

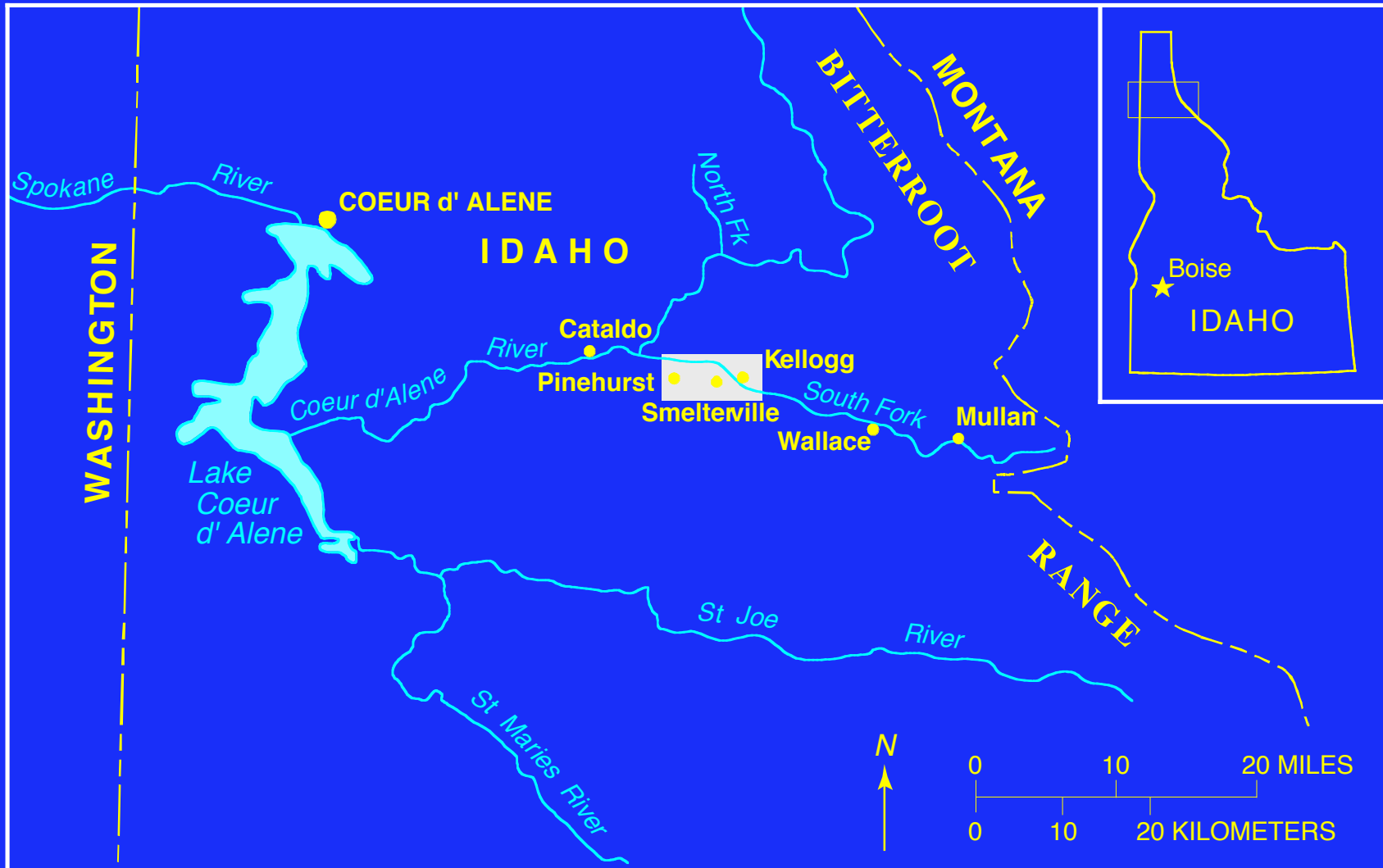
The Impact of Mining and Related Activities on the Sediment Chemistry of Lake Coeur d' Alene and the Spokane River System

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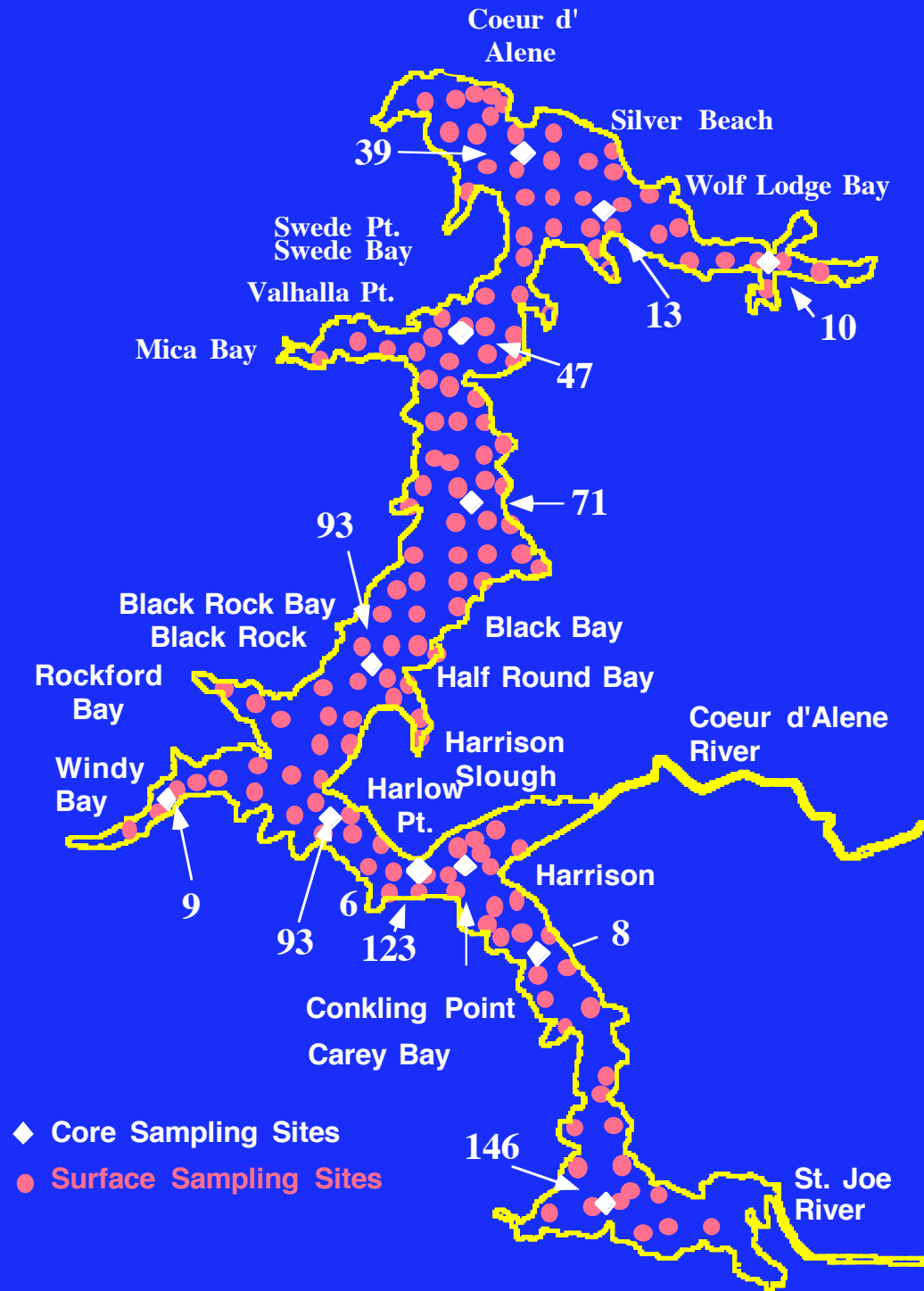
**TESNAR Workshop
Odanah, WI
September 12 - 14, 2011**

The Coeur d'Alene River Basin

General Location Map for the Coeur d'Alene Lake Study

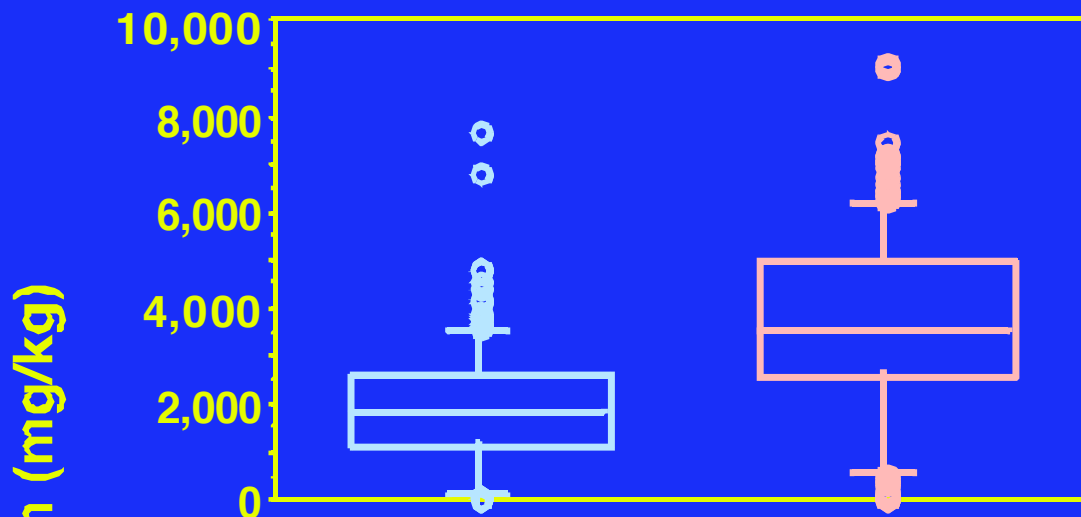


Sampling Locations in Lake Coeur d'Alene

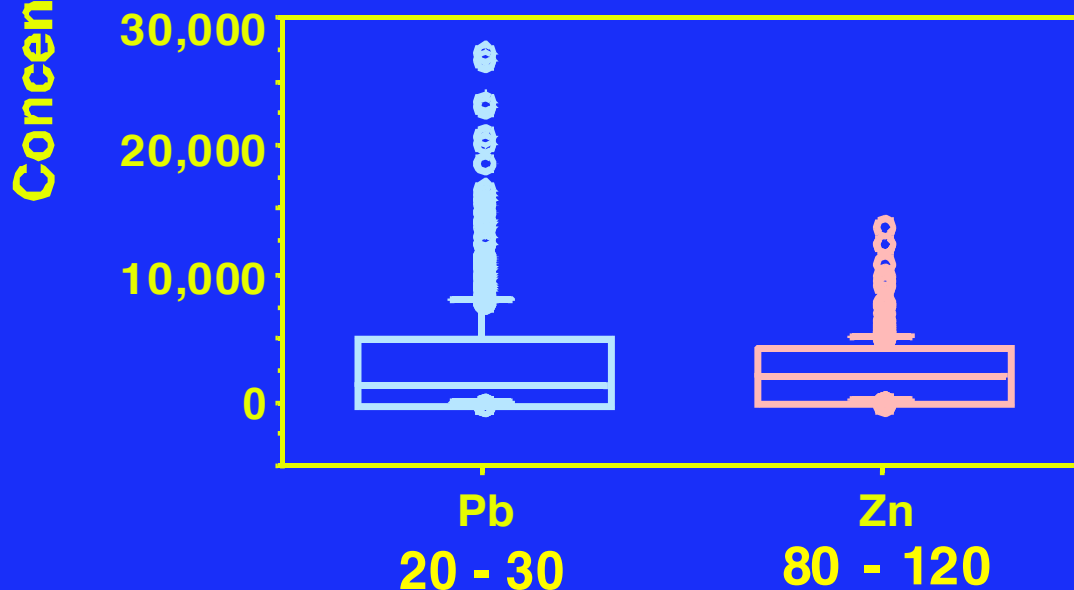


Box plots of Selected Sediment-Associated Trace Element Data from Lake Coeur d'Alene

Surface Sediments

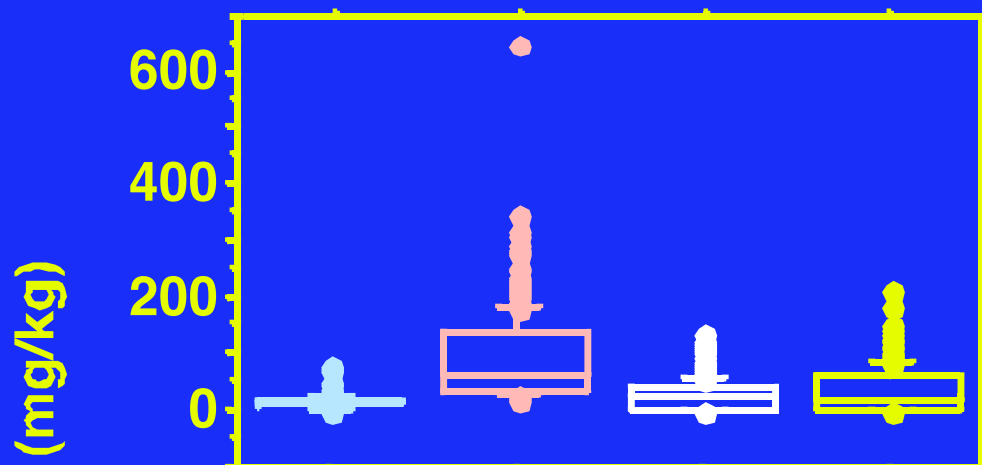


Subsurface Sediments

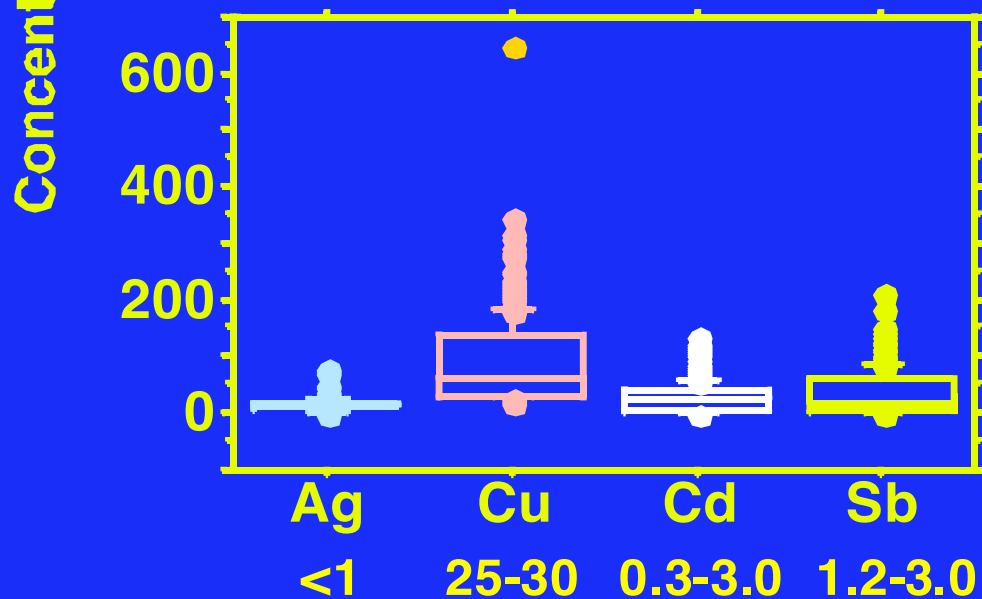


Box plots of Selected Sediment-Associated Trace Element Data from Lake Coeur d'Alene

Surface Sediments

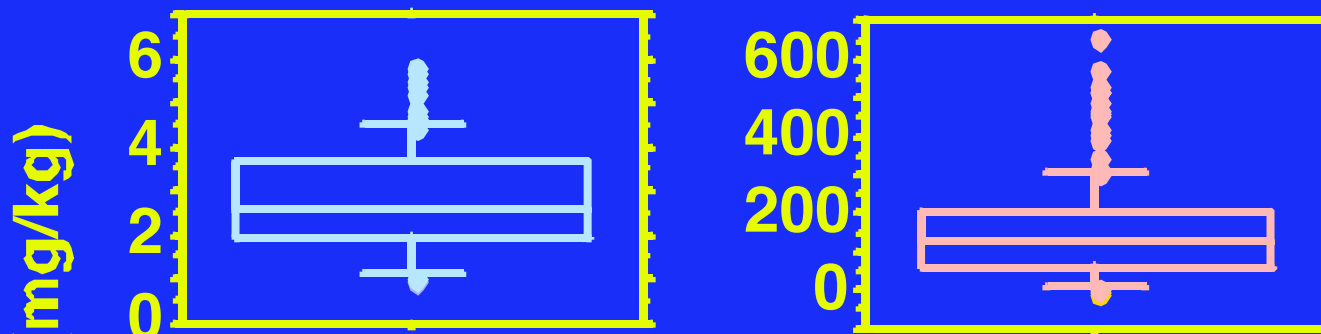


Subsurface Sediments

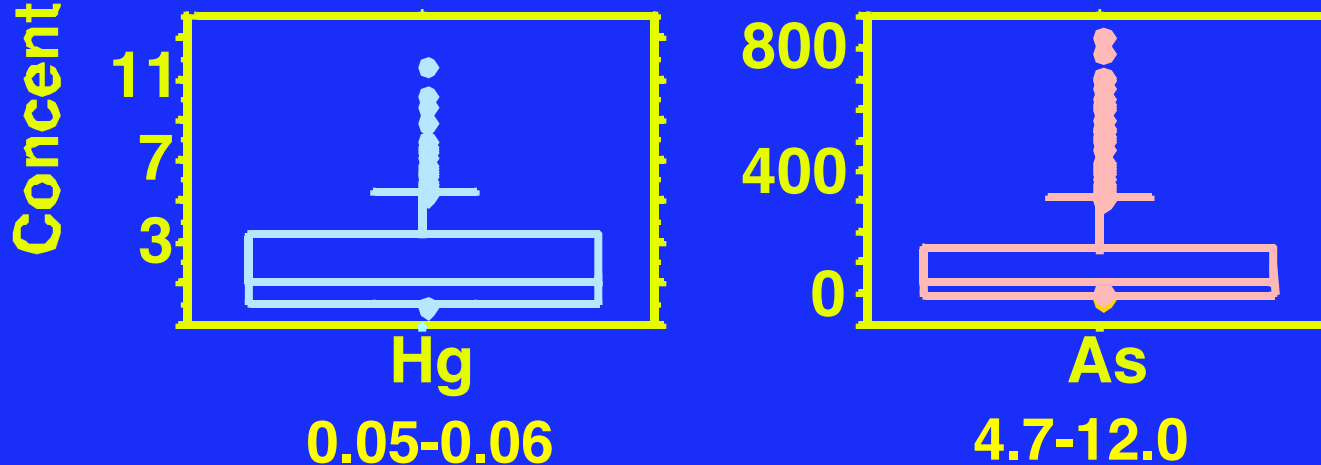


Box plots of Selected Sediment-Associated Trace Element Data from Lake Coeur d'Alene

Surface Sediments

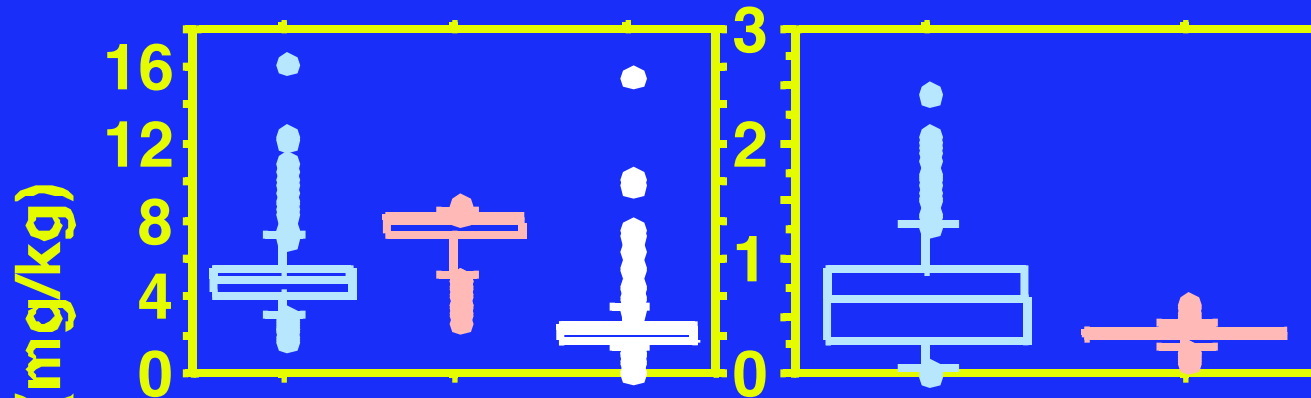


Subsurface Sediments

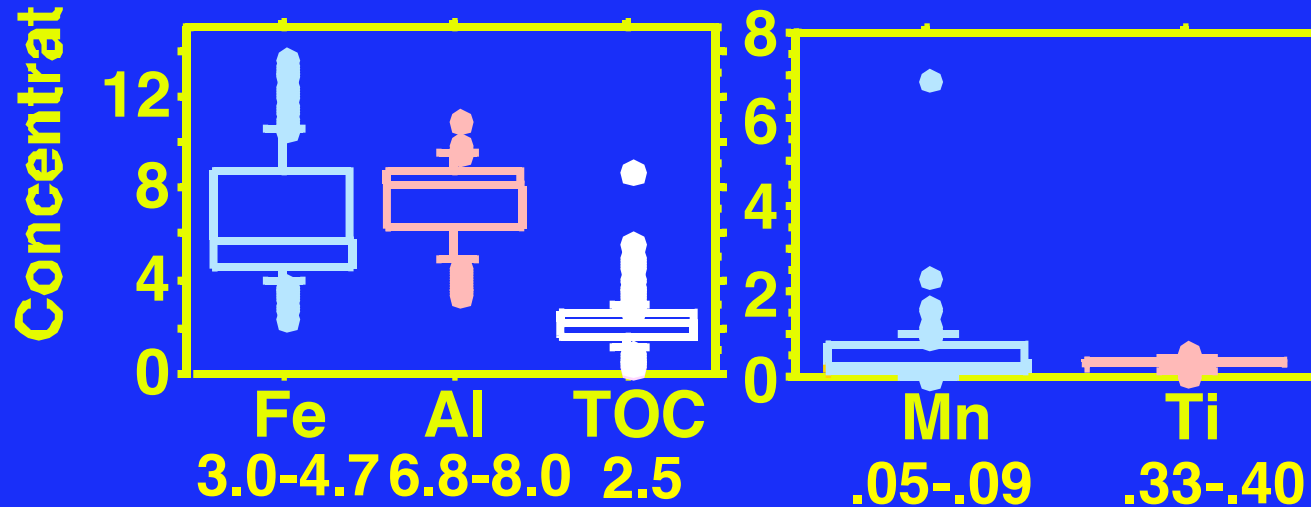


Box plots of Selected Sediment-Associated Trace Element Data from Lake Coeur d'Alene

Surface Sediments

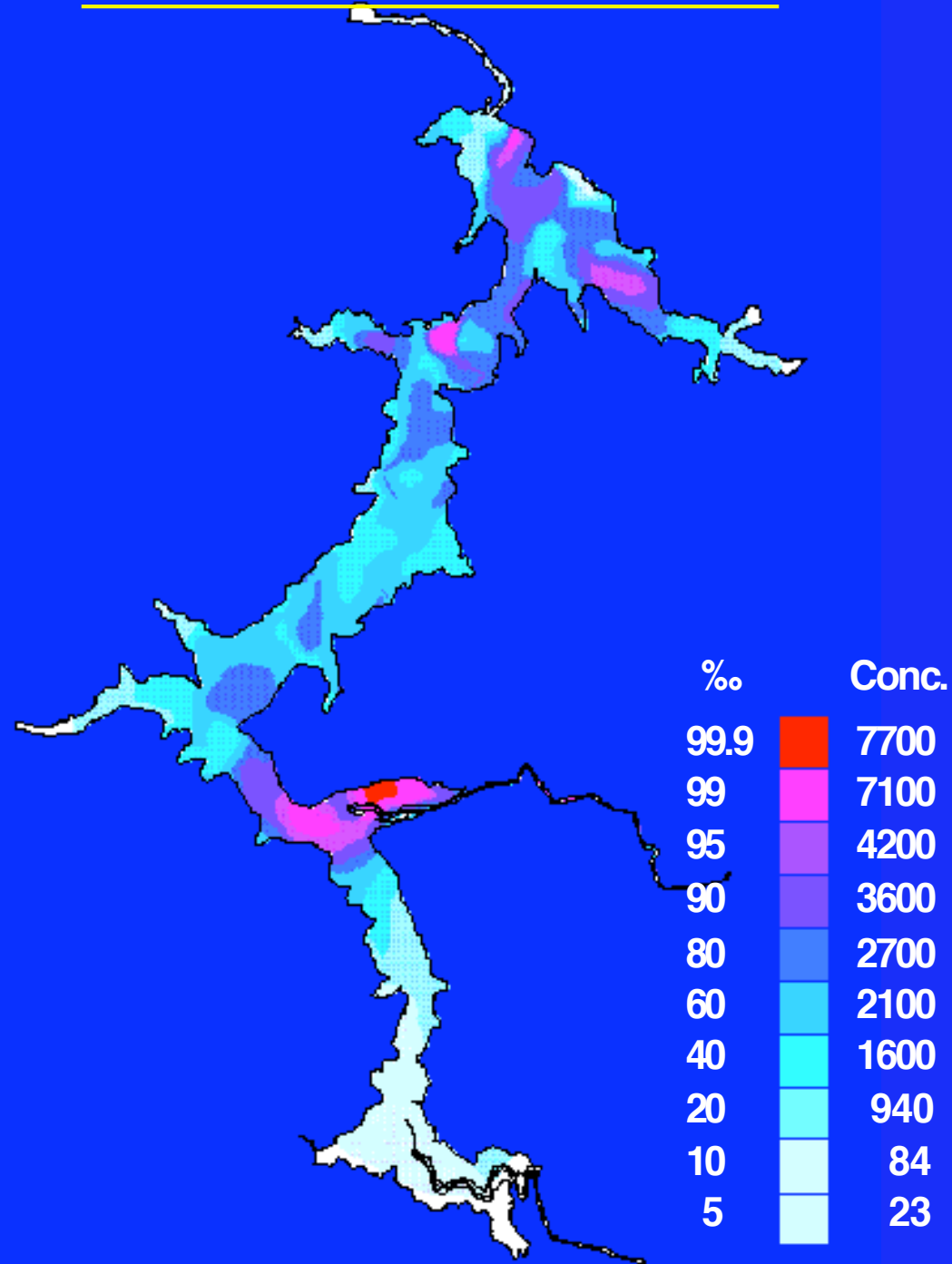


Subsurface Sediments

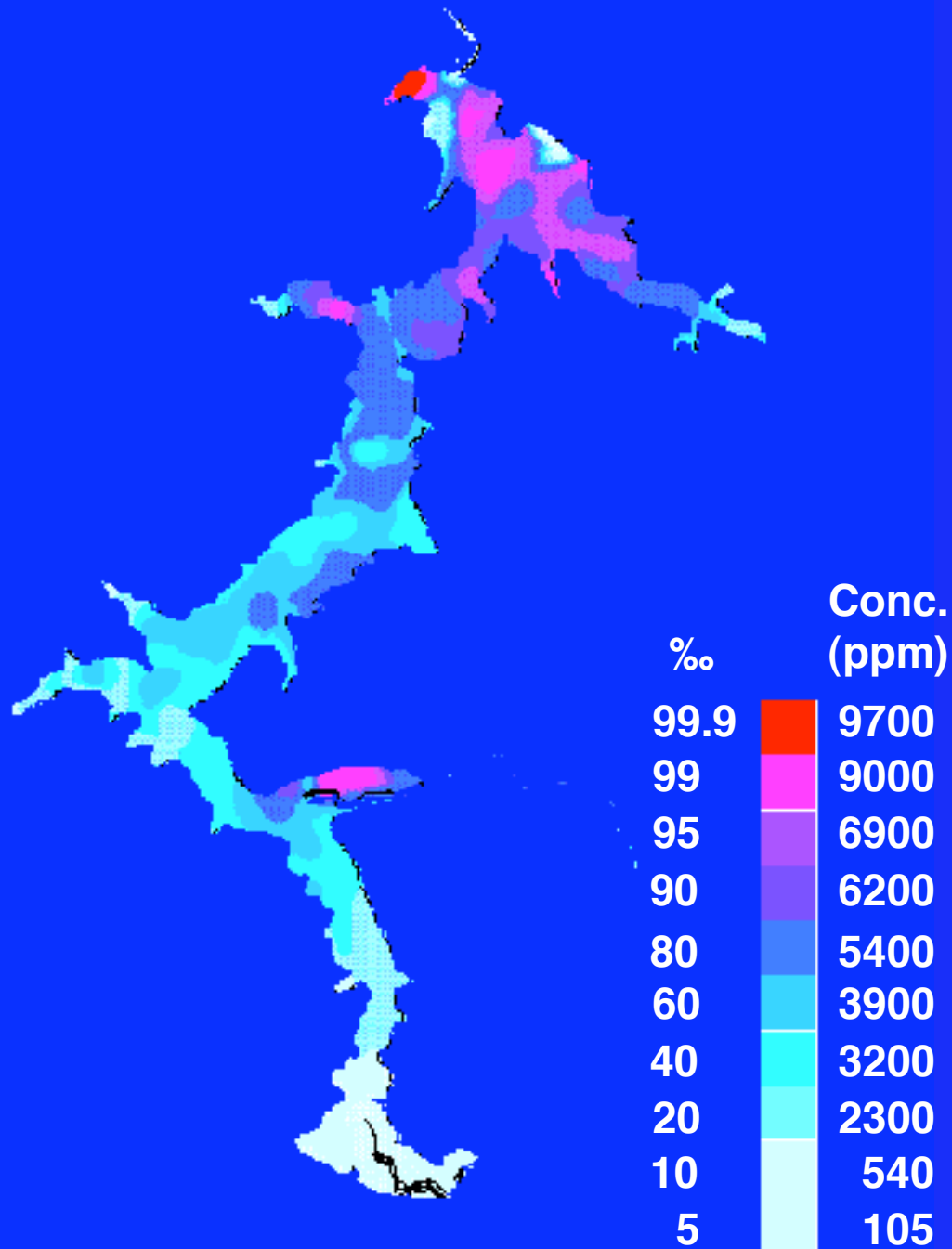


Spatial Distributions of Sediment-Associated Trace Elements

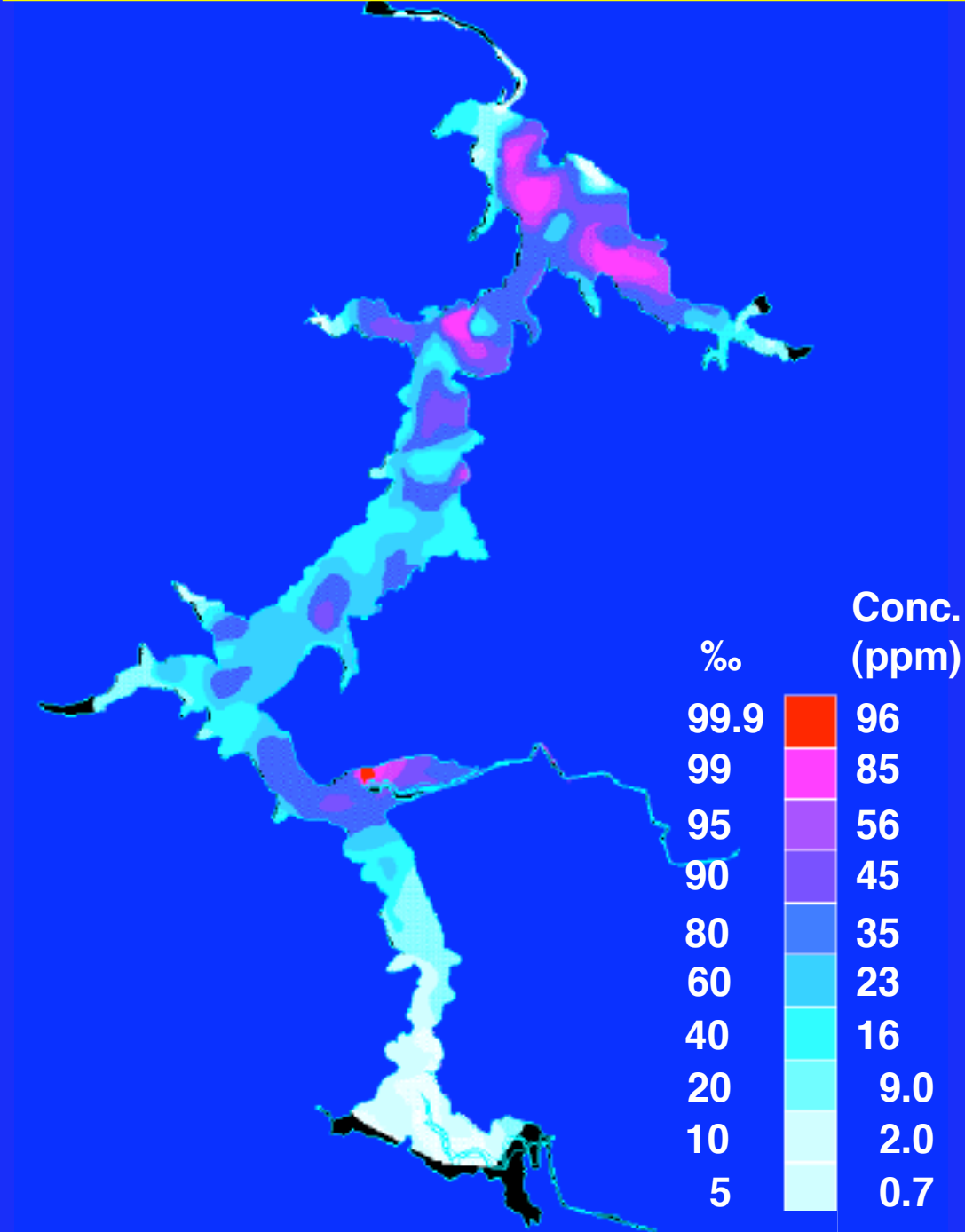
The Distribution of Lead in Lake Coeur d'Alene Surface Sediments



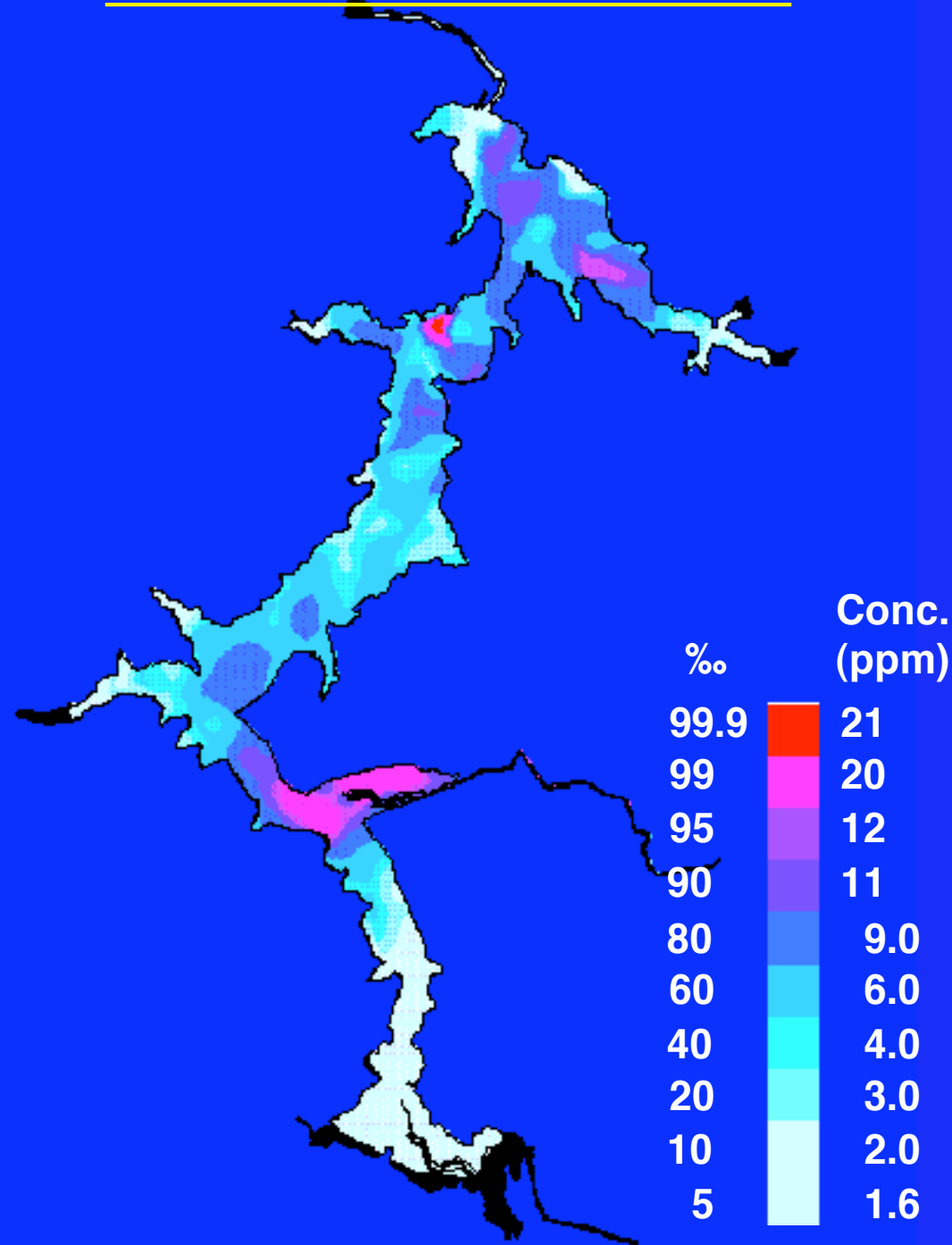
The Distribution of Zinc in Lake Coeur d'Alene Surface Sediments



The Distribution of Antimony in Lake Coeur d'Alene Surface Sediments



The Distribution of Silver in Lake Coeur d'Alene Surface Sediments



The Geochemistry of Bank and Floodplain Deposits from the Coeur d'Alene River

Chemical Concentrations for Selected Samples from the South Fork, Coeur d'Alene River

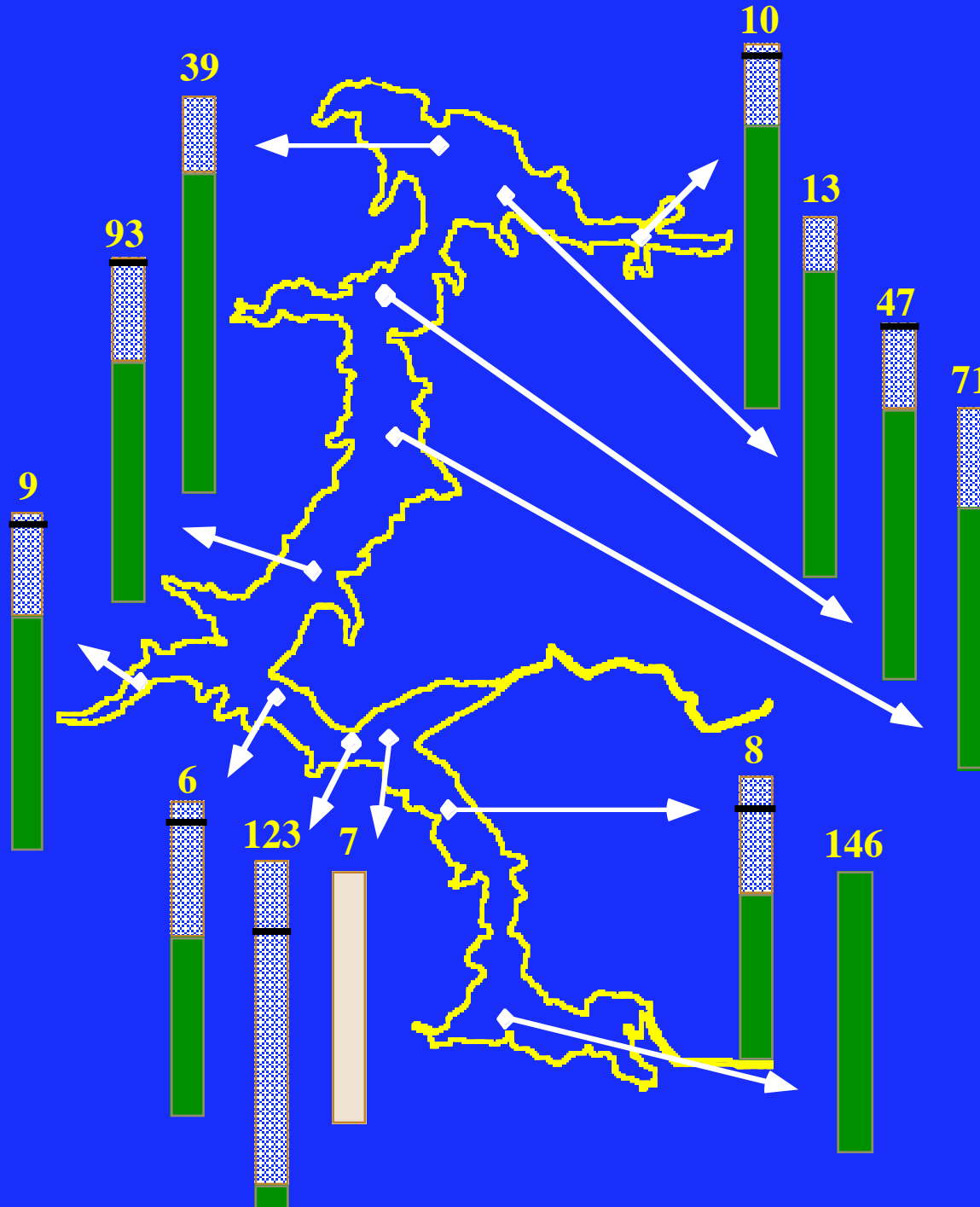
Sample	%	Ag	Cu	Pb	Zn mg/kg	Cd	Hg	As	Sb	Fe	Mn %	Al	Ti
South Fork @ Smelterville , Right Bank													
Bulk		150	590	63,000	12,000	43	18	90	160	17	0.62	3.4	0.13
Light	41	36	150	8,100	3,700	16	3.3	30	130	4.9	0.14	4.2	0.11
Heavy	58	140	730	80,000	16,000	51	18	120	240	24	0.83	3.0	0.14
South Fork @ Smelterville I, Left Bank													
Bulk		170	650	55,000	8,800	20	21	100	320	15	0.58	3.9	0.15
Light	40	73	260	21,000	3,600	13	7.0	40	220	5.4	0.13	4.4	0.11
Heavy	59	180	920	58,000	12,000	24	28	140	340	24	0.90	3.3	0.15
South Fork @ Smelterville II, Left Bank													
Bulk		180	670	71,000	9,000	19	18	96	300	15	0.51	4.0	0.15
Light	42	67	240	16,000	3,200	7.5	7.5	40	200	5.1	0.13	4.5	0.11
Heavy	58	230	930	76,000	13,000	23	23	140	400	24	0.77	3.4	0.15
Downstream from the Confluence of the North and South Fork Coeur d'Alene River													
Bulk		16	240	5,600	4,500	64	3.4	170	85	9.2	0.56	4.9	0.24
Light	81	9.7	160	4,900	3,300	49	4.3	100	50	4.1	0.15	5.2	0.17
Heavy	17	42	430	7,300	7,300	56	5.7	330	160	39	2.6	2.0	0.38

Chemical Concentrations for Selected Samples from Cataldo Flats

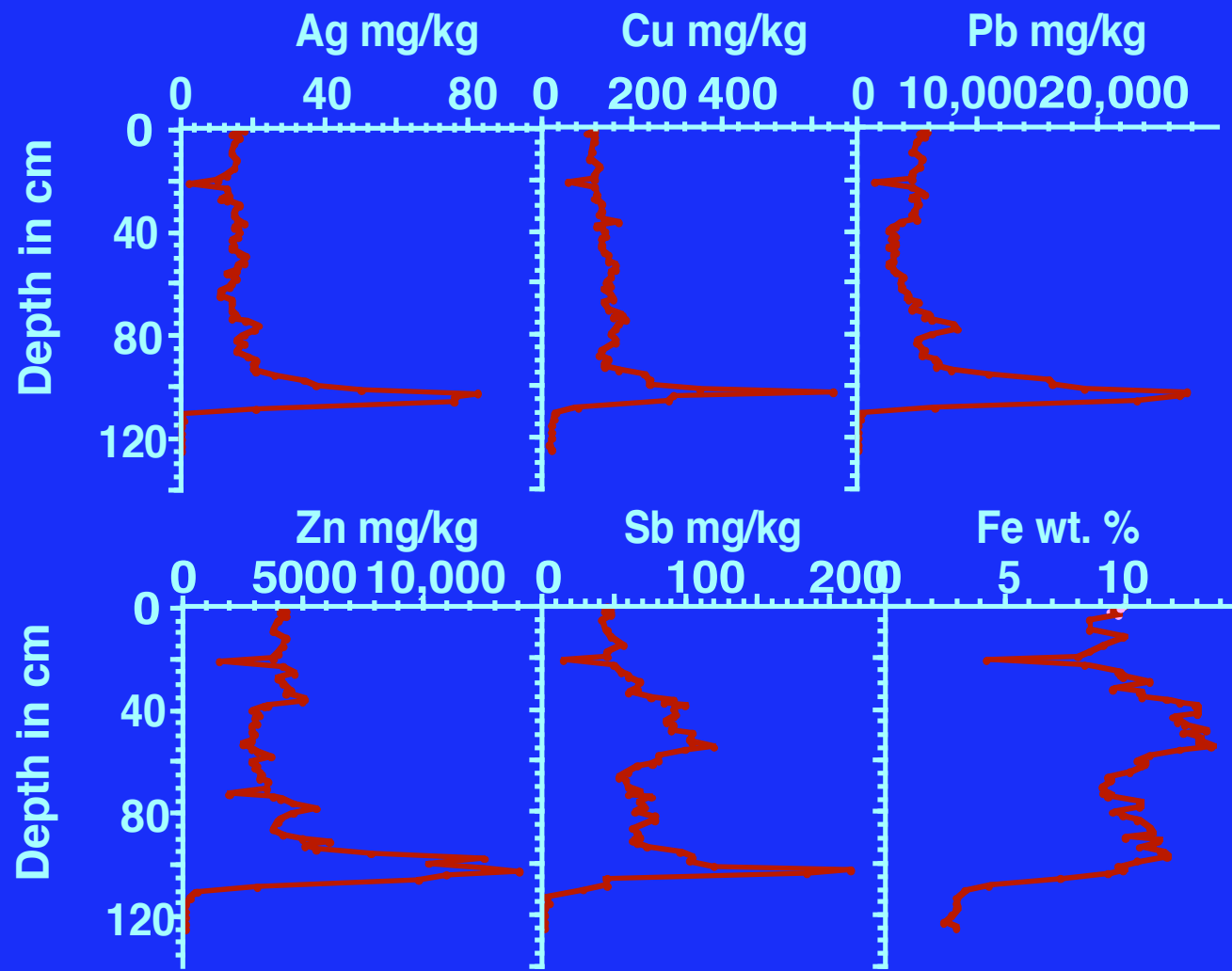
Sample	%	Ag	Cu	Pb	Zn mg/kg	Cd	Hg	As	Sb	Fe	Mn %	Al	Ti
Sediment at Bottom of Drop													
Bulk		10	76	2,800	7,700	14	0.67	150	48	8.7	0.90	3.2	0.13
Light	78	15	47	1,400	5,100	6.4	0.45	80	35	2.8	0.33	3.6	0.11
Heavy	21	20	180	7,000	15,000	27	1.5	330	70	33	3.0	1.9	0.14
Mid-Stream at Seep Bottom													
Bulk		12	84	2,500	6,500	8.4	0.72	140	49	7.6	0.85	3.3	0.13
Light	78	5.8	38	1,400	3,700	3.1	0.3	75	26	2.7	0.30	3.7	0.12
Heavy	21	27	220	8,600	16,000	35	1.4	500	70	38	3.3	1.6	0.14
Seep Solids at River Edge													
Bulk		12	100	3,800	7,800	13	1.9	160	52	8.8	0.89	3.9	0.17
Light	78	7.4	62	2,600	5,400	8.1	1.2	80	33	3.8	0.33	4.4	0.15
Heavy	20	25	250	8,600	14,000	29	2.8	420	60	37	3.0	1.8	0.16
Surface Floc from Seep													
Bulk		11	89	2,000	19,000	9.4	1.6	170	48	15	0.85	3.4	0.14
Light	75	9.0	54	2,800	17,000	6.1	1.2	100	29	8.4	0.31	3.7	0.11
Heavy	23	20	180	6,800	27,000	20	2.4	430	70	37	2.6	1.9	0.16

Downcore Chemical Distribution Patterns

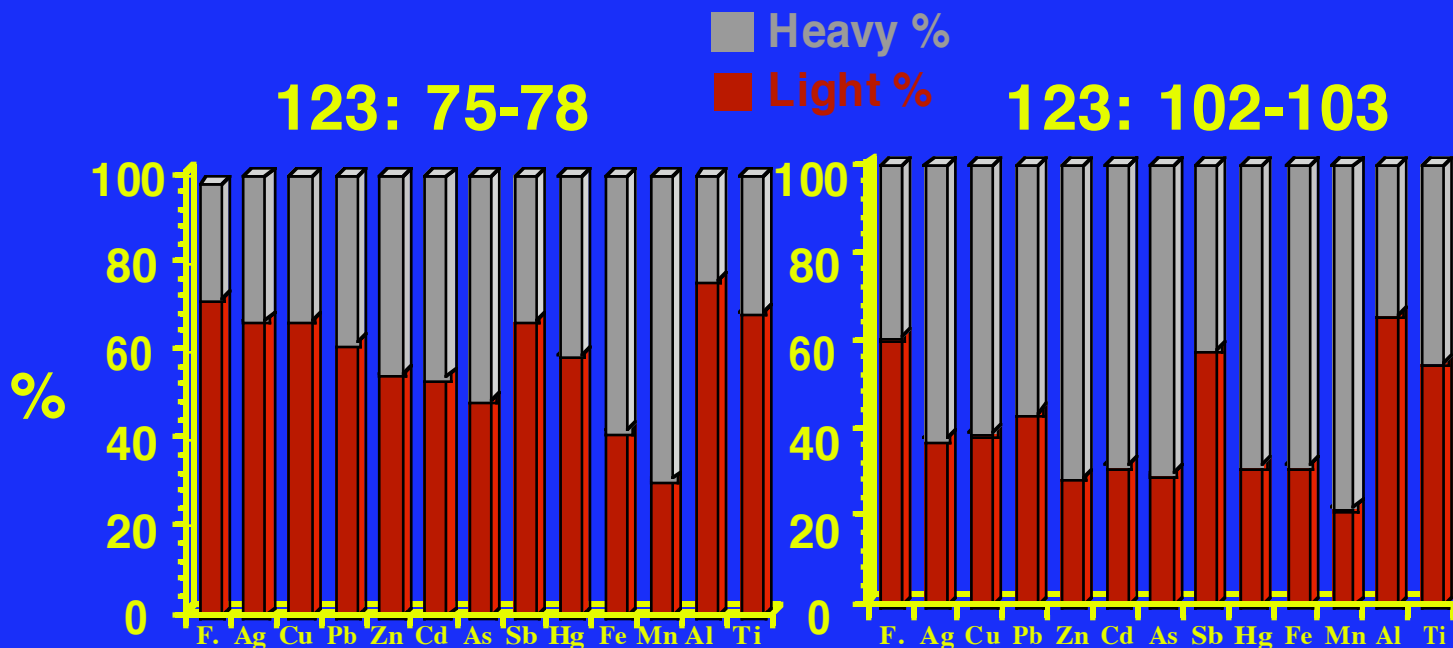
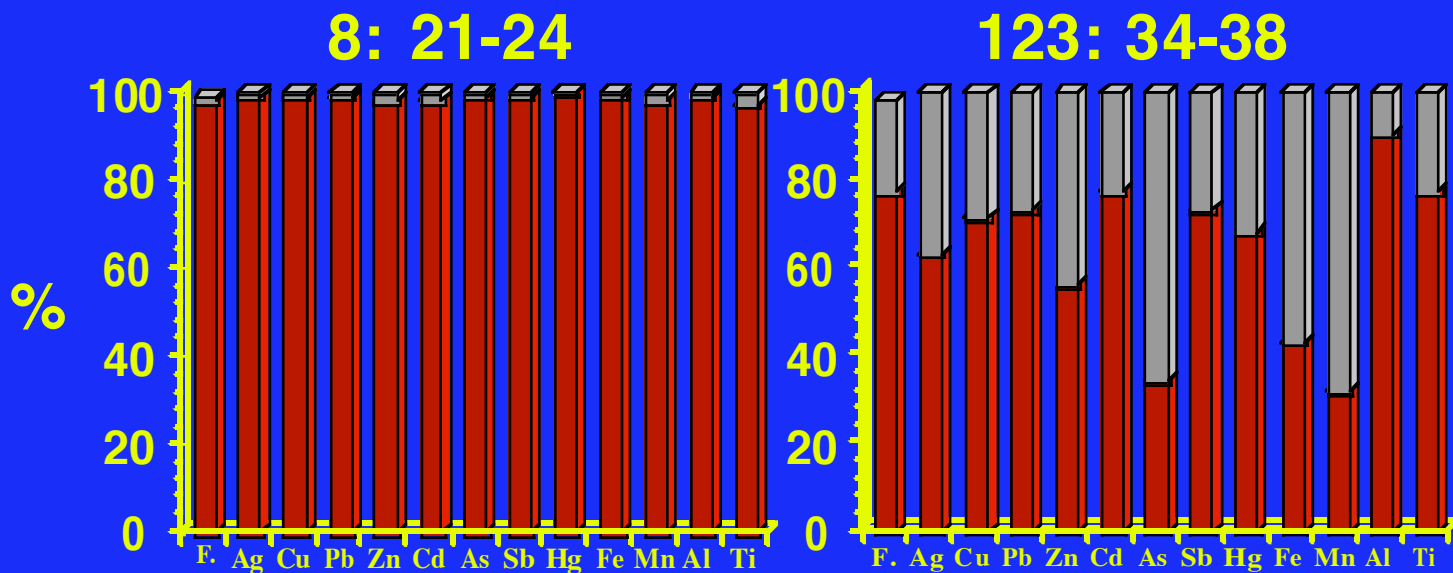
Downcore Physical Comparisons



Downcore Trace Element Distribution Patterns - Core 123



Heavy/Light Fraction Geochemistry of Selected Core Samples



Estimated Masses of Enriched Sediments and Associated Trace Elements

Estimation of Masses

- 1) The lake was divided into 12 separate zones; each zone contained one core.
- 2) The area of each zone was determined using U.S.G.S. topographic maps and a digitizing table.



Estimation of Masses con't.

3) For purposes of this estimate, it was assumed that each core represented the thickness and chemical content (median concentration) of the entire zone within which it was located.

Core Number	Total Length (cm)	Thickness of Enriched Zone (cm)
Core 10	130.0	25.0
Core 13	128.5	17.0
Core 39	140.5	23.5
Core 47	128.0	26.0
Core 71	129.0	30.0
Core 93	124.0	31.0
Core 9	122.0	34.0
Core 6	114.5	41.0
Core 123	126.0	119.0
Core 7	97.5	97.5
Core 8	105.0	35.0
Core 146	105.0	0.0

Estimation of Masses con't.

4) For purposes of this estimate, it also was assumed that each core represented the chemical content (median concentration) of the entire zone within which it was located.

Constituent	Unit	Core Number											
		10	13	39	47	71	93	9	6	123	7	8	146
Ag	mg/kg	7.9	16	18	23	24	20	8.3	20	20	16.00	15	<0.5
Cu	mg/kg	92	137	140	170	160	160	83	160	160	130	130	35
Pb	mg/kg	3,400	7,000	7,100	8,300	8,900	6,400	2,700	6,300	6,300	5,100	4,800	23
Zn	mg/kg	3,600	4,700	4,800	4,700	4,200	4,600	2,100	4,500	4,500	4,100	3,700	130
Cd	mg/kg	41	48	51	50	54	44	22	39	37	46	32	0.2
Hg	mg/kg	1.3	2.3	3.2	3.6	3.3	3.6	1.1	3.7	3.8	5.10	1.9	0.07
As	mg/kg	41	45	80	78	120	120	32	240	270	320.0	78	6.6
Sb	mg/kg	24	52	58	70	83	73	27	73	74	59	47	0.7
Fe	%	4.9	6.3	6.5	7.4	7.6	8.0	5.1	9.7	10	10	6.5	4.6
Mn	%	0.29	0.44	0.54	1.2	0.83	0.69	0.32	0.82	0.86	0.91	0.42	0.05
Area	km ²	6.3	13.7	11.9	15.7	15.3	16.0	6.1	9.0	1.4	6.0	6.7	19.6

Estimation of Masses con't.

5) The volume of enriched sediment for each zone was determined by multiplying the area of the zone by the thickness of the trace element-rich section of each core.

Zone 1: area = $6.34 \text{ km}^2 = 6.34 \times 10^{10} \text{ cm}^2$; thickness = 25 cm
Therefore, volume = $(6.34 \times 10^{10} \text{ cm}^2) (25) = 1.59 \times 10^{12} \text{ cm}^3$

6) The mass of enriched sediment in each zone was calculated by multiplying the volume of each zone by the assumed density of the sediment (2.00 g/cm^3).

Therefore, for Zone 1: $(1.59 \times 10^{12} \text{ cm}^3) (2.00 \text{ g/cm}^3) = 3.18 \times 10^{12} \text{ g} = 3.18 \text{ Mt}$

Estimation of Masses con't.

7) The mass of enriched sediment for the entire lake was determined by summing the results from each of the zones.

Therefore, for the entire lake, the mass of enriched sediment =
Zone 1 (mass) + Zone 2 (mass) + Zone 3 (mass) ... + Zone 11
(mass) = 75 Mt.

8) The mass of each enriched trace element, in each zone, was calculated by multiplying the mass of sediment in that zone by the median chemical concentration from the appropriate core.

Therefore, for Zone 1, to determine the mass of Pb, with a median concentration of $3,400 \mu\text{g g}^{-1}$:
 $(3.18 \times 10^{12} \text{ g}) (3,400 \mu\text{g g}^{-1})$
 $= 10.8 \times 10^{15} \mu\text{g of Pb} = 10,800 \text{ t.}$

Estimation of Masses con't.

8) By substituting baseline median chemical concentrations obtained from Core 146 and the unbanded zones of the other cores, normal (unaffected) trace element masses were calculated for the same volume as the enriched sediments

Therefore, for the entire lake, to determine the mass of Pb in 75 Mt of sediment, with a median concentration of $23 \mu\text{g g}^{-1}$: $(75 \times 10^{12} \text{ g}) (23 \mu\text{g g}^{-1}) = 1.73 \times 10^{15} \mu\text{g of Pb} = 1725 \text{ t of Pb.}$

9) The excess mass of each sediment-associated trace element was calculated by subtracting the results for the unaffected mass from the affected mass.

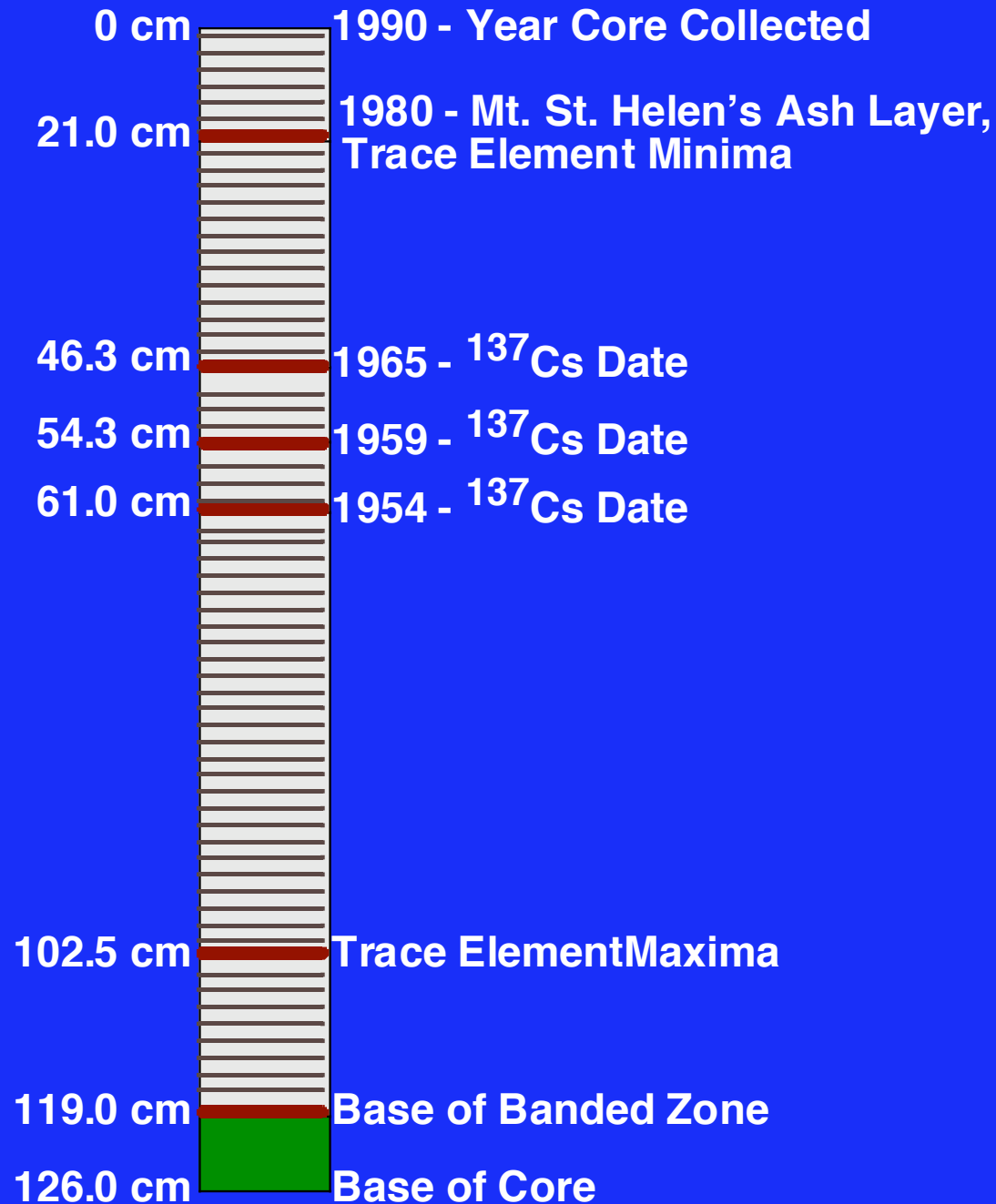
Therefore, for the lake, to determine the excess mass of enriched Pb, subtract the calculated background mass (1725 t) from the calculated enriched mass (470,000 t) which equals 468,000 t of excess Pb.

Estimation of Masses con't.

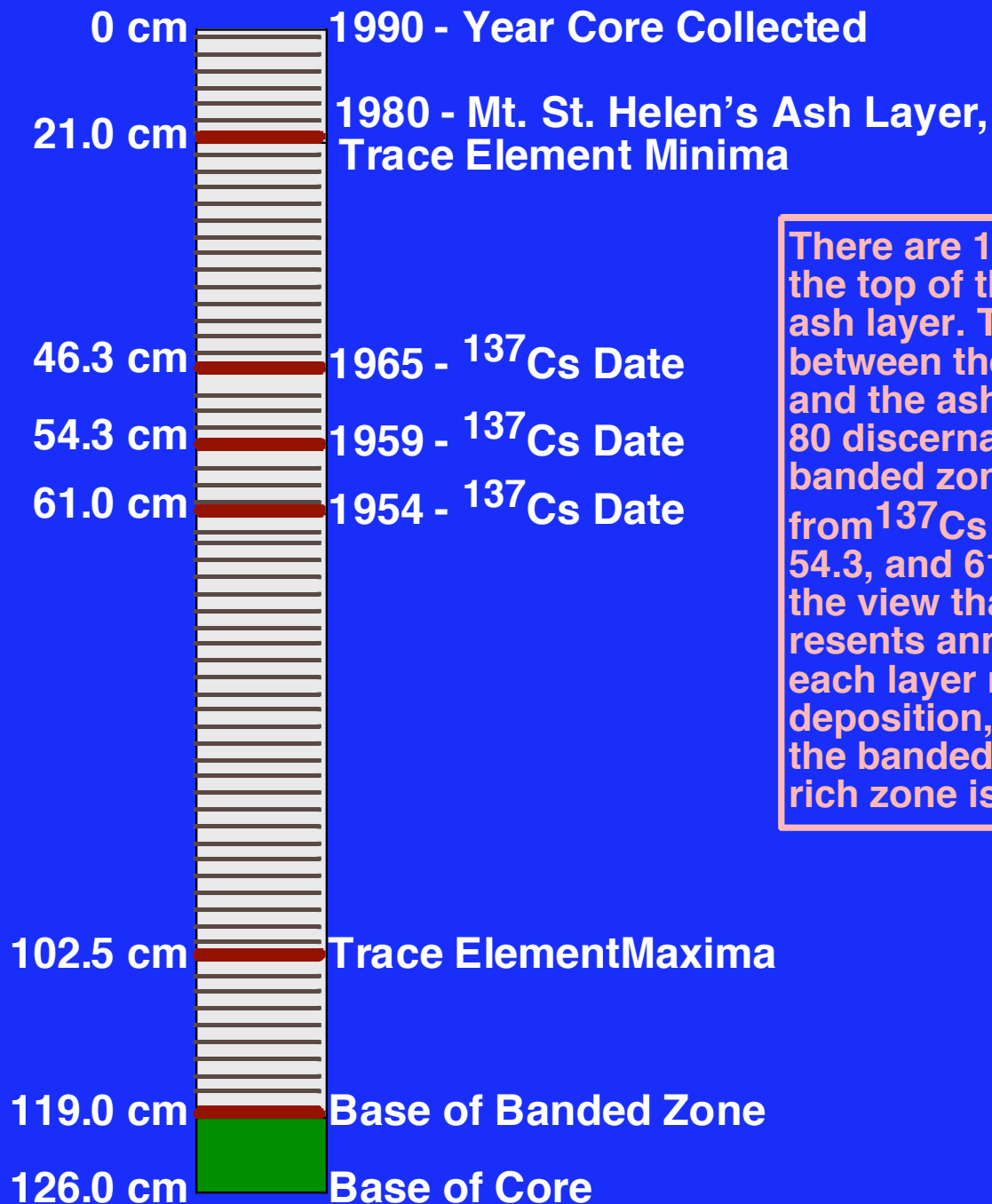
Constituent	Total Mass in Enriched Zone (t)	Total Mass from Baseline Levels (t)	Excess Due to Enriched Sediment (t)
Ag	1,350	<38	>1,300
Cu	10,000	2,600	7,400
Pb	470,000	1,700	470,000
Zn	240,000	9,600	230,000
Cd	3,300	16	3,300
Hg	270	5.3	260
As	12,000	500	12,000
Sb	4,700	53	4,600

Sediment Geochemical History of Lake Coeur d'Alene

Chronology and Major Physical and Chemical Features of Core 123

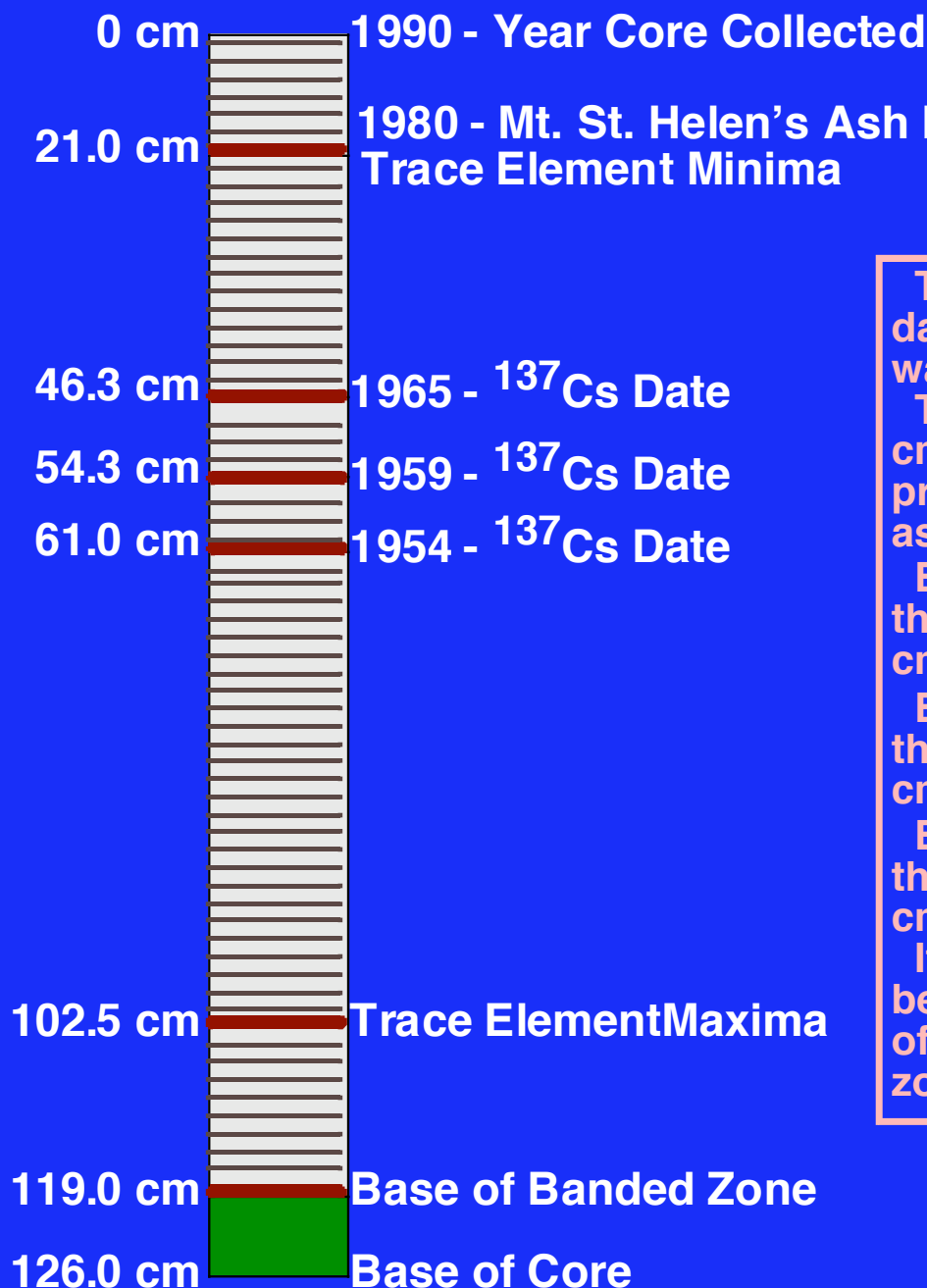


Estimated Age of the Base of the Trace Element-Rich Zone in Core 123 - Method 1



There are 10 years between the top of the core and the ash layer. There are 10 layers between the top of the core and the ash layer. There are 80 discernable layers in the banded zone. Ages estimated from ^{137}Cs activities at 46.3, 54.3, and 61.0 cm, support the view that each layer represents annual deposition. If each layer represents annual deposition, then the base of the banded, trace element-rich zone is 1990 - 80 = 1910.

Estimated Age of the Base of the Trace Element-Rich Zone in Core 123 - Method 2



The top of the core can be dated at 1990 because that was when it was collected.

The age of the core at 21.0 cm is 1980 based on the presence of a Mt. St. Helen's ash layer.

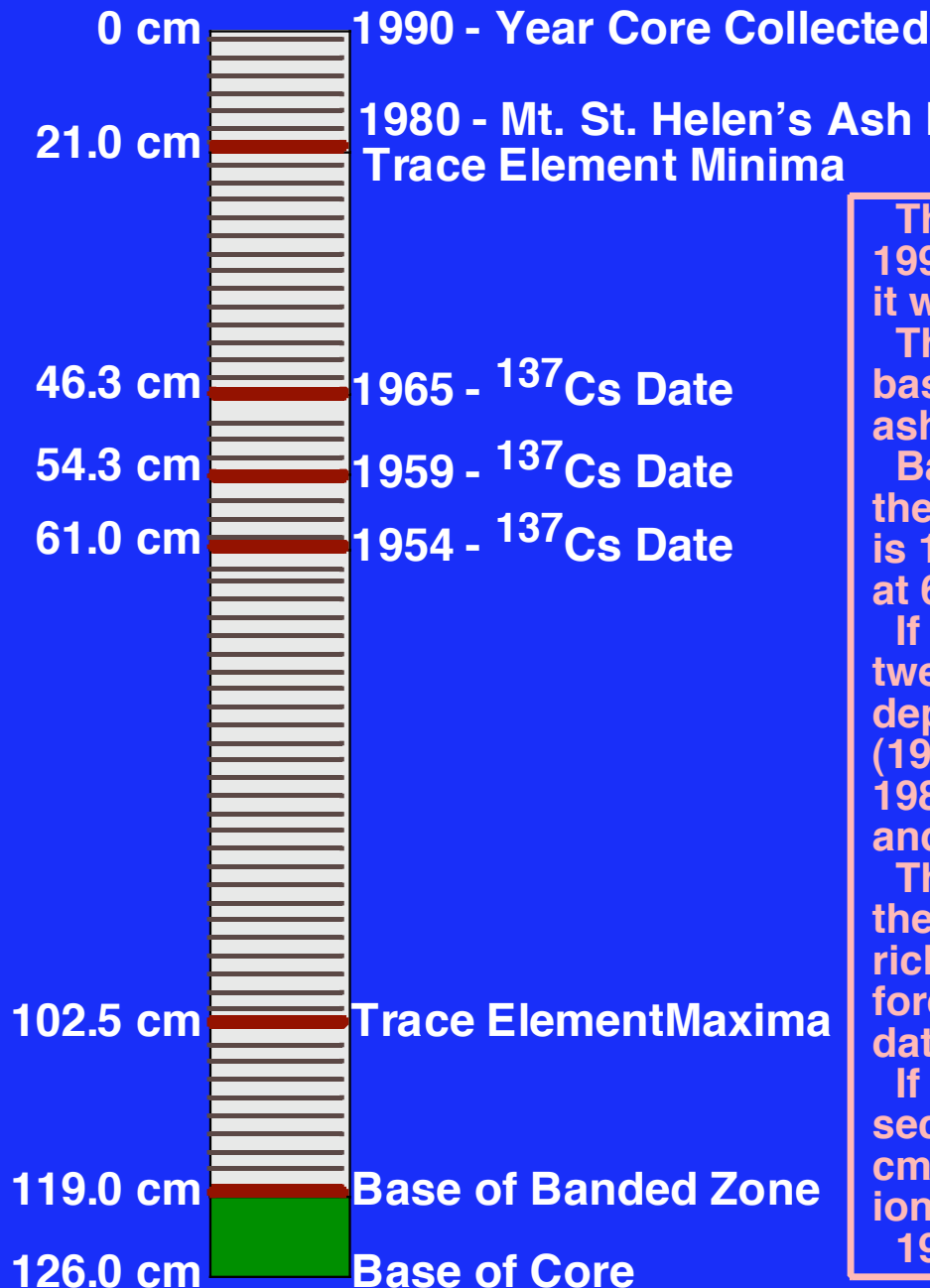
Based on ^{137}Cs activities, the age of the core at 46.3 cm is 1965.

Based on ^{137}Cs activities, the age of the core at 54.3 cm is 1959.

Based on ^{137}Cs activities, the age of the core at 61.0 cm is 1954.

If deposition is assumed to be constant, then the base of the trace element-rich zone is estimated as 1895.

Estimated Age of the Base of the Trace Element-Rich Zone in Core 123 - Method 3



The age of the core top is 1990 because that was when it was collected.

The age at 21.0 cm is 1980, based on a Mt. St. Helen's ash layer.

Based on ¹³⁷Cs activities, the age of the core at 46.3 cm is 1965, at 54.3 it is 1959, and at 61.0 it is 1954.

If deposition is constant between dates, average annual deposition rates are 2.1 cm/y (1980-1990), 1.7 cm/y (1965-1980), 1.3 cm/y (1959-1965), and 1.4 cm/y (1954-1959).

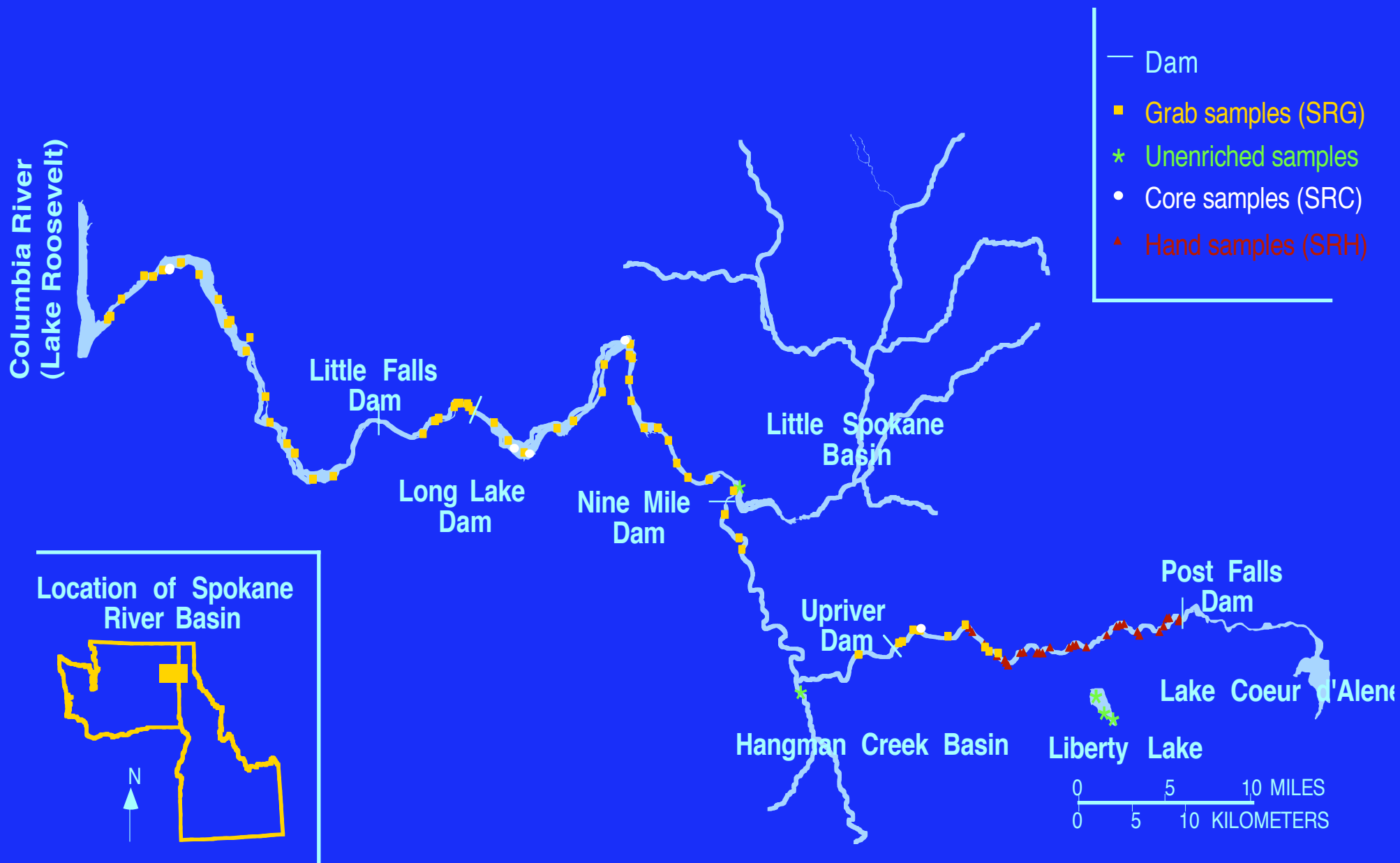
The 1954 layer is at 61.0 cm, the base of the trace element-rich zone is at 119.0 cm; therefore, the thickness of the undated portion is 58 cm.

If the deposition rate for this section is assumed to be 1.35 cm/y, then the undated section represents 43 years.

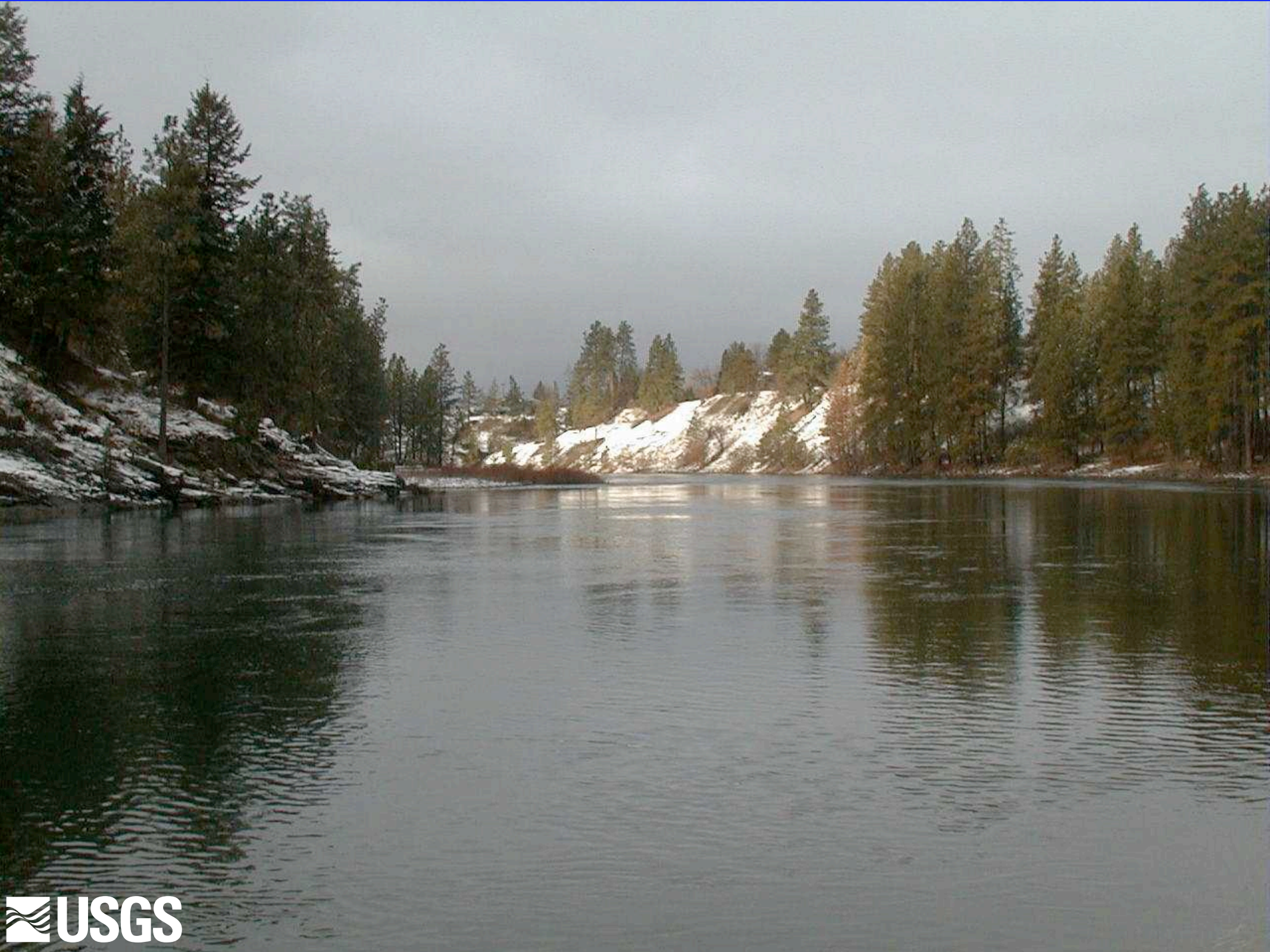
1954 - 43 years = 1911.

The Spokane River Basin

Sampling Sites in the Spokane River Basin







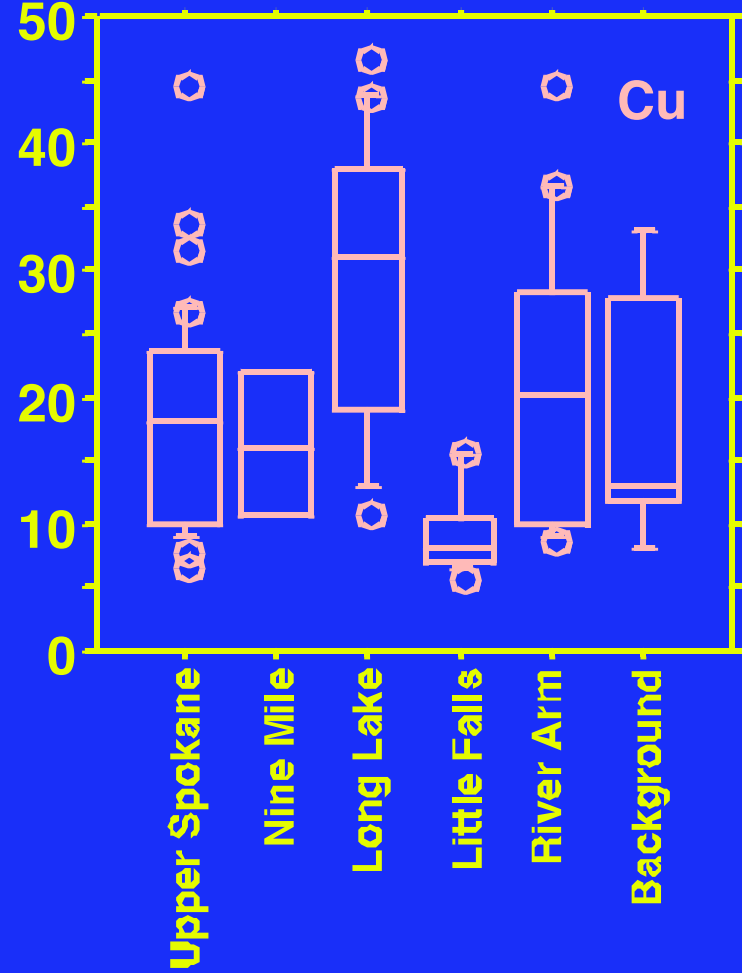
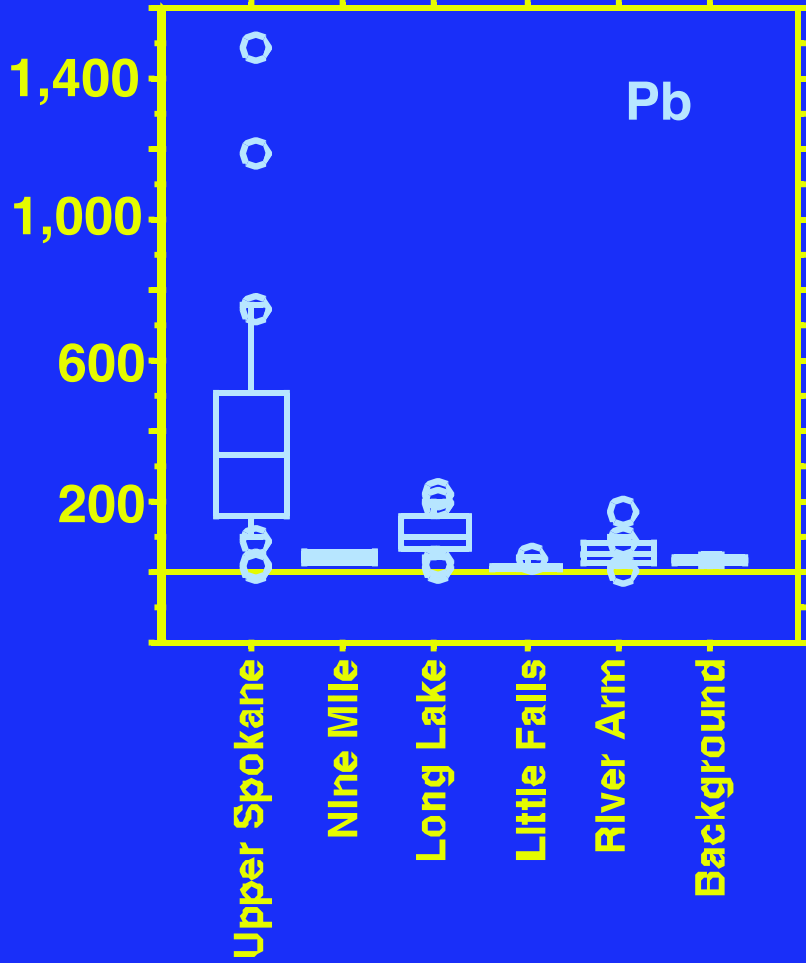






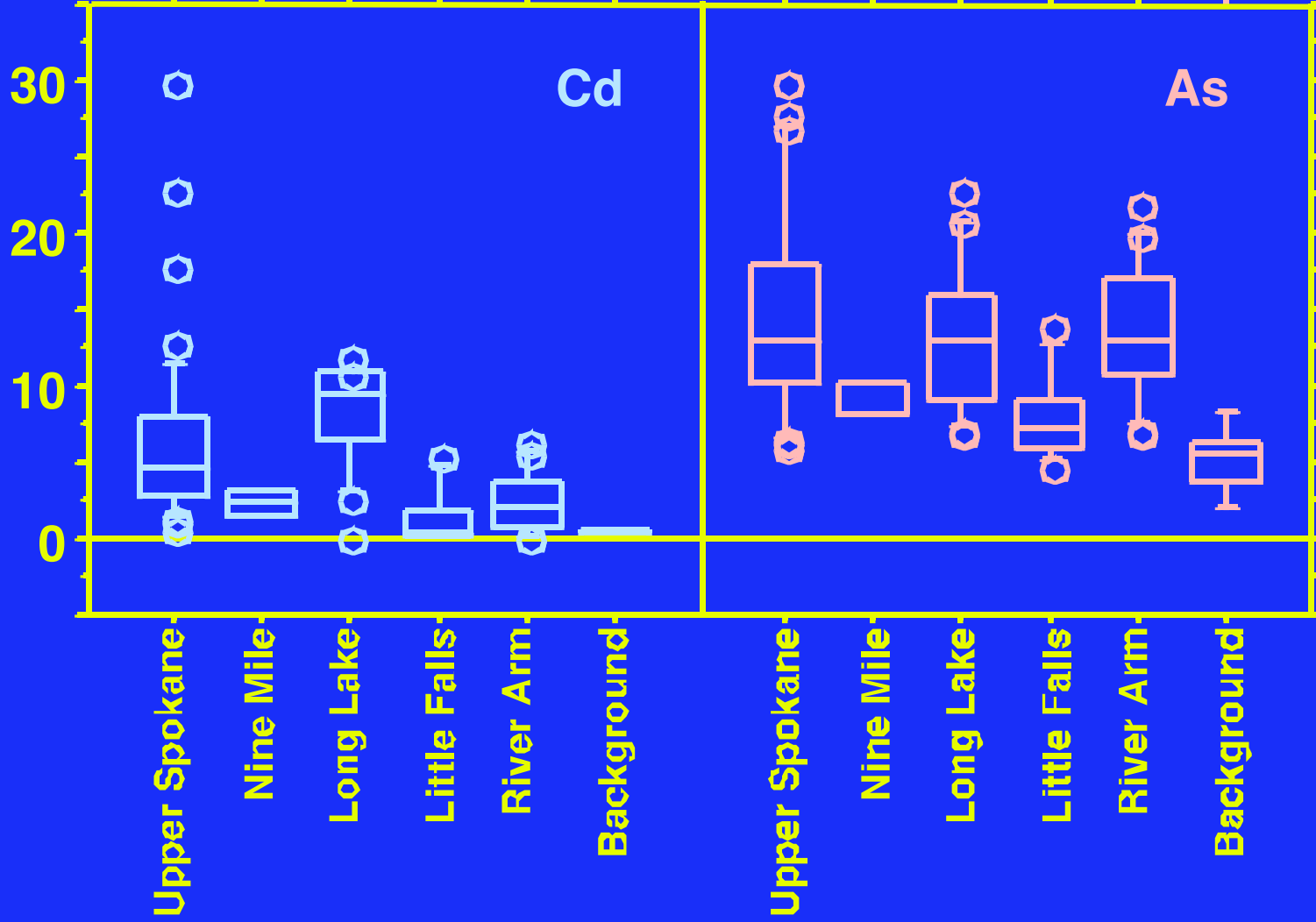
Boxplots of Pb and Cu in the Spokane River Basin

Concentration (mg/kg)



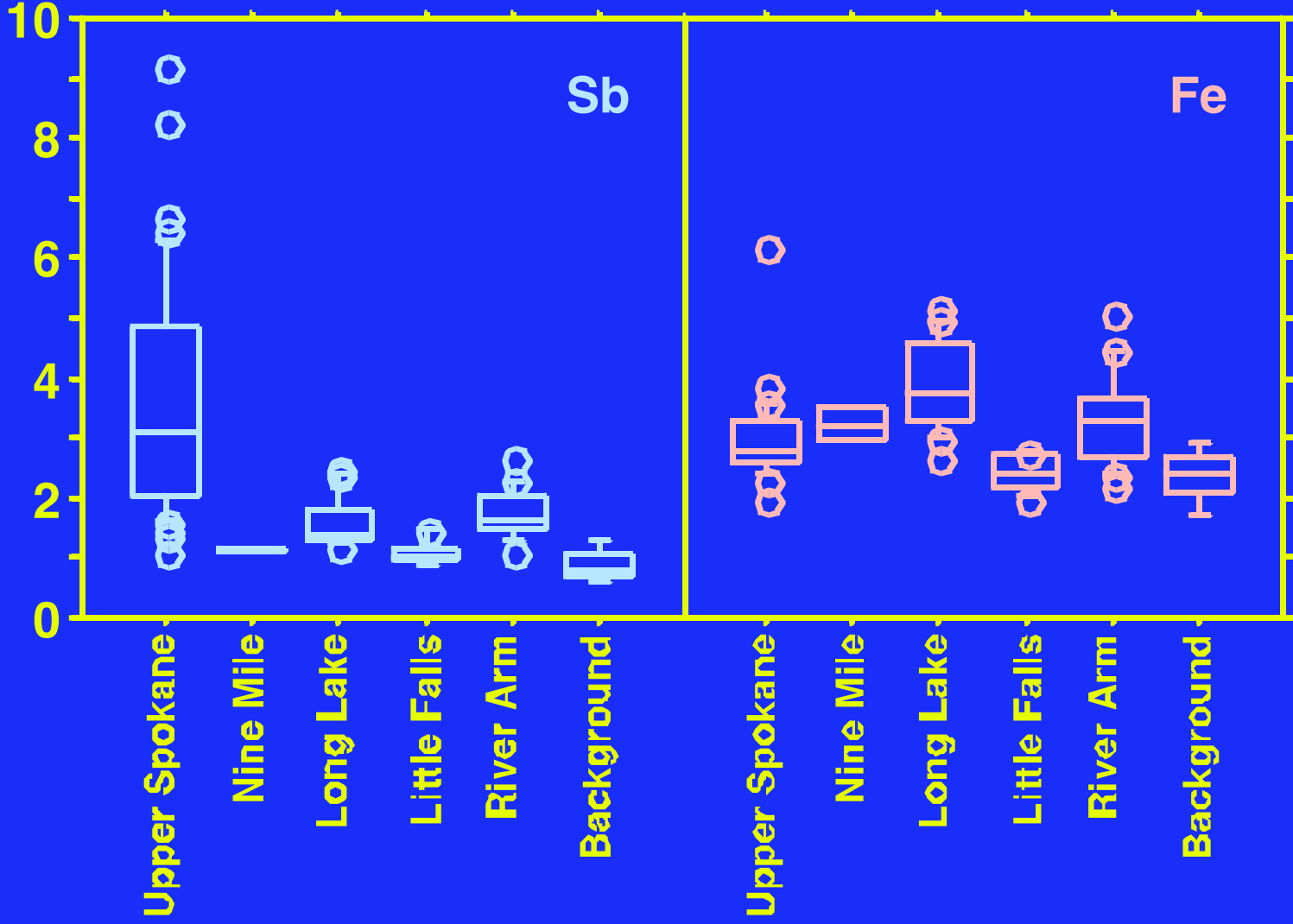
Boxplots of Cd and As in the Spokane River Basin

Concentration (mg/kg)



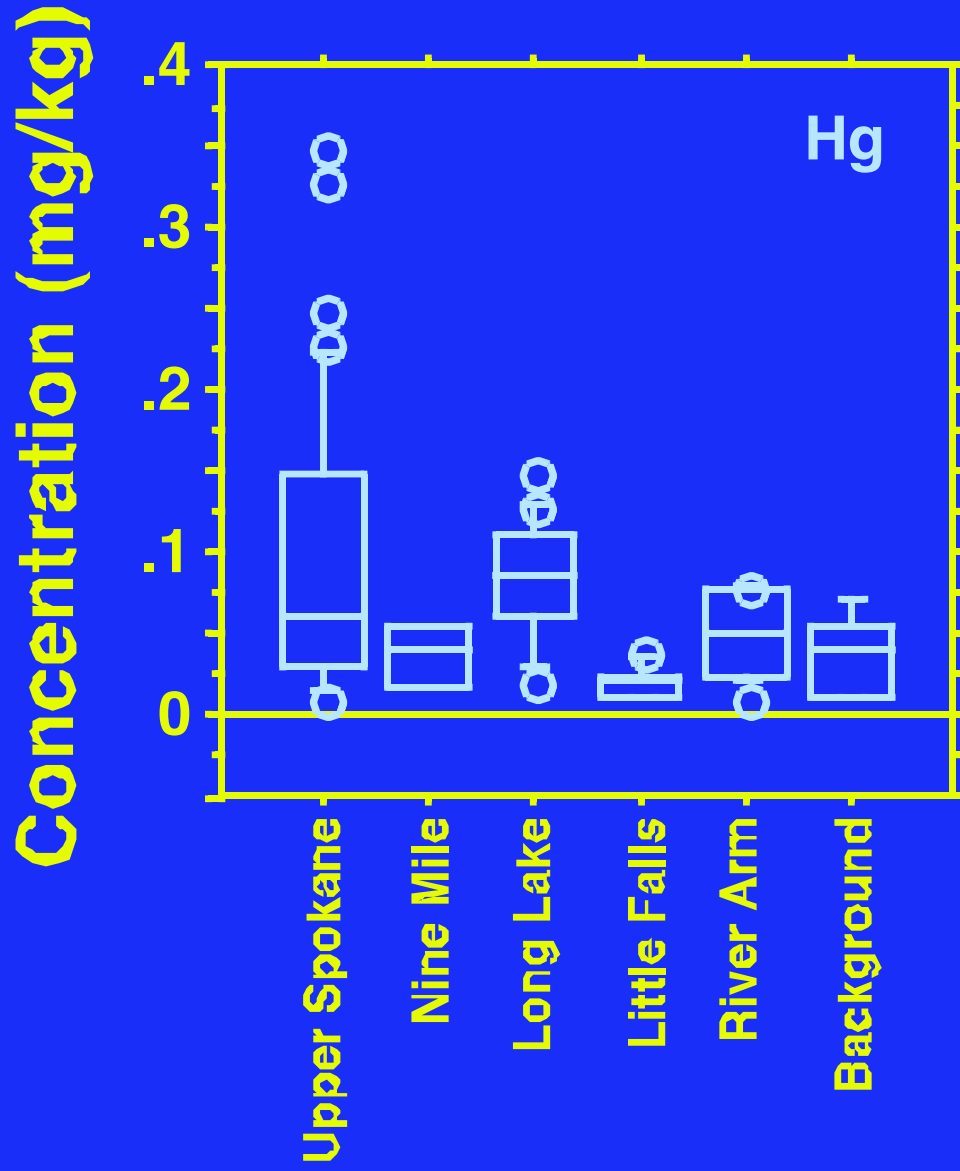
Boxplots of Sb and Fe in the Spokane River Basin

Concentration (mg/kg)

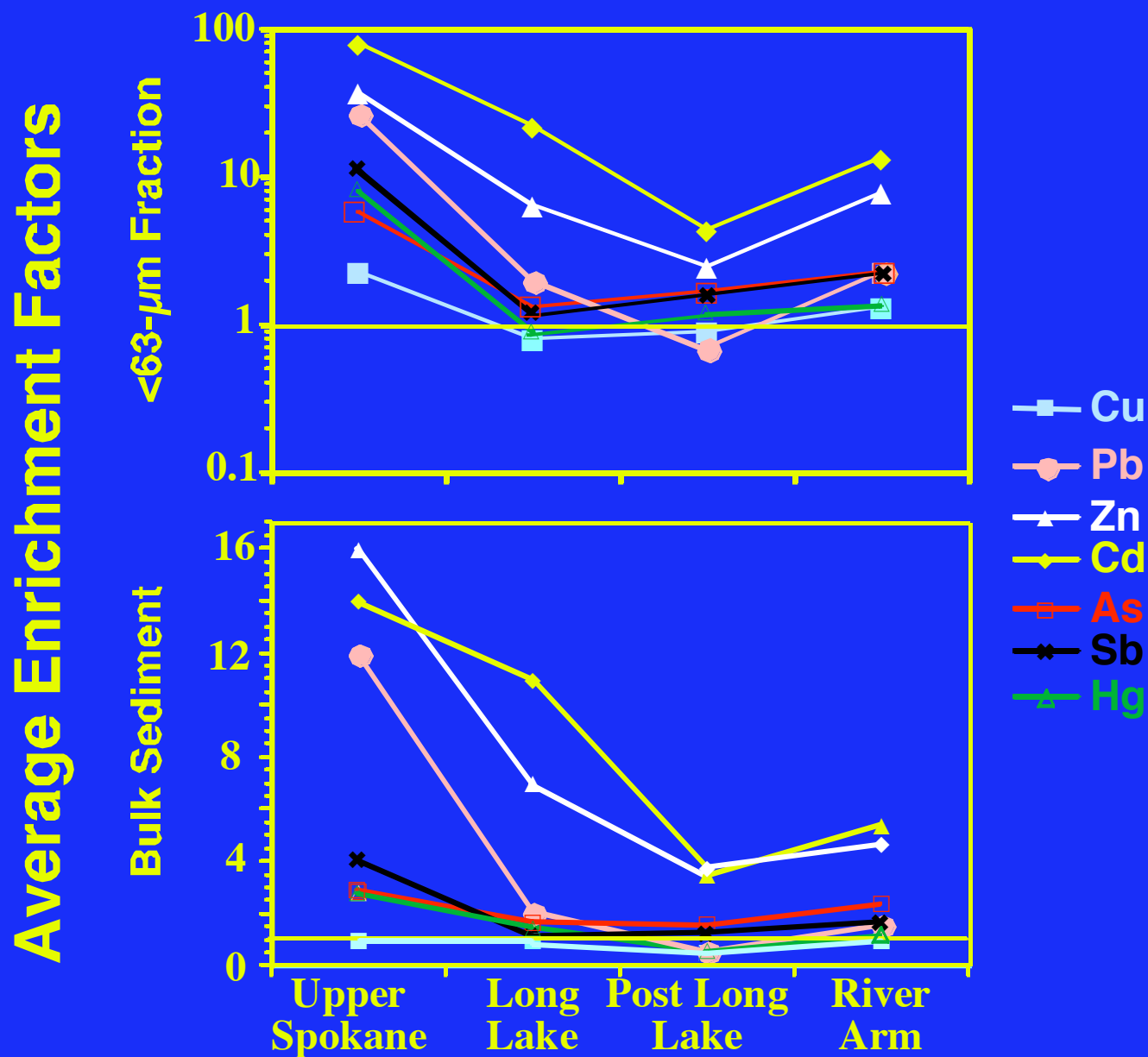


Concentration (%)

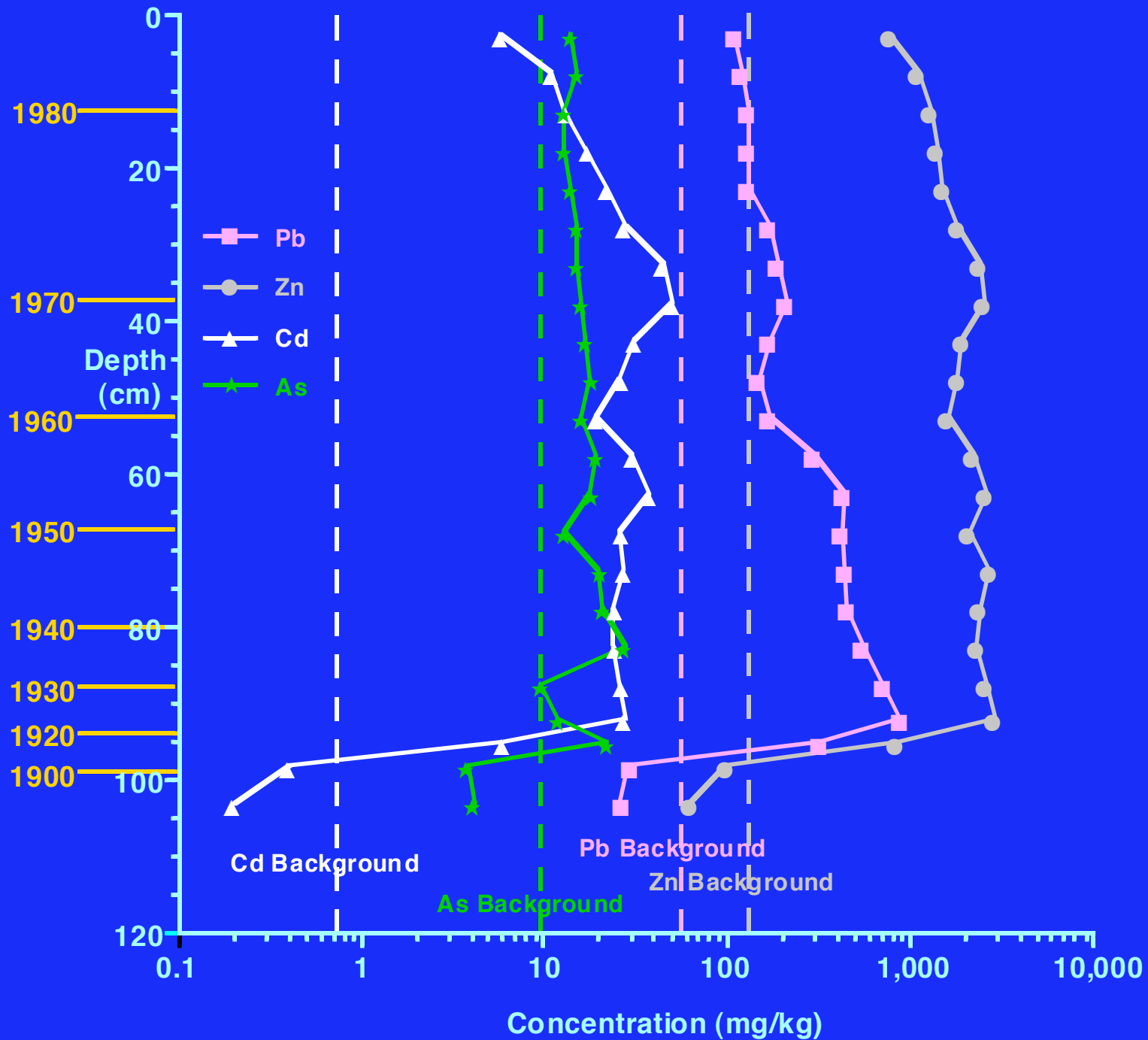
Boxplot of Hg in the Spokane River Basin



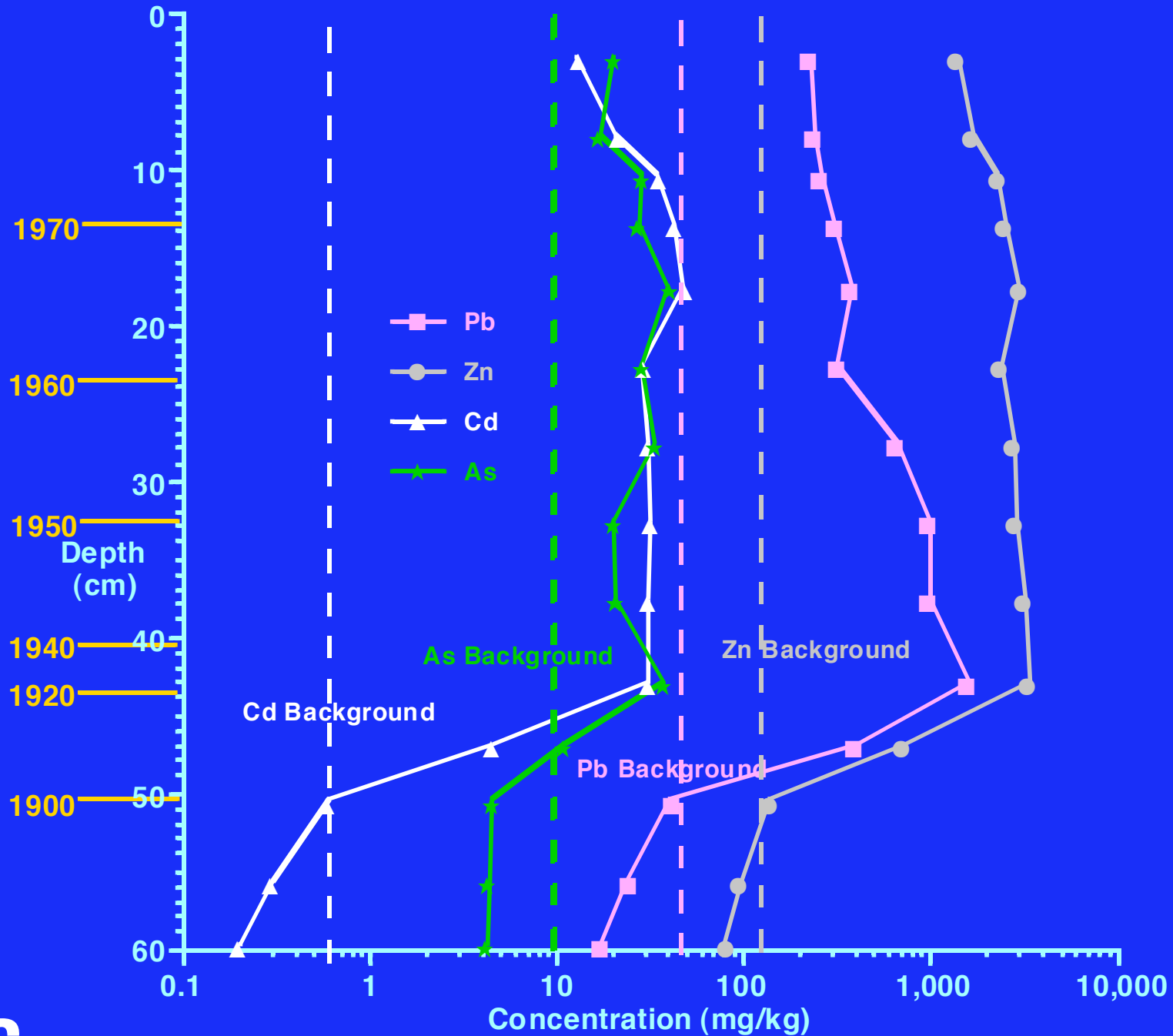
Average Downstream Enrichment Factors/Patterns for Selected Sediment-Associated Trace Elements in the Spokane River Basin



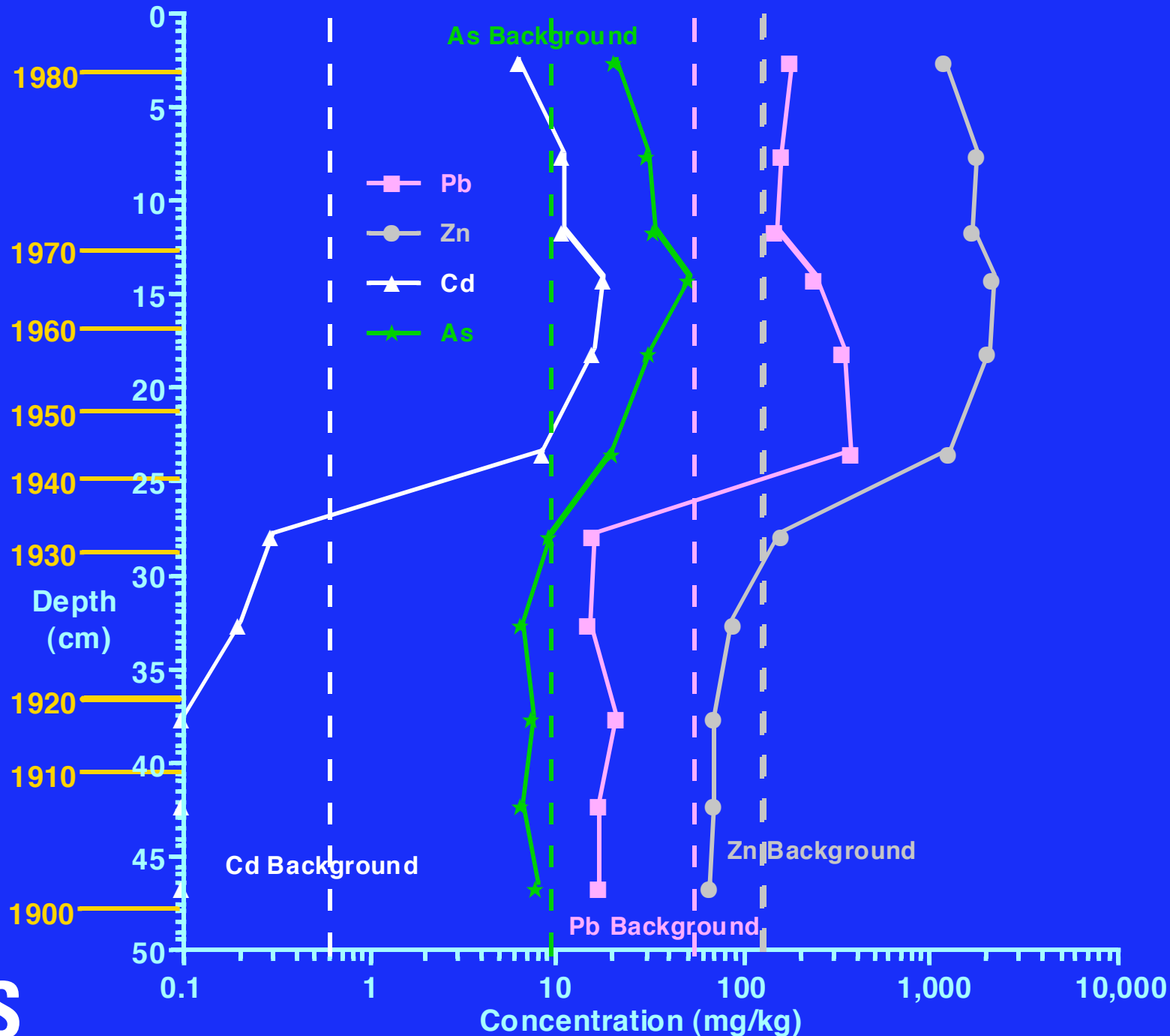
Core SRC 1 - Upper-Mid Long Lake



Core SRC 2 - Lower Long Lake



Core SRC 5 - Spokane River Arm of Lake Roosevelt



Conclusions

- **Substantial portions of the surface and subsurface sediments on or in 85% of the bed of Lake Coeur d'Alene are enriched in Ag, As, Cd, Cu, Hg, Pb, Sb, and Zn.**
- **The Coeur d'Alene River appears to be acting as a point source for the delivery of the majority of the trace element-rich sediments to the lake.**
- **There appears to be some 75 Mt of trace element-rich bed sediments in Lake Coeur d'Alene with masses ranging from a high of 470,000 tonnes of Pb to a low of 260 tonnes of Hg.**

Conclusions con't.

- Based on the presence of a Mt. St. Helen's ash layer, three dates based on ^{137}Cs activity, and calculated sedimentation rates for a core from Lake Coeur d'Alene, the age of the onset of trace element enrichment appears to fall between 1895 and 1910.
- The onset of trace element enrichment appears to coincide with the onset of silver mining in the area.
- Surface sediments in the Spokane River basin also are enriched in Pb, Zn, As, Cd, Sb, and Hg; the presumptive source for the enrichment is the Coeur d'Alene River Basin.

Conclusions con't.

- On average, trace element enrichment in the Spokane River Basin decreases downstream, apparently reflecting both increased distance from the source, as well as dilution with locally derived, but unenriched material.
- Subsurface sediments in the Spokane River Basin also are enriched in Pb, Zn, As, Cd, Sb, and Hg relative to local baseline levels.
- Based on ^{137}Cs and excess ^{210}Pb dating, trace element enrichment began in the middle of the basin between 1900 and 1920, contemporaneously with Lake Coeur d'Alene.

Conclusions con't.

- The retention of at least some of the trace element-rich sediments in the middle portion of the Spokane River Basin may be due, at least in part, to the construction and closure of dams on the Spokane River.
- Also, based on ^{137}Cs and excess ^{210}Pb dating, trace element enrichment in the most downstream section of the Spokane River Basin began much later, between 1930 and 1940, probably as a result of the closure of Grand Coulee Dam.