Mercury, Arsenic and Selenium in Channel Catfish from the Allegheny, Monongahela and Ohio Rivers near Pittsburgh PA: Implications for metallotoxin source identification and fish consumption by local anglers.

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Why Fish in Public Health Work? The Basis for Biomonitoring Ecological Receptors as Sentinels for Water Quality and Human Exposure

- Contaminants in sediments and water bioaccumulate in aquatic food chains and concentration levels can be magnified well over 100X in higher trophic level feeders.
- Lipophylic chemicals are more rapidly exchanged between the water and organism than they are excreted or biodegraded by the organism.
- The channel catfish is a high fat, higher trophic level, piscivirous fish (piscivirous fish eat other fish).
- Fish classically bioaccumulate methylmercury and selenium and lipophylic pharmaceutical estrogens and estrogen mimicking chemicals such as nonylphenol.
- Semi-subsistence anglers eat appreciable quantities of river caught fish and recreational anglers are also exposed to toxins in fish through ingestion.
- Fish are the “Canaries in the Coal Mine” for water quality. Biomonitoring fish can lead to informed hypothesis regarding deposition of air contaminants as well as sources of water pollution.

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Initial Hypothesis

- Channel catfish caught near the Edger Thompson Works, on the Monongahela River and at Point State Park will have significantly higher fillet levels of Hg, Se and As than catfish from the Allegheny River at Highland Park Dam because of legacy and current iron and steel pollution and the because there are over 300 combined and sanitary sewer overflows (CSO/SSO) within a 10 mile radius of these points.
- Channel catfish caught near the Kittanning Dam, approximately 40 miles upstream from Pittsburgh, will contain the lowest levels of Hg, As and Se in flesh since the closest industrial production sites are far upstream of this site (Oil City PA) and only one CSO/SSO is within 3 miles of this site.

Fisherman from focus groups suggest that they would eat fish from the Kittanning PA area because they come from water with far less pollution loads than the rivers nearer to Pittsburgh.

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Objective A:

To determine if the levels of mercury, arsenic and/or selenium in channel catfish fillet vary by locations of catch in Southwestern PA and with store-bought fish.

Objective B:

To determine if we can use catfish as sentinels to identify the ultimate source(s) of contaminants in water.

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Objective C:

To establish the safety of channel catfish as a food for semi-subsistence and recreational fishers.

Objective D:

To engage individual anglers and fishing groups in a Community Based Participatory Research project.

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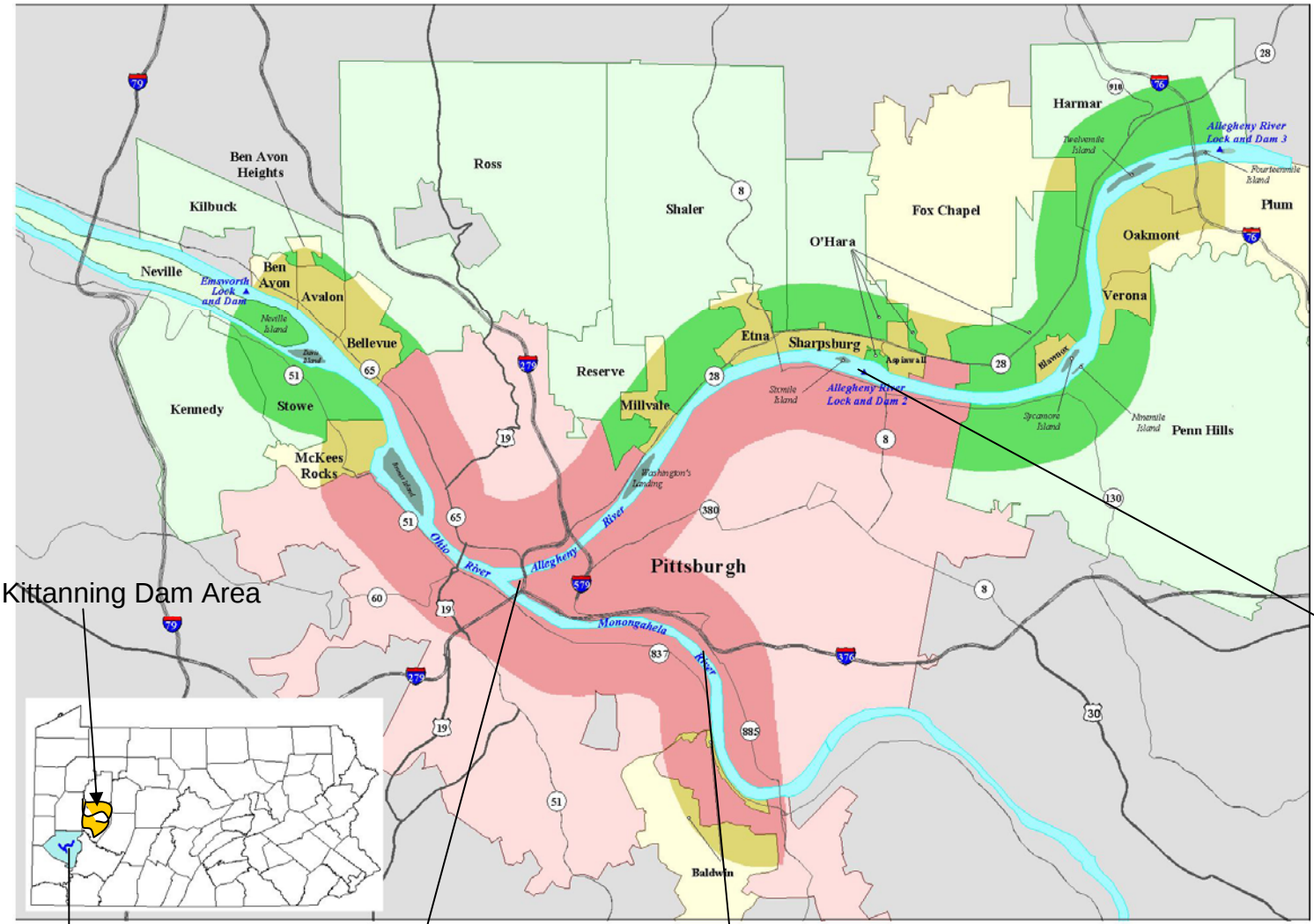
Locations of Channel Catfish Sampling in Southwestern Pennsylvania



Kittanning Dam Area

Three Rivers Area-Allegheny County

Point State Park

Monongahela River near the U. S. Steel Edger Thompson Works-Braddock Dam

Highland Park Dam

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Methods

Fish were caught by rod and reel method using a Community Based Participatory Research approach (scientists catch smaller fish than anglers). Local anglers were recruited to catch fish.

The geo-coordinates of all fish collection locations were determined on a Garmin, GPS Map 60CSx device and were used in ArcView 9.2 map production.

10-15 catfish were caught at each location and 10 channel catfish were store-bought.

0.5 gram of catfish fillet was microwave digested in nitric acid. As and Se were analyzed by collision cell ICP-MS with calibration by the method of standard additions. Mercury was analyzed by isotope dilution cold vapor ICP-MS.

Data were log-transformed and analyzed by ANOVA with Tukey post hoc tests using SPSS 15.0.

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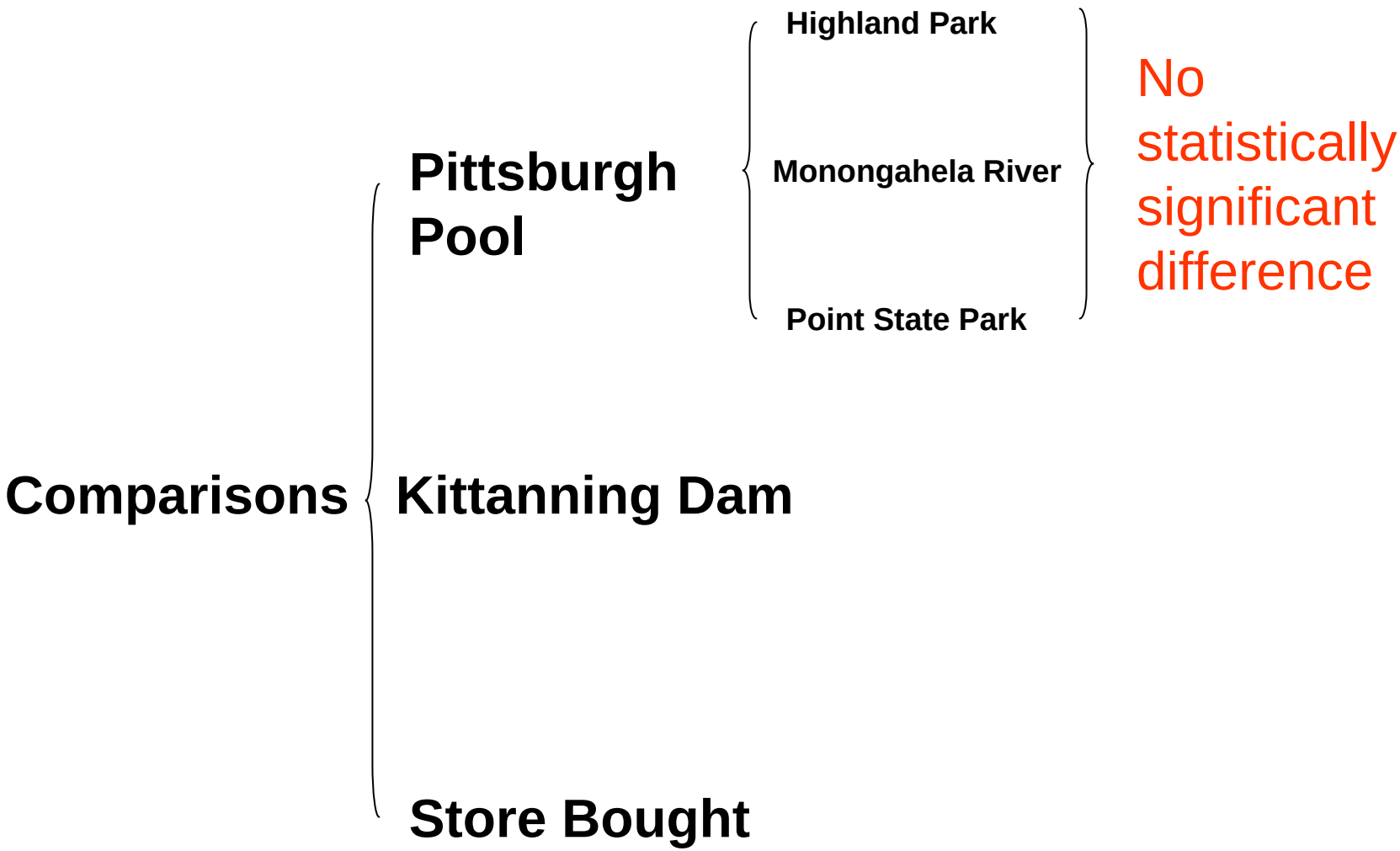
ANOVA Tukey Post Hoc Comparisons



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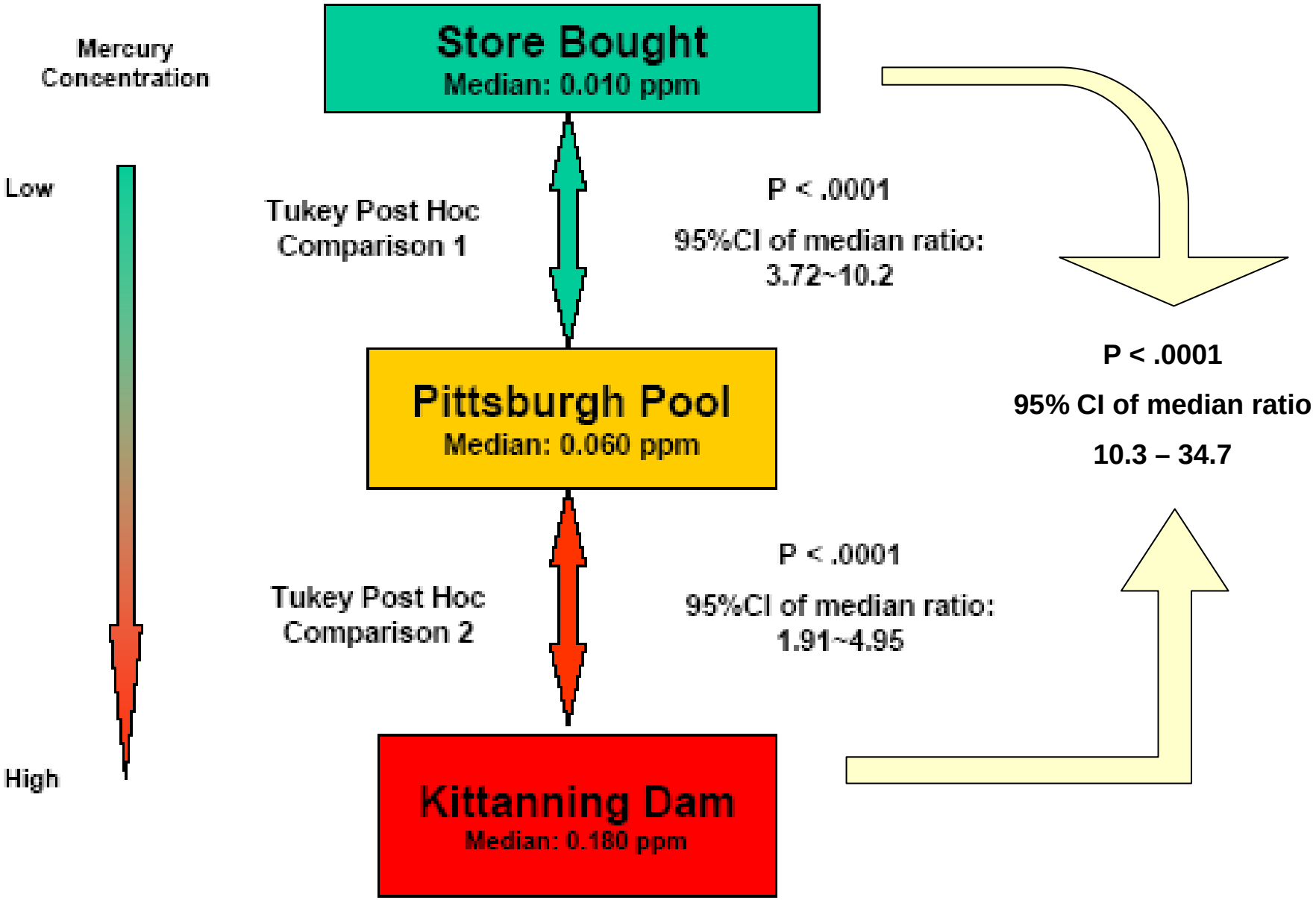

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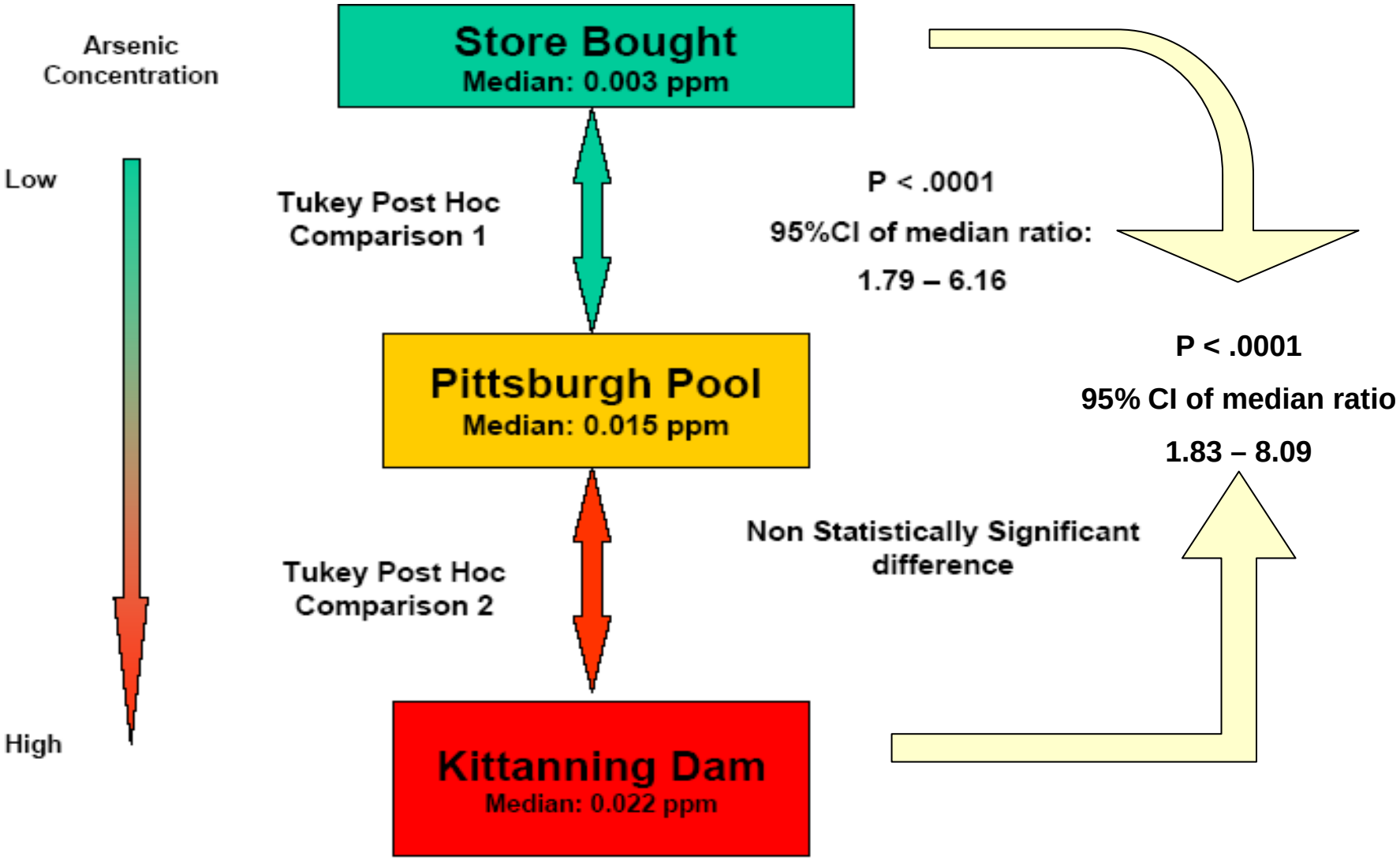

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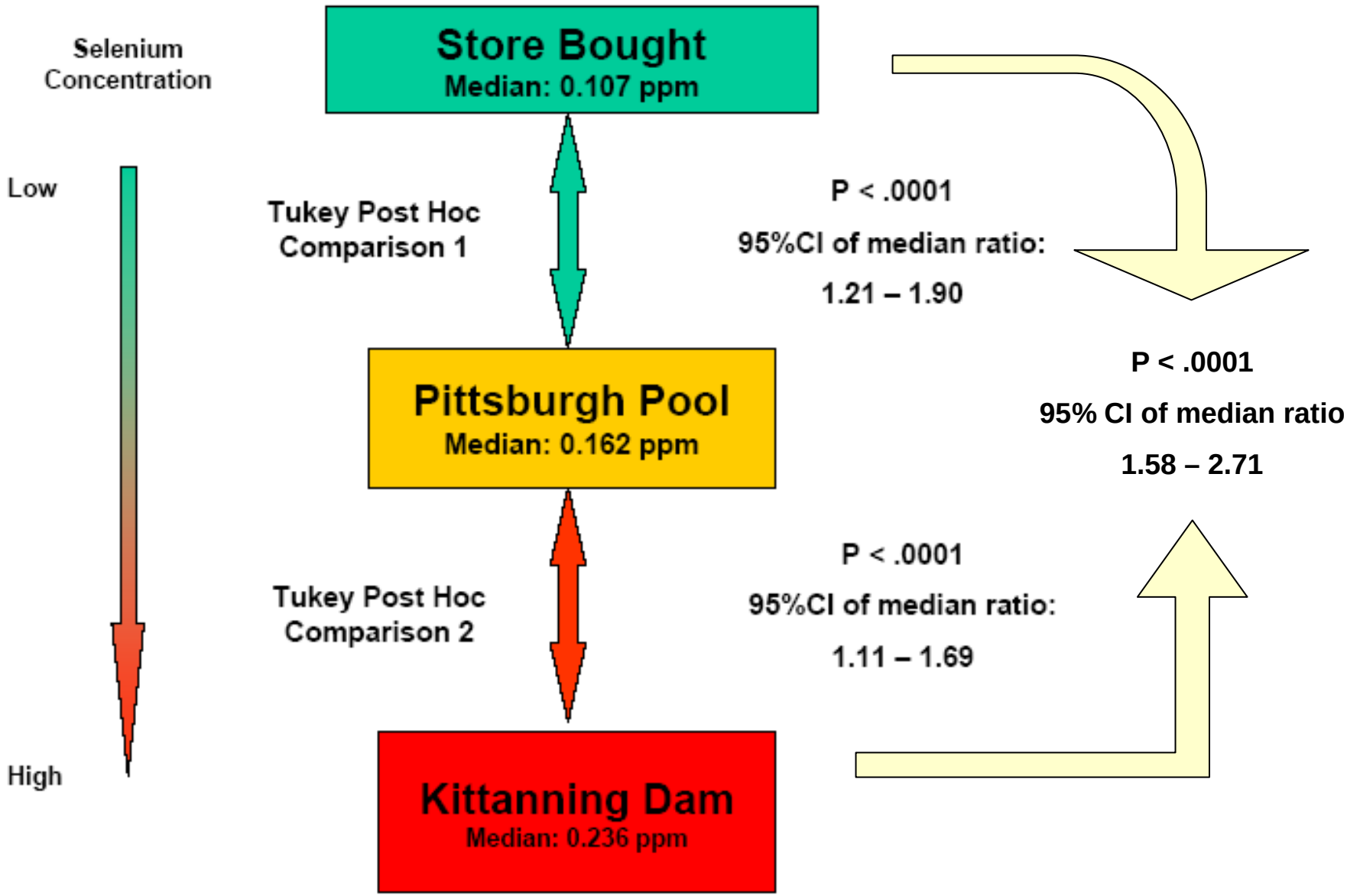

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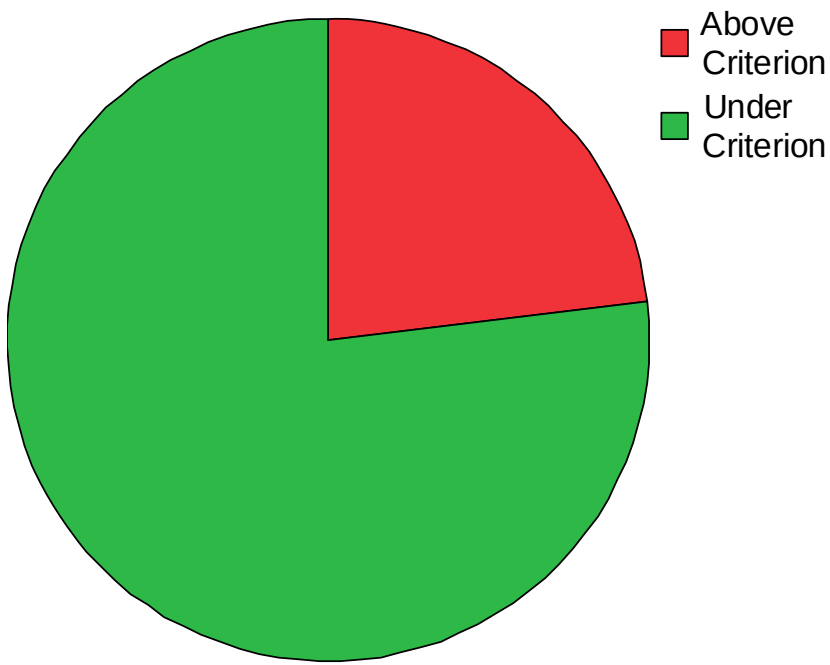
Percentage of Channel Catfish Samples Caught in the Kittanning Dam Area Over EPA Fish Tissue Residue Criterion for Mercury



EPA fish tissue residue criterion = 0.3 (mg methylmercury/kg fish)

23% of samples caught within 500 yards of the Kittanning Dam had higher mercury levels than the EPA criterion.

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Weight and Length of River Caught Channel Catfish by Location

Locations		Mean of Weight (g)	Mean of Length (cm)
Pittsburgh Pool 	Highland Park Dam	1219.2	48.5
	Monongahela River	1018.9	46.1
	Point State Park	1028.3	45.9
Kittanning Dam Area 		470.1	37.1

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Mean of Weight

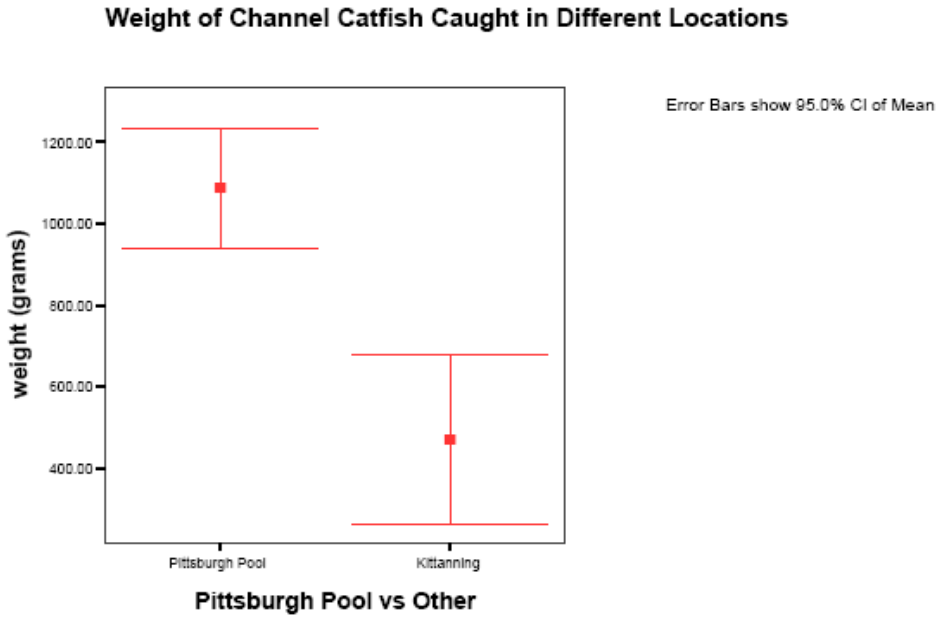
Pittsburgh Pool: 1086.8g

Kittanning Dam: 470.5g

T-Test P-value < 0.0001

95% CI of Mean Diff:

[343.8, 888.7] g



Mean of Total Length

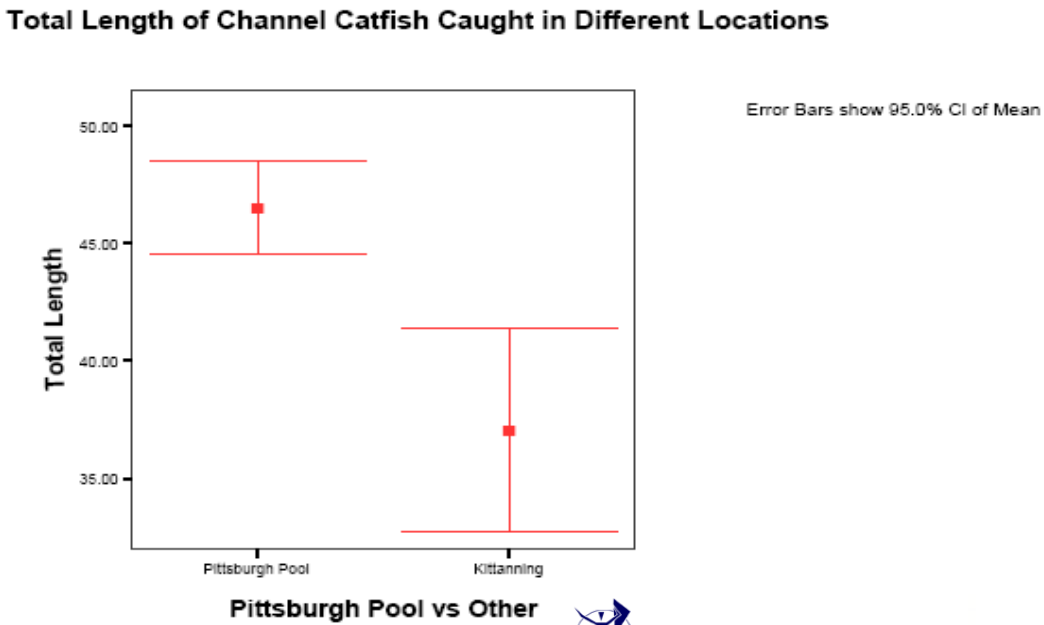
Pittsburgh Pool: 46.5 cm

Kittanning Dam: 37.1 cm

T-Test P-value < 0.0001

95% CI of Mean Diff:

[5.4, 13.5] cm



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Pearson Correlation Coefficient Between As, Se and Hg

	Arsenic Vs Selenium	Selenium Vs Mercury	Arsenic Vs Mercury
Correlation Coefficient	0.07	0.50	0.16
P-value	0.574	0.001	0.205

Significantly positive correlation between Se and Hg concentrations in channel catfish tissue.

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Risk Assessment for Population Subgroups Consuming Channel Catfish Caught Near Kittanning Dam

Study Population

- Children 3-8 yrs
- Children 9-15 yrs
- Women of childbearing age
- Adults

Exposure Frequency → 1 meals/day, 4 meals/week

Intake Rate (kg fish/meal)

- 0.114 kg for children <9 yr
- 0.228 kg for others

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$$ADD = \frac{C_{fish} * IR_{fish} * EF * ED}{BW * AT}$$

Where

ADD = Average Daily Dose (ingestion of contaminated fish, mg/kg-day)

C_{fish} = Concentration of contaminants in fish (mg/kg fish)
95% CI: (.154 - .282) mg/kg fish (Kittanning Area)

IR_{fish} = per capita intake rate of fish (kg fish/meal)

EF = exposure frequency (meals/day)

ED = exposure duration (day/week)

BW = body weight (kg) and

AT = averaging time (days/week)

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The hazard quotient is be calculated by:

Hazard Quotient = ADD/RfD

Where,

RfD: the oral reference dose (10^{-4} mg/kg-day)

Hazard Quotient
- >1, excess non-carcinogenic health risk
- <=1, no excess non-carcinogenic health risk

Subgroup	ADD (range, mg/kg-day)	Hazard Quotients (range)
3-8 yr	4.6×10^{-4} - 8.3×10^{-4}	5 – 8
9-15 yr	4.4×10^{-4} - 8.1×10^{-4}	4 – 8
Women of childbearing age	3.1×10^{-4} - 5.7×10^{-4}	3 – 6
Adults	2.9×10^{-4} - 5.2×10^{-4}	3 – 5

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Conclusions

- Hg, As and Se concentrations in channel catfish fillet were not significantly different in the Pittsburgh Pool as originally hypothesized. Channel catfish caught in highly legacy contaminated areas of the Monongahela River did not differ in flesh concentrations of Hg, As or Se from fish caught in the same pool but in the Allegheny River portion of the pool.

- ✓ The Pittsburgh Pool may be considered a locked water system due to the lock and dam system on all area rivers.
- ✓ Pollution discharged into the Pittsburgh Pool from industrialized sources and sewer overflows may be evenly distributed through the water body.
- ✓ Fish caught at each location within the Pittsburgh Pool may range throughout the pool.

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Conclusions

- The original hypothesis that fish from Kittanning would be lower in the monitored contaminants than fish from heavily contaminated legacy areas nearer to Pittsburgh is rejected.
- Hg and Se levels in catfish fillet tissue did vary significantly between the Pittsburgh Pool and 40 miles upstream at the Kittanning Dam. Fish from the Kittanning area had approximately 3 and 1.5 times the Hg and Se, respectively than fish from the Pittsburgh area.

- ✓ Modeling of area coal-fired power plant emissions and deposition patterns, wastewater effluent containing high levels of Se and the leaching and runoff from piles of flyash stored near the Allegheny River or within the watershed is hypothesized as being the source of the higher Hg and Se levels in fish in the Kittanning Dam area.
- ✓ As concentrations in fish flesh may not be higher in the Kittanning fish vs. Pittsburgh fish because As is not classically bioaccumulated in fish and is thought to be highly internally regulated.
- ✓ Nevertheless, the median As concentration in both Kittanning and Pittsburgh Pool fishes were between 1.8 to 8.1 times (with 95% confidence) the median As concentration of storebought fish (farm raised-Georgia, USA).

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Public Health Implications

- Anglers and their families who consume channel catfish from Kittanning are at significantly higher risk of health effects (mainly neurological health endpoints) from ingestion of Hg.
- This risk assessment may actually represent an underestimation of true risk since fish were taken in the fall season and not during the summer when bioaccumulation rates are highest. Some depuration may have occurred in fish.
- Channel catfish are not the highest trophic level in this riverine system. Walleye and pike, more prized by anglers as table fare, are expected to have even higher levels of Hg in fillet tissue.
- High mercury and selenium levels in fish from Kittanning as well as the elevated As levels over store-bought are thought to occur because of pollution from coal powered electrical generation facilities. This implies that people living in the affected areas near Kittanning may have high total body burdens of Hg and other heavy metals through inhalation and ingestion of other locally grown food and untested drinking water. We plan a program of Hg and other metal and metalloid biomarker assessment in discrete population groups living near Kittanning to begin to assess total exposure to Hg, As, Se and other metals associated with power plant emissions.

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Public Health Implications

- More fish need to be sampled from more sampling locations on the river so that more specific fish consumption advisories can be issued to anglers.
- The Community Based Participatory Research approach performed beyond our expectations and energized the local fishing community to become stewards of the rivers.
- Because of the publication of the research results in local public media, local anglers are more actively energized to volunteer in the upcoming research in Spring, 2008, using fish as sentinels to further identify multiple pollution sources.

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Acknowledgements

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