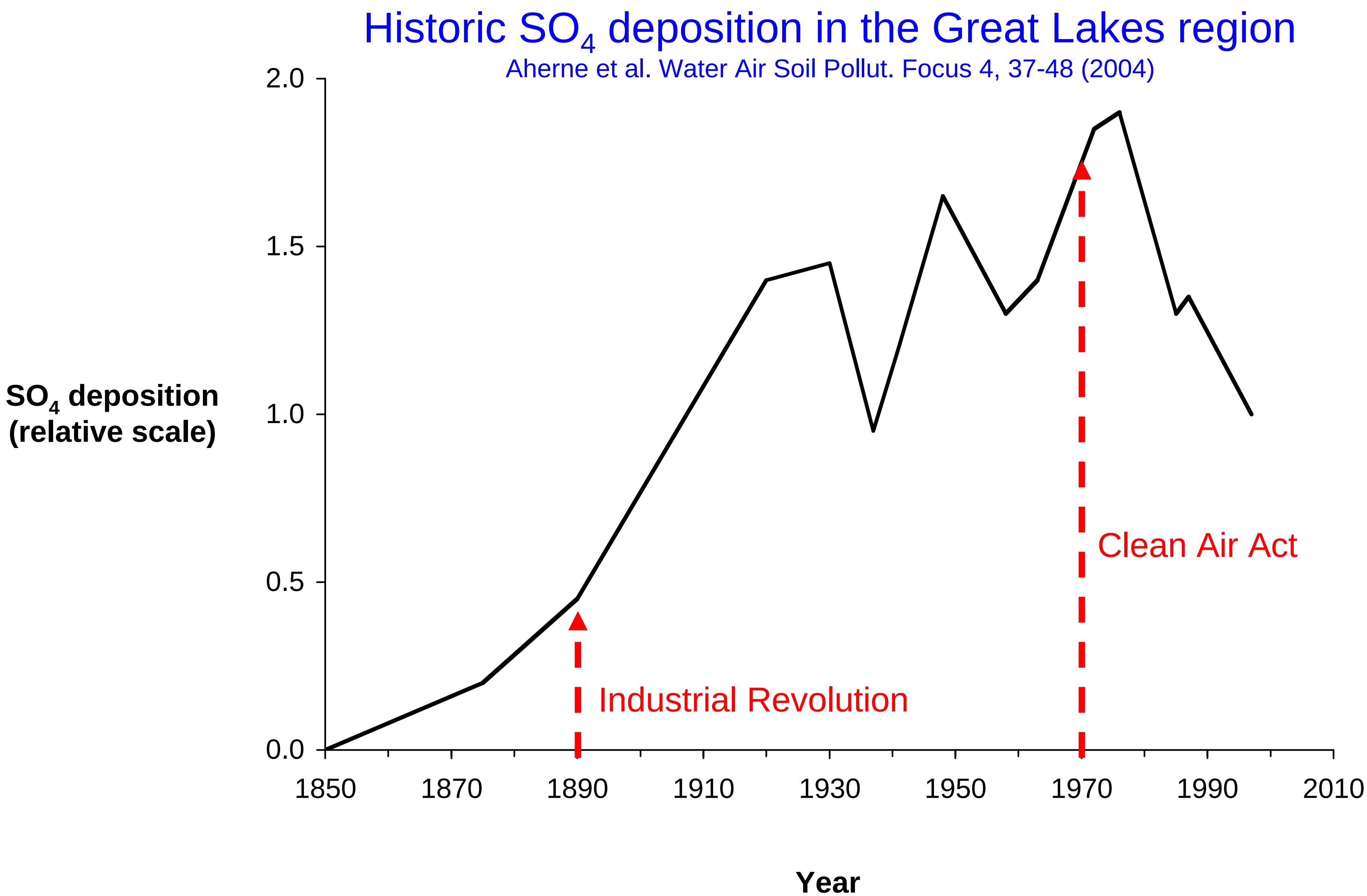
- Intact sediment cores
- Wetland mesocosms
- Whole lake

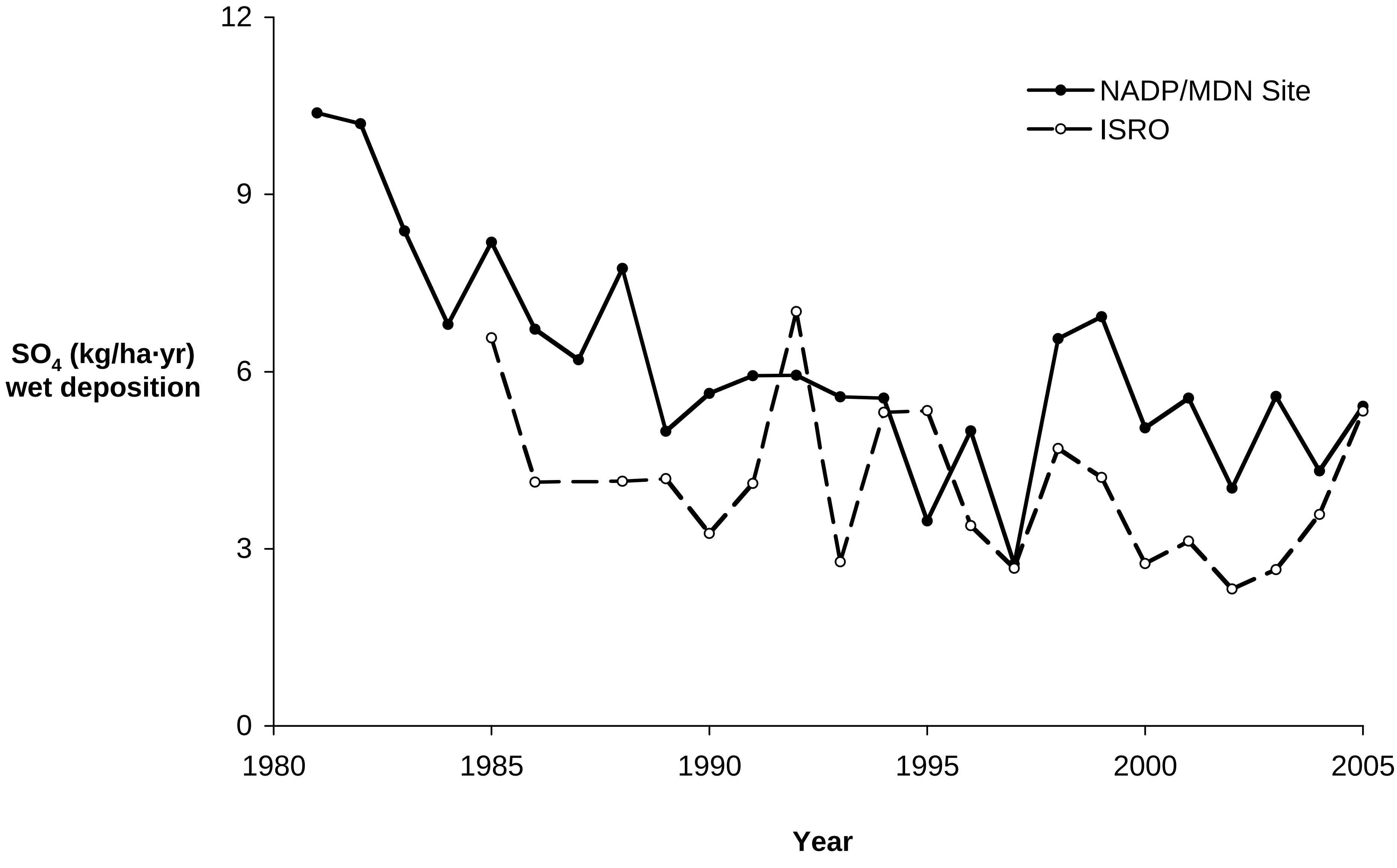
Source: loer.tamug.tamu.edu




Sulfate
Water
Sediment
Oxic
Anoxic
Sulfide oxidation
Inorganic mercury
?
Methyl- mercury
Sulfate reduction
Sulfide
Sulfide complexation
Inorganic mercury
?
Methyl- mercury

SO_4 is a primary component of acid rain





12
9
6
3
0
SO4 (kg/ha·yr)
wet deposition
1980
1985
1990
1995
2000
2005
Year
NADP/MDN Site
ISRO

SO_4 in inland lakes of Isle Royale National Park

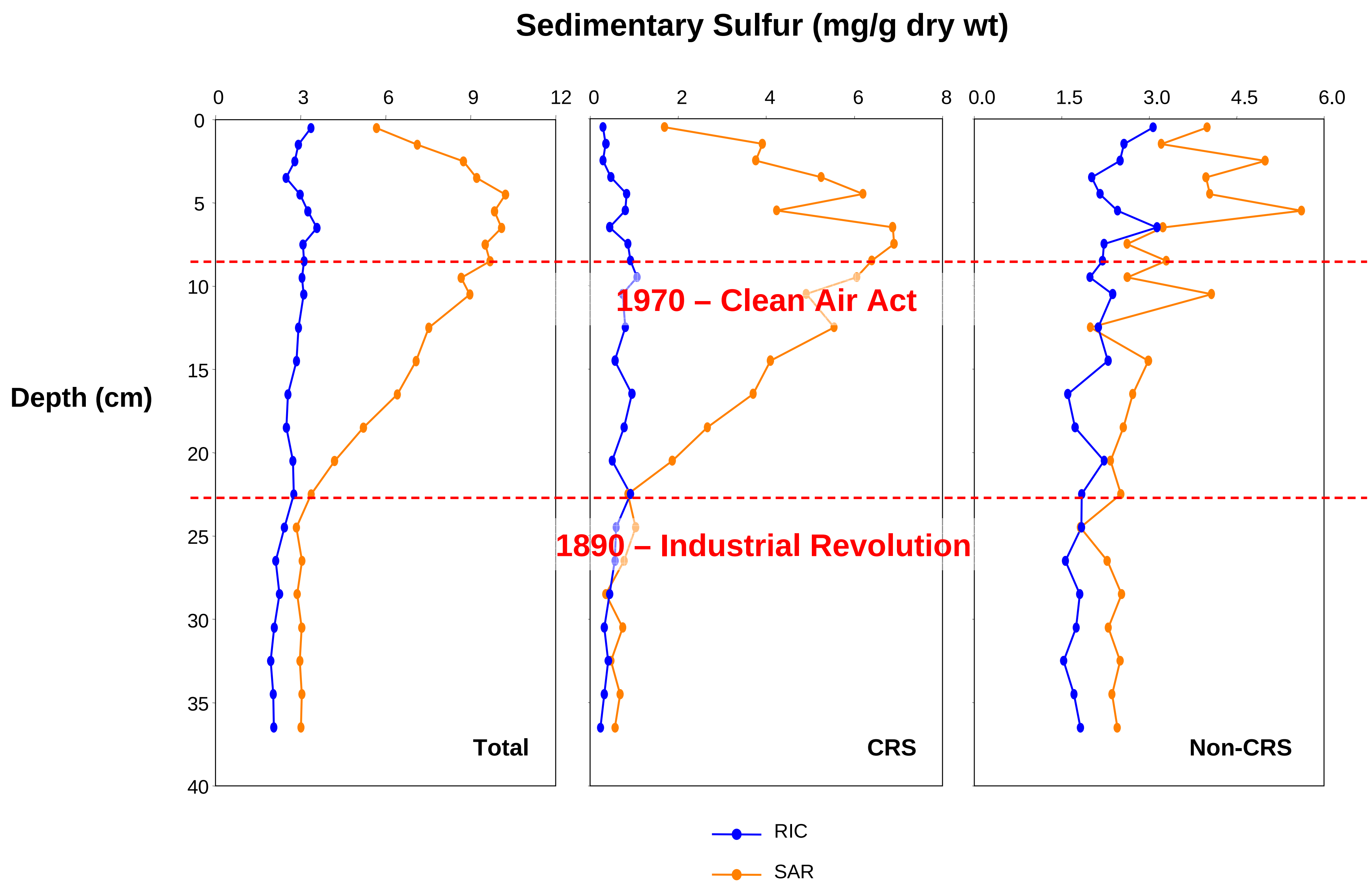
Lake	SO_4 concentration (µM) 1980-1981	1995-1996	2006
AHM	.	21	
AMY	52	26	
ANG	64	32	
BEA	.	34	
BEN	.	23	
CHI	49	31	
DES	45	27	
DUS	48	31	
EPI	45	15	
EVA	.	22	
FEL	.	33	
FOR	46	15	
GEO	39	24	
HAL	49	18	
HAR	.	28	
HAT	46	24	
INT	66	31	12
JOH	62	19	
LES	.	30	
LIN	.	28	
LIV	44	31	
MAS	.	33	
MCD	.	35	
NEW	34	.	
OTT	.	29	
PAT	.	12	
RIC	59	34	17
SAR	.	34	
SCH	52	28	
SHE	.	18	
SIS	.	47	35
THE	27	.	
WAG	.	35	
WHI	48	28	24

Hypothesis

Declines in SO_4 deposition have inhibited SO_4 reduction, resulting in less methylation of Hg and thus less CH_3Hg bioaccumulation into fish

Hypothesis Test

Reconstruct the history of SO_4 reduction by exploring sulfur concentrations in sediment profiles



Sedimentary Sulfur (mg/g dry wt)
Depth (cm)
0
3
6
9
12
0
2
4
6
8
0.0
1.5
3.0
4.5
6.0
0
5
10
15
20
25
30
35
40
1970 – Clean Air Act
1890 – Industrial Revolution
Total
CRS
Non-CRS
RIC
SAR

Hypothesis

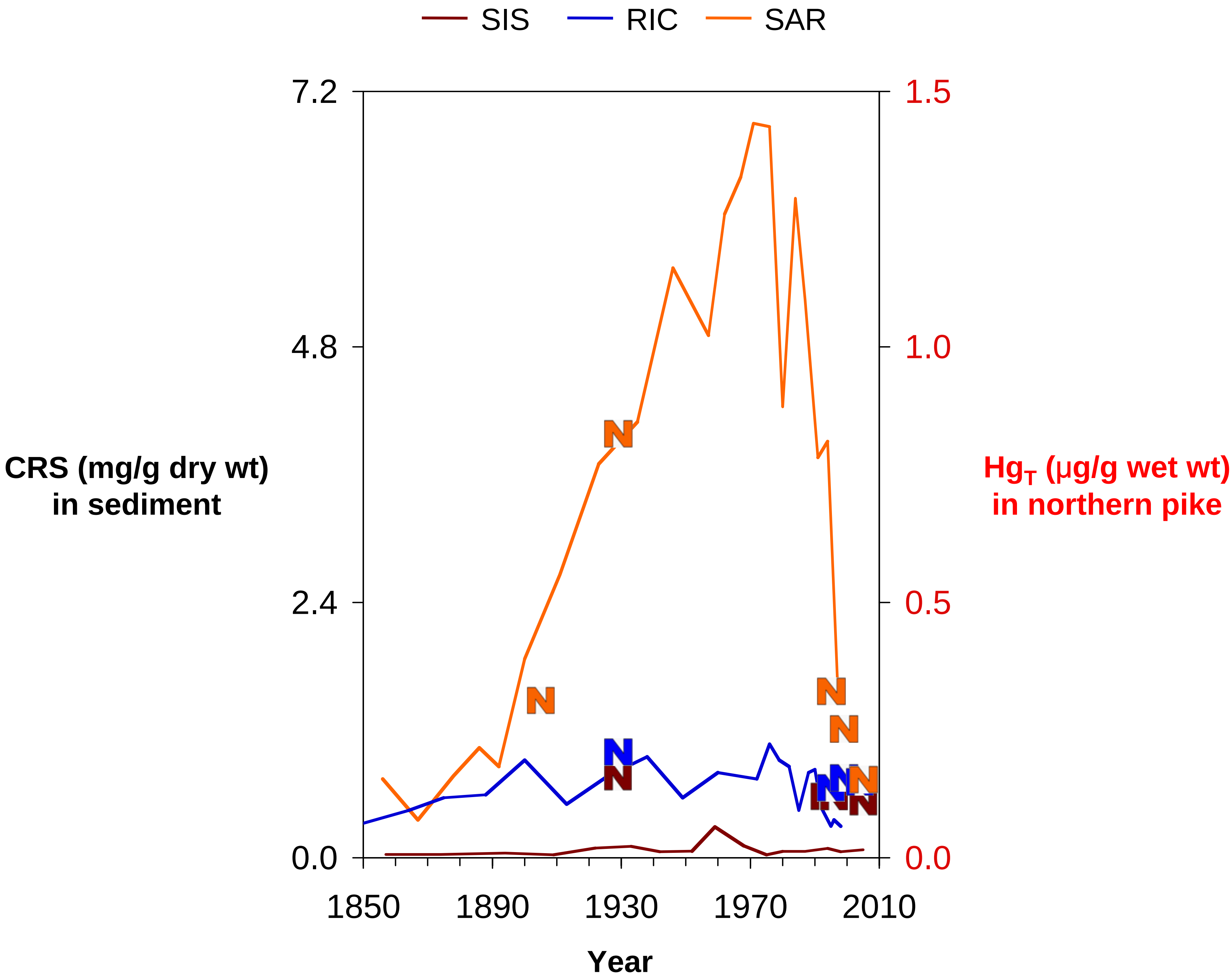
CH_3Hg bioaccumulation in fish primarily a function of SO_4 deposition and SO_4 reduction during past century

Hypothesis Test

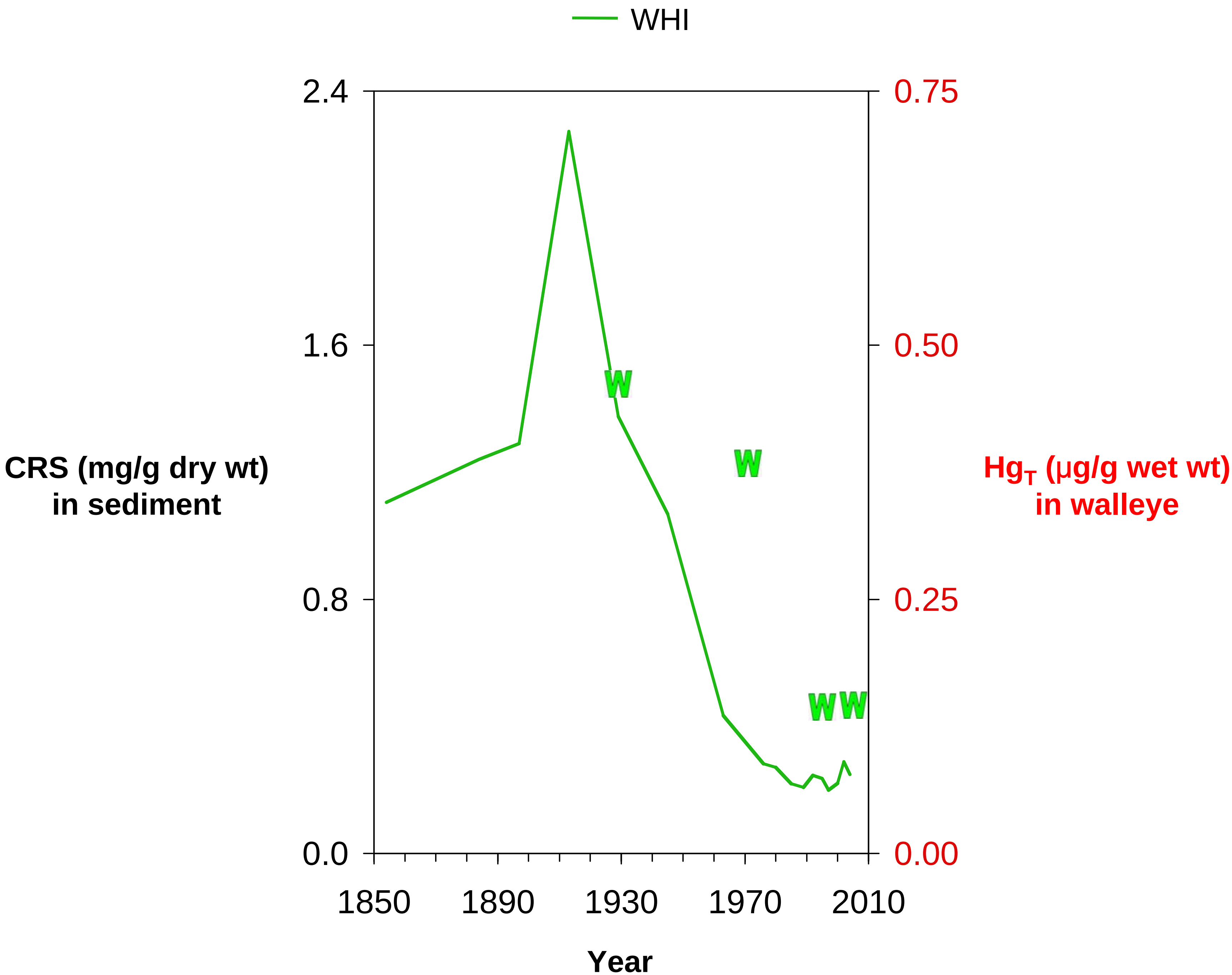
Compare Hg_T in fish to time-equivalent CRS in sediment

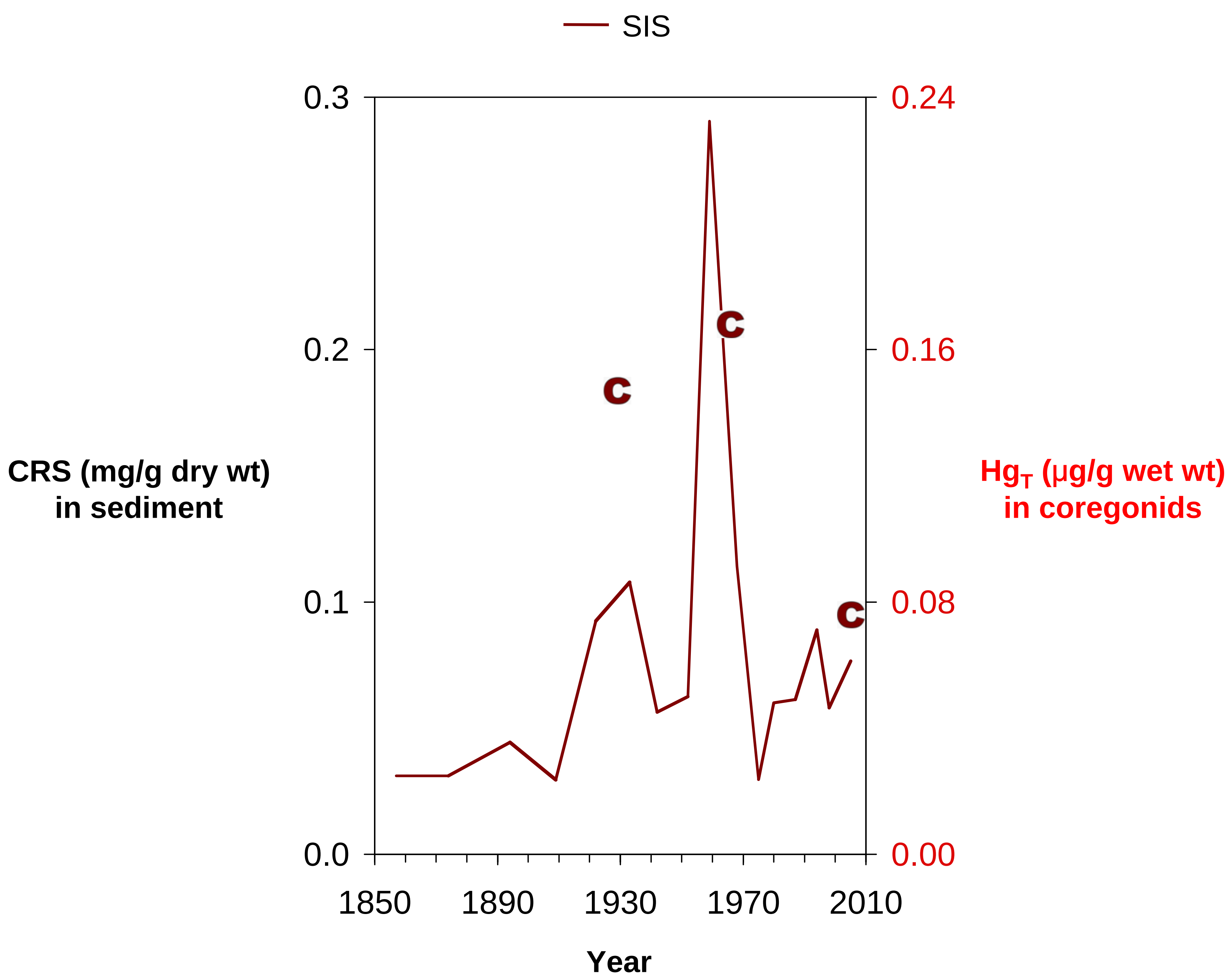

We·no·nah


Tank 22A
103011
lucius
Sargent Lake
Isle Royale
Gelson and Mc Creary
VII:16:1905



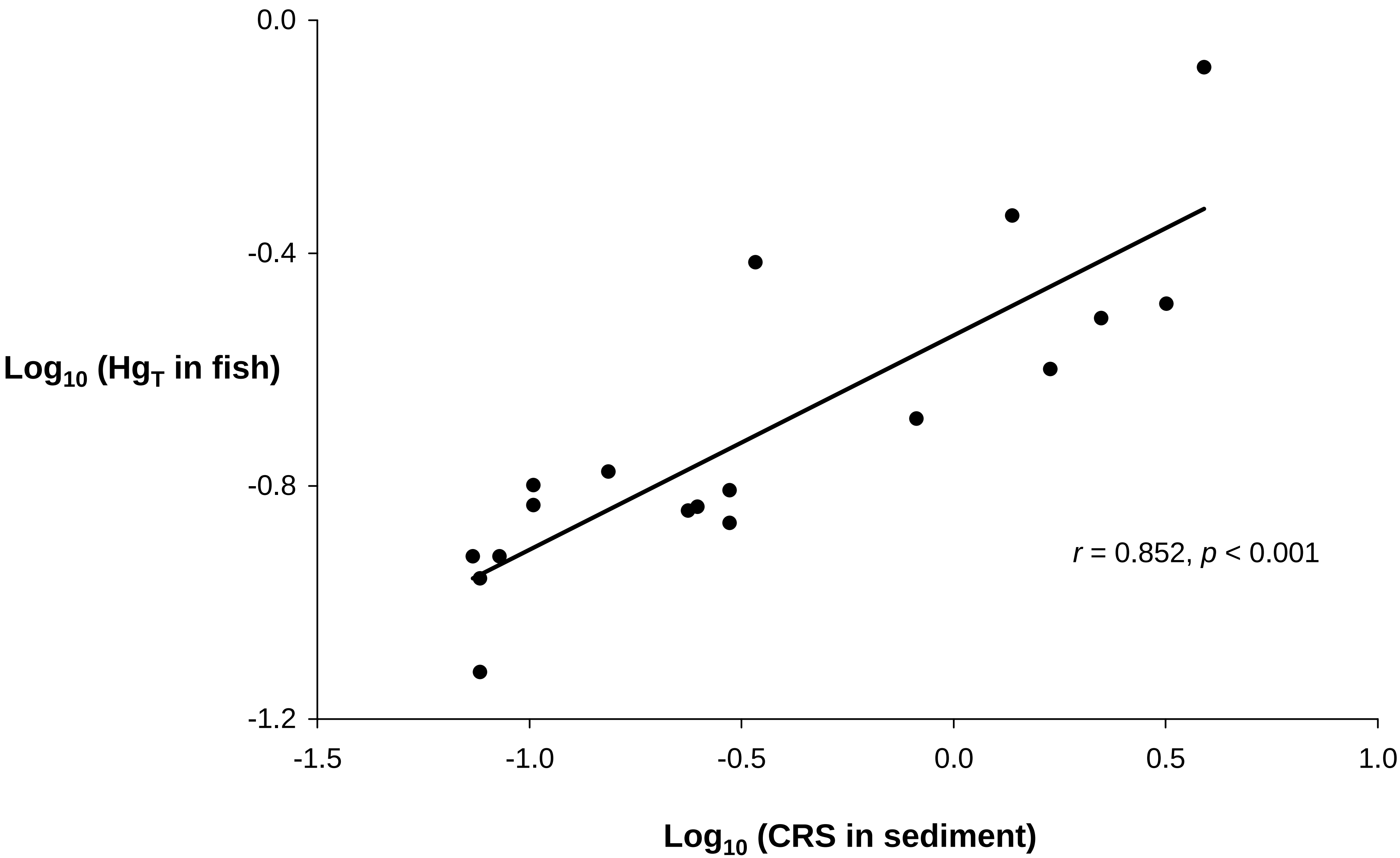
SIS
RIC
SAR
7.2
4.8
2.4
0.0
1.5
1.0
0.5
0.0
CRS (mg/g dry wt) in sediment
Hg_T (μg/g wet wt) in northern pike
1850
1890
1930
1970
2010
Year


WHI
2.4
1.6
0.8
0.0
0.75
0.50
0.25
0.00
CRS (mg/g dry wt) in sediment
Hg_T (μg/g wet wt) in walleye
W
W
W
W
1850
1890
1930
1970
2010
Year

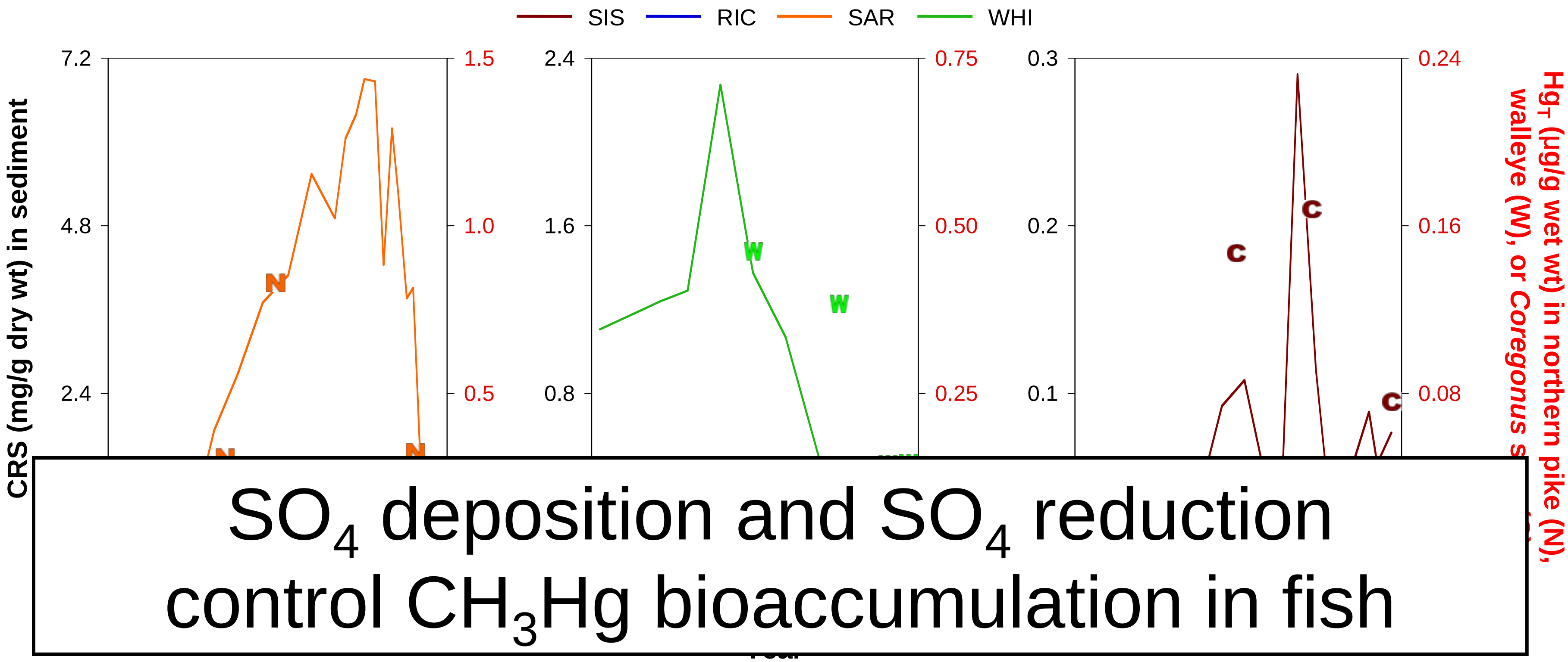


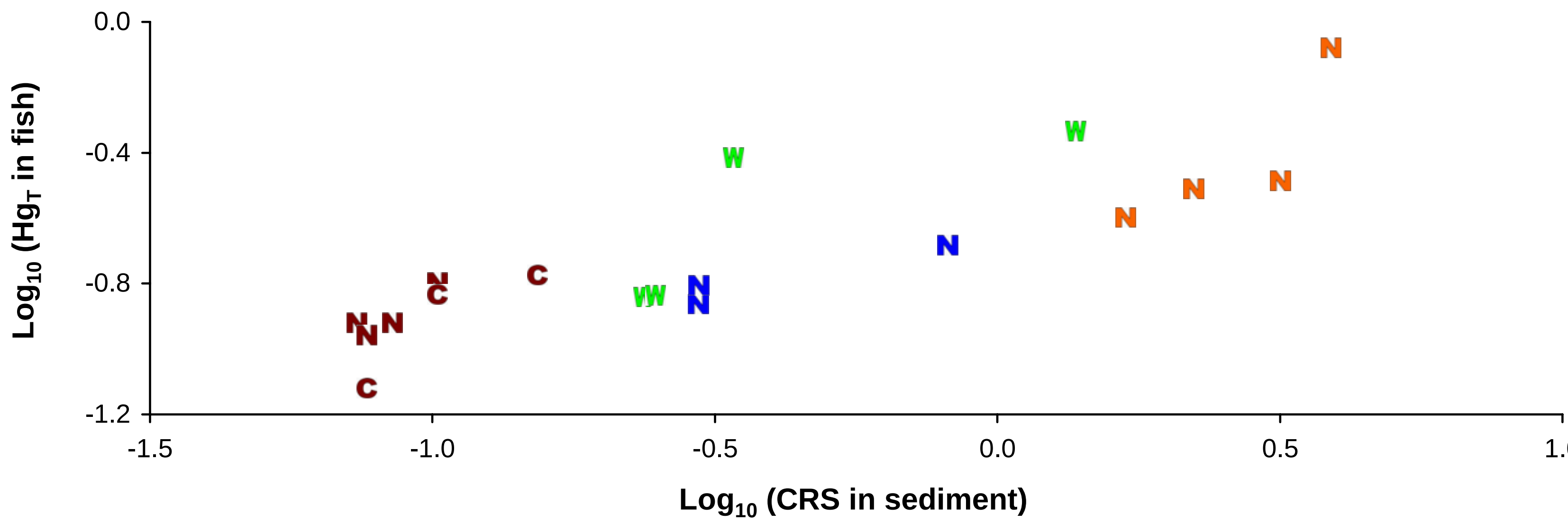
SIS
0.3
0.2
0.1
0.0
0.24
0.16
0.08
0.00
CRS (mg/g dry wt)
in sediment
Hg$_T$ (µg/g wet wt)
in coregonids
c
c
c
1850
1890
1930
1970
2010
Year

SO_4 deposition and SO_4 reduction control CH_3Hg bioaccumulation in fish



SO_4 deposition and SO_4 reduction control CH_3Hg bioaccumulation in fish





Conclusions

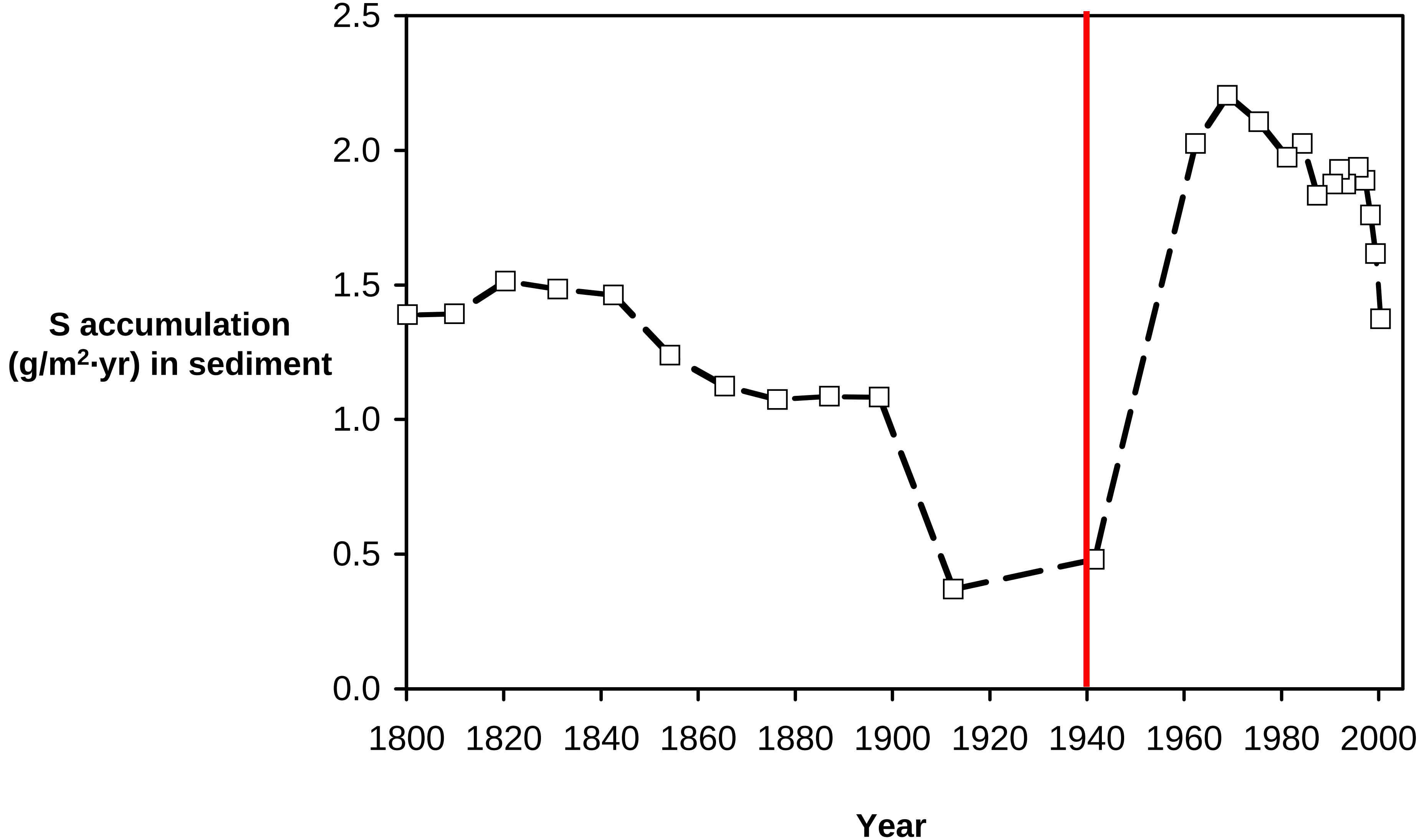
Reductions in CH_3Hg possible without reductions in Hg

Reductions in CH_3Hg possible with reductions in SO_4

To solve Hg problem in SO_4-limited lakes:

Local: Don’t unnecessarily add SO_4 (e.g., $CuSO_4$)

Houghton Lake, MI: $CuSO_4$ additions



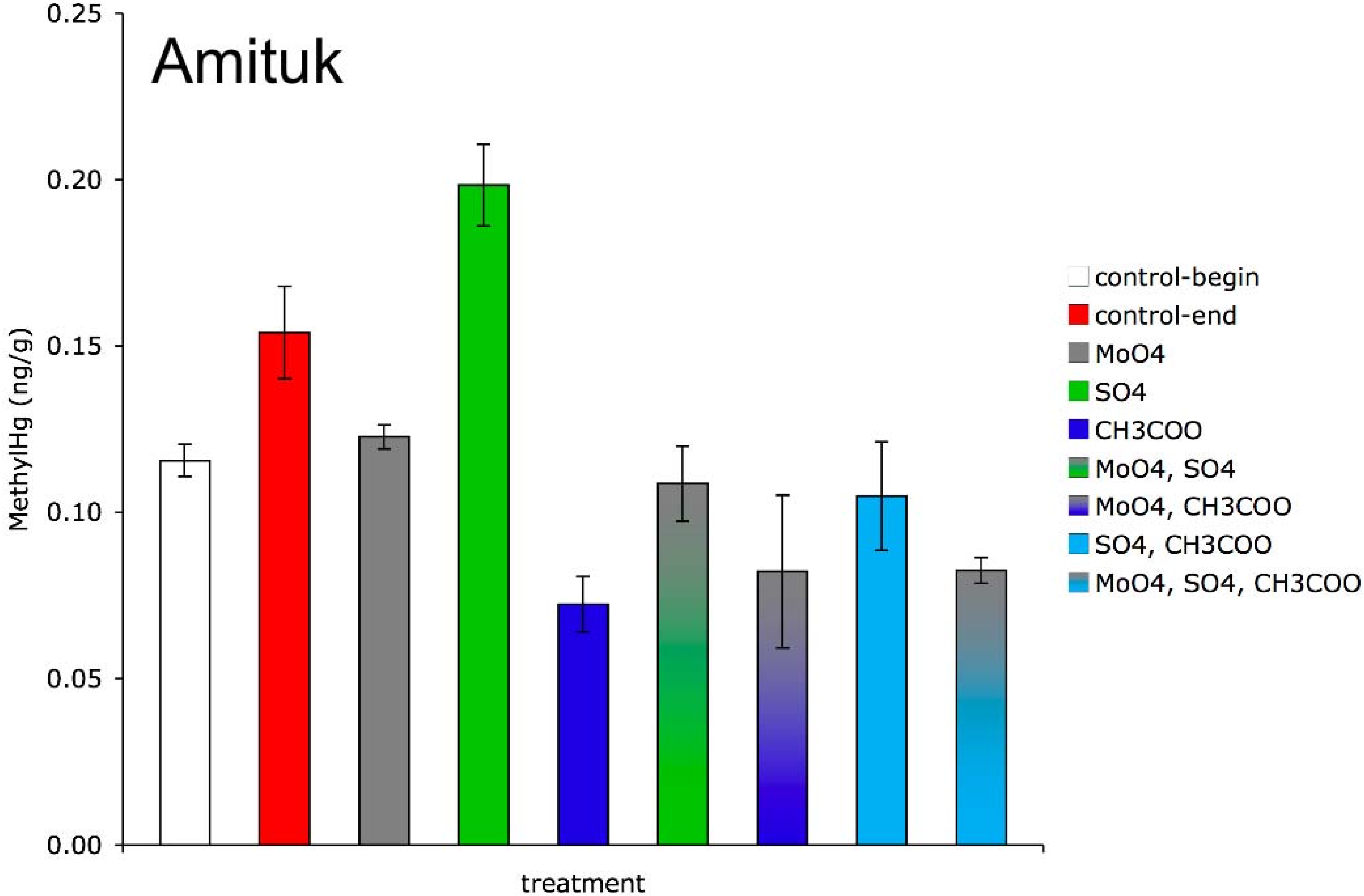
Conclusions

Reductions in CH_3Hg possible without reductions in Hg

Reductions in CH_3Hg possible with reductions in SO_4

To solve Hg problem in SO_4-limited lakes:

- Local: Don't unnecessarily add SO_4 (e.g., $CuSO_4$)
- Regional: Continue existing acid rain programs
- Global: Don't add SO_2 to atmosphere to slow climate change


Amituk
0.25
0.20
0.15
0.10
0.05
0.00
MethylHg (ng/g)
treatment
control-begin
control-end
MoO4
SO4
CH3COO
MoO4, SO4
MoO4, CH3COO
SO4, CH3COO
MoO4, SO4, CH3COO

[redacted]