# MERCURY, ARSENIC AND SELENIUM IN CHANNEL CATFISH CAUGHT IN SOUTHWESTERN PENNSYLVANIA; IMPLICATIONS FOR COAL-FIRED POWER PLANT EMISSION SOURCE IDENTIFICATION AND FISH CONSUMPTION SAFETY

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MERCURY, ARSENIC AND SELENIUM IN CHANNEL CATFISH CAUGHT IN SOUTHWESTERN PENNSYLVANIA; IMPLICATIONS FOR COAL-FIRED POWER PLANT EMISSION SOURCES IDENTIFICATION AND FISH CONSUMPTION SAFETY

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Abstract

This study recruited local anglers to catch catfish from 3 locations within the Pittsburgh Pool and an upstream location on Allegheny River at Kittanning Dam to compare the As, Hg and Se levels in catfish fillet. The objectives were: to find if there exist locational differences of As, Hg and Se levels in catfish flesh; use catfish as sentinels to identify the sources of pollution; determine if any catfish had mercury levels above the EPA criterion; and assess the consumption risk for semi-subsistence anglers and their families. Local store-bought catfish are also compared with river-caught samples.

Fish tissue was prepared following EPA method 3052. As and Se were analyzed by collision cell ICP-MS with calibration by standard addition methods. Mercury was analyzed by isotope dilution cold vapor ICP-MS. Data were log-transformed and analyzed by ANOVA with Tukey Post-Hoc Comparisons.

There were no significant differences in As, Hg and Se concentrations among the Pittsburgh Pool catch, so we combined these data. Significantly higher levels of Hg and Se were found in Kittanning-caught fish even given significantly smaller fish sizes compared to those caught in the Pittsburgh Pool. The store-bought fish were significantly lower in As, Hg and Se than those caught in the Pittsburgh Pool. In addition, 23% of samples caught in Kittanning had higher mercury levels than the EPA criterion. Hg and Se levels in samples are significantly positively correlated. Using upper 95% CI of mean mercury level in Kittanning-caught catfish flesh, the maximum monthly allowable fish consumption limit for adult anglers is 4 meals, for children below 16 years old is 2 meals, and for women of childbearing age is 3 meals.

**Conclusions:** The Hg and Se levels in catfish in Pittsburgh Rivers vary significantly by location. Fishers are exposed to higher Hg and Se levels when they eat the fish caught near Kittanning and Pittsburgh pool than bought from the fish market.

**Public health implications**: River areas upstream from Pittsburgh may have higher mercury levels than those nearer Pittsburgh because of deposition of emissions from coal-fired power plants. Location specific fish consumption advisories are needed for local fishers.

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## PREFACE

**The project is funded by the DSF Charitable Trust, the Heinz Endowments and the Highmark Foundation, Healthy People-Healthy Communities Project, through the Center for Environmental Oncology of the University of Pittsburgh Cancer Institute. Additional funding was also provided by the Centers for Disease Control and Prevention, Environmental Public Health Tracking Network (EPHT) through the University of Pittsburgh Academic Center of Excellence EPHT.**

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# 1.0 INTRODUCTION

Fish consumption has generally increased in the United States over the last few years, largely because of the perceived and documented nutritional benefits of eating fish and the availability of a wide range of fish in supermarkets and fish markets. Fish provide omega-3 fatty acids, which reduce cholesterol levels and the incidence of heart disease, stroke, and preterm delivery (Wiener 1995; M. Daviglus 2002; Patterson 2002). These benefits are particularly correlated with consumption of cold-water fish from regions such as the Bering Sea and North Pacific. As an important source of protein, river-caught fish is the major diets for semi-subsistence anglers, who often belong to minority and are at low socio-economical status (Volz, C.D, 2007). Besides the nutritional aspects, fishing is also a popular pastime sport, and is an important aspect of the culture of many groups of people throughout the word, especially in regions where the fishing season extends to many months. (J. Burger 1992; J. Burger 1993; F. Toth Jr. 1997; Burger 2002; B. Knuth 2003). With hundreds of miles of waterways winding through this region, there are tremendous opportunities for fishing in the city and around the Pittsburgh Region. According to the report of Pennsylvania Fishing and Boat Commission, in 2006, 133864 fishing licenses and permits were sold in study area (PFBC, 2007).

Recently, however, there has been widespread concern about possible adverse health effects from consuming fish with toxic contaminants. Concern is particularly high for developing fetuses because chemicals and metals can be transferred across the placenta to the fetus during maternal exposure (B.L. Gulson 1997; B.L. Gulson 1998). Effects on human health from exposure to mining-derived metals have been documented, as have effects on aquatic organisms and wildlife (Beyer et al., 2004; Shmitt e al., 1993, Schmitt, Whyte, Brumbaugh, & Tillitt, 2005; Wildhaber et al., 2000; Yoo & Janz, 2003). For example, there is a positive relationship between the mercury level in fish, fish consumption by pregnant women, and deficits in neurobehavioral development in children (Kjellstrom 1986; Kjellstrom 1989; Davidson 1995; Myers 1995a; Myers 1995b; Myers 1995c; Grandjean 1997; Myers 1997; Davidson 1998). Metals or metalloids released from anthropogenic activities, such as the coal burning process used to generate electricity, only change forms (chemical and physical states) and are not destroyed during combustion, the amount of metals in the original fuel will be equal to the amount of metals found in the ash plus those metals emitted from the stacks and metals in effluent or runoff water (Harold F. Hemond 1999). Metals deposited in aquatic environment, lead to high metal concentrations in sediments. A report has demonstrated that the sediment arsenic concentrations in a coal ash setting basin and downstream drainage in South Carolina were as high as 70.8 and 116.6 ug/g dry weight respectively (Rowe et al., 1996). Metal/metalloid contaminants in aquatic environment can be biotransformed from inorganic forms to organic forms by bacteria and bioaccumulate or accumulate in the aquatic food chain. Piscivorous fish, like channel catfish can bioaccumulate high metal concentration through the food chain, gill transfer, and through skin absorption.

The water quality of Pittsburgh’s Three Rivers has been improving since the 1980s due to the Clean Water Act and the declination of iron and steel industry. This has resulted in an increase in recreational fishing and subsistence fishing within the Three Rivers. Although the water quality has improved, river sediments can be a persistent reservoir of particle-bound contaminants and might act as a source of contaminants that in turn, can cycle through the food web and bioaccumulate in high tropic level fish. Moreover, coal/oil is the main fossil fuels used to produce electricity in Pittsburgh. According to the statistics from Reliant Energy, Inc.(Reliant Energy), there are 7 coal/oil-fired power plants owned by Reliant Energy in the vicinity of Pittsburgh city, with total electricity generation capacity of 2470 megawatts. Heavy metal contaminants are emitted from those power plants and deposited within local rivers. Additionally, other industrial discharge flows are also affecting the metal concentrations in water. Thus, the local anglers are raising concern about fish consumption because of the contaminants released from different sources along Pittsburgh's three rivers. The deposition of power plant emissions can result in increased Hg, As and Se levels in catfish and potentially affect anglers and their families' health through fish consumption.

To assess local angler's exposure to metal contaminants through fish consumption, and to identify the possible contaminant sources, this study chose catfish as a biomonitor and selected several locations where local anglers said they preferred fishing. We wanted to explore the As, Hg and Se levels in fish tissue caught from different sites. We wanted to determine if we can use catfish as sentinels to identify the environmental contaminant sources and we were interested in whether there were location effects that might affect risk to consumers of catfish.

## 1.1 BACKGROUND

Coal is the main fossil fuel used to produce electricity in Southwestern Pennsylvania and the Tri-State Area. Several power generation stations are major contributors to the air pollution in this area. Conemaugh Generating Station located in Indiana County, Cheswick Generating

Station located in Springdale, 18 miles northeast of Pittsburgh, Elrama Generating Station located along the Monongahela River, 25 miles southwest of Pittsburgh, and Seward plant, located 80 miles east of Pittsburgh near Johnstown, Pennsylvania all add As, Hg and Se through stack emissions, fly ash leaching, and water effluent that ultimately bioconcentrate in our aquatic system. Discharges exceeding PA Department of Environment Protection (DEP) and EPA standards from those sources, including wastewater and air contaminants continuously raise public concern. An example is the Conemaugh Generating Station which, discharges 3 million gallons of wastewater a day containing selenium, manganese, aluminum, boron and iron in concentrations that frequently exceed pollution limits set by the EPA and enforced by the state to protect water quality in the Conemaugh River. The Conemaugh River flows to the southwest and finally joins with the Allegheny River. Reliant Energy was sued, accused of polluting the Conemaugh River by the Pennsylvania State DEP in April, 2007 (Don Hopey, Pittsburgh Post-Gazette, April 12, 2007).

Another example is Edison International's EME Homer City power plant, a 1,884 megawatt coal-fired power plant in Indiana County which discharges excessive levels of selenium, suspended solids and wastewater on numerous occasions since 2001 in violation of the Pennsylvania Clean Streams Law. The Pennsylvania Department of Environmental Protection said the illegal water discharges from the power plant were linked to a smokestack "scrubber" system designed to reduce air emissions of sulfur dioxide, a major component of acid rain. And in July, 2007, Edison International's EME Homer City power plant is fined $200, 000 by the Pennsylvania Department of Environmental Protection for discharging excessive levels of selenium, suspended solids and wastewater on numerous occasions into the Conemaugh drainage (Don Hopey, Pittsburgh Post-Gazette, July 14, 2007).

## 2.0 WHY DO WE STUDY ARSENIC, MERCURY AND SELENIUM

### 2.1 MERCURY, ARSENIC AND SELENIUM IN ENVIRONMENT

Arsenic, mercury and selenium are naturally occurring elements that are found in environmental media such as air, water, and soil, as well as biota. They are also released into the environment by anthropogenic sources, including fossil-fuel-fired electric utility plants. During combustion the volatile species in the coal evaporate in the boiler and recondense as sub micrometer aerosol particles, or on the surfaces of ash particles as the flue gas cools. The concentrations of arsenic, mercury and selenium increase markedly with decreasing particle size from bottom ash through fly ash, from control devices, to stack fly ash (stack dust) emitted into the atmosphere (PACYNA 1987). More than 90% of the mercury in coal is released as vapor (Billings and Harley 1973). Combustion temperature in the boiler is one of the key parameters affecting the amounts of metals released. Table 1 shows the concentrations of arsenic and mercury in coal and crude oil (PACYNA 1987).

Table 1. **Concentrations of As and Hg in Coal and Crude Oil (in µg/g)**

| Metal | Coal | Crude oil |
|---|---|---|
| **As** | 0.34-130.0 | 0.0024-1.63 |
| **Hg** | 0.01-1.6 | 0.014-30.0 |

The arsenic air concentrations in areas near some combustion facilities can be significantly higher than uninfluenced areas, as evidenced by measurements taken outside and inside of the United States (Eisler 1994; Schudlark 1994; Wu 1994).

Table 2. **Reported Arsenic Air Concentrations in Remote Area and near coal-fired Power Plant**

| Type | Mean ($ng/m^3$) | Max ($ng/m^3$) | Reference |
|---|---|---|---|
| Remote areas | <21 | | Eisler 1994 |
| Kaarvatn, N.Europe | 0.5 | 1 | Pacyna et al. 1989 |
| Nordmoen, N. Europe | 1.2 | 2 | |
| Prestebaake, N. Europe | 0.5 | 1.8 | |
| Chesapeake Bay (Wye, Elms) | 0.69, 0.625 | 1.96, 1.56 | Wu et al. 1994 |
| Near coal-fired power plant (Czech) | 19000-69000 | | Eisler 1994 |
| Urban areas | <160 | | |

In addition to the fly ash emitting contaminants and particulates into the atmosphere, As, Hg and Se are also released into the aquatic environment by wastewater effluents discharge and the improper storage of coal ash, allowing contaminants to leach into groundwater and eventually reach surface water. Waste sediment settling ponds are a major source of selenium transfer to sediment and water.

After entry into the aquatic environment, inorganic arsenic, mercury and selenium will be transformed to organic forms by bacteria. Organic forms of mercury and selenium will bioconcentrate and bioaccumulate in aquatic organisms (Figure 1). Organic formed arsenic does not appear to bioaccumulate or bioconcentrate in freshwater finfish and is much less toxic than inorganic arsenic (EPA 1998). The species of arsenic present in fish appears to be somewhat variable. For freshwater fish, it is conservatively assumed that 10% of the arsenic is inorganic arsenic (EPA 1998).

Metallic mercury is converted to methylmercury by the methylating action of bacteria. Methylmercury is highly toxic and can build up in fish, shellfish and animals that eat fish including birds, mammals and humans. Fish and shellfish consumption are the main sources of methylmercury exposure to humans. The levels of methylmercury in fish and shellfish depend on what they eat, how long they live, how high they are in the food chain and the concentration of methylmercury in water and sediments. Figure 2 shows the process of mercury's emission, deposition, transformation and bioaccumulation.

Like mercury, selenium can be bioaccumulated by aquatic organisms and may also biomagnify in aquatic organisms. One study showed that the Se concentrations in fish from sites receiving seepage and effluents from fly ash disposal ponds were significantly greater than those in fish from upstream, where Se concentrations were near background concentrations (Besser, Giesy et al. 1996).

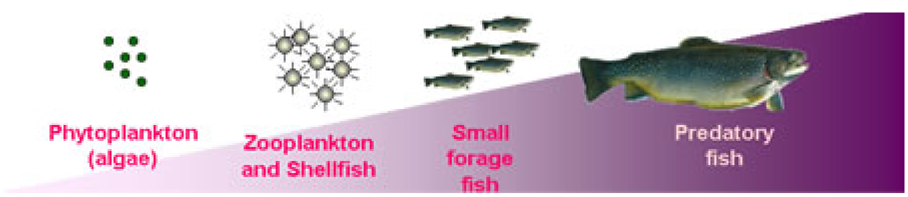


Figure 1. **Metal Bioaccumulation in Food Chain**

(Figure cited from http://www.epa.gov/mercury/exposure.htm)

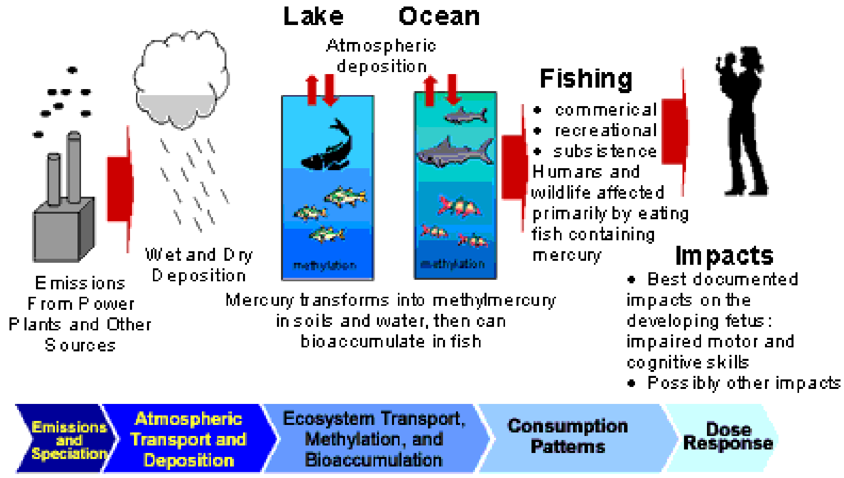


Figure 2. **Fate and Transport of Mercury in Environment**

(Figure cited from http://www.epa.gov/mercury/exposure.htm)

Given the historical anthropogenic impacts to which the Three Rivers have been subjected over the century, especially from the iron and steel, foundry and power plant operations, the contaminants of concern in this area are well known. In the Pittsburgh Fish Consumption project, contaminants of concern analyzed in fish tissue samples included arsenic, copper, selenium, mercury, barium, lead and zinc. Of those contaminants As, Hg and Se are of special concern; among them Hg and Se are given off during coal combustion and bioaccumulate with each aquatic tropic level. Arsenic is also associated with coal combustion and ash storage.

## 2.2 TOXICOLOGY PROFILE OF MERCURY, ARSENIC AND SELENIUM

### 2.2.1 Mercury

The nervous system is sensitive to all forms of mercury. Methylmercury and metallic mercury vapors are more harmful than other forms, because more mercury in these forms reaches the brain. Exposures to high levels of metallic, inorganic, or organic mercury can permanently damage the brain, kidneys, and developing fetus. Effects on brain functioning may result in irritability, shyness, tremors, changes in vision or hearing, and memory problems (ATSDR 1999). The first documented widespread human methylmercury poisoning occurred in Minamata, Japan, between 1953 and 1960. The consumption of contaminated fish and seafood from Minamata Bay where waste containing mercury were directly discharged from an industrial plant caused approximately 2,200 Minamata disease cases in adults. The most common clinical signs observed in adults were paresthesis, ataxia, sensory disturbances, tremors, impairment of hearing and difficulty in walking (Takeuchi et al. 1975). In the case of maternal exposure, symptoms didn't appear until 5 to 8 years after the birth of child. A number of children were born with congenital cerebral palsy. These children experienced symptoms such as mental retardation, primitive reflex, cerebellar ataxia, disturbance in physical development and nutrition and other problems (Harada, 1995). Because almost all of the mercury the fish take from the water will be transformed to organic forms (Bloom 1992; Akagi 1995; Becker 1995; Kim 1995; USEPA 2006), in this thesis, we will focus on discussion of the toxic effects of methylmercury.

### 2.2.2 Arsenic

Analysis of the toxic effects of arsenic is complicated by the fact that arsenic can exist in several different valence states and many different inorganic and organic compounds. Most cases of human toxicity from arsenic have been associated with exposure to inorganic arsenic. A number of studies have noted differences in the relative toxicity of these compounds, with trivalent arsenites tending to be somewhat more toxic than pentavalent arsenates (TB. 1960; Byron WR 1967; CC. 1981; Sardana MK 1981; Maitani T 1987a). Because it targets a number of metabolic processes, arsenic affects nearly all organ systems of the body by different exposure pathways. By acute ingestion exposure, inorganic arsenic can cause vomit, diarrhea, gastrointestinal hemorrhage, and death. The chronic non-carcinogenic effects from oral arsenic exposure include black-foot disease (Tseng 1977), gastrointestinal lesions(Armstrong CW 1984; Bartolome B 1999; Lee DC 1995), hematological effects and renal effects (ATSDR, Toxfile for As, 2005). Arsenic is known to cause cancer in humans. Ingested inorganic arsenic is strongly associated with lung and skin cancers and may cause other cancers in organs such as the bladder, kidneys, and liver (ATSDR 2005). Although organic arsenicals are usually viewed as being less toxic than the inorganics, several methyl and phenyl derivatives of arsenic that are widely used in agriculture are of possible human health concern. Several organic arsenicals tend to accumulate in planktivorous fish species (and also sculpins, Cottus spp.) to a greater degree than in other fishes (Wageman 1978; Spehar, Fiandt et al. 1980; Hunter 1981; Schmitt 1990) and can be further accumulated by fish (Spehar, Fiandt et al. 1980; Hunter 1981). Although the organic arsenicals accumulated in fish tissue are not considered as essentially toxic, a study done by Lehmann and Ebeling et al (Lehmann, Ebeling et al. 2001) indicated that the main organic arsenic form in fish, represented by arsenonetaine, is not easily eliminated from human body after ingestion the contaminated fish.

### 2.2.3 Selenium

Eating a nutritious diet is adequate to assure meeting the Recommended Daily Allowance (RDA) for selenium, which is an essential elemental nutrient. However, selenium compounds can be harmful at daily dietary levels that are higher than needed. In epidemiological studies of populations exposed to high levels of selenium in food and water, discoloration of the skin, pathological deformation and loss of nails, loss of hair, excessive tooth decay and discoloration, garlic odor in breath and urine, lack of metal alertness and listlessness were reported (Yang et al., 1983, Yang et al., 1989b, Longnecker et al., 1991),. The seriousness of the effects of excess selenium depends on how much and how often selenium is eaten (USEPA 1986; ATSDR 1996). Selenium is extremely toxic to aquatic organisms. High selenium concentrations are believed to cause teratogenic deformities in fish, and massive reproductive failure (Lemly 1993; Lemly 1997). Selenium-exposed sunfish show histopathological and hematological abnormalities in both the kidney and liver (Sorensen, Bell et al. 1983; Sorensen, Cumbie et al. 1984).

# 3.0 JUSTIFICATION OF THE STUDY

## 3.1 THE PUBLIC HEALTH SIGNIFICANCE OF EATING CONTAMINATED FISH

Fish consumption is the major source for human exposure to mercury and selenium outside of occupational exposure and can be a major source of arsenic exposure depending on the fish flesh concentrations. The consumption of contaminated fish by humans has caused widespread health problems and related deaths worldwide, notably in Japan (Harada, 1995), Iraq (Amin-Zaki et al., 1974), New Zealand (Kjellstrom et al., 1986, 1989), Canada (Mckeown –Eyssen et al., 1983a, 1983b, 1983c), Seychelles (Myers et al., 1995a, b, c, Davidson et al., 1995, 1998) and South America (USEPA 2001). In the United States, approximately 840 sport-fish consumption advisories exist due to mercury contamination and the U.S. FDA advises that pregnant women limit consumption of top predators to be less than once a month. One study indicated that the blood mercury levels in fishermen who ate twice as much fish as a reference group were 10-15% higher than the control group (Svensson, Nilsson et al. 1995).

## 3.2 CATFISH CAN ACT AS A BIO-MONITORING MODEL

Channel Catfish are good indicators of ecological health and human fish consumption safety because they can be used as indicators of (1) the health of the catfish itself, (2) the species that prey upon the catfish, (3) the food web that the catfish is part of, (4) the community, and (5) humans that depend upon the catfish for food (J. Burger 2004). Channel catfish are piscivorous fish, meaning they eat other fish. They are at middle tropical levels in aquatic environment, and they can bioaccumulate the contaminants mercury and selenium, and accumulate arsenic. Also they are widespread, numerous, a popular sport fish commonly eaten by anglers. They pose a consumption risk to higher-level carnivores, such as raccoons, osprey, eagles and humans.

Channel Catfish are also useful as bioindicators of contamination. EPA determined that it is more appropriate to base the methylmercury criterion on a fish tissue residue concentration than on an ambient water concentration. This determination was partly based on the current scientific understanding of the fate of mercury and its conversion to methylmercury and its bioavailability (USEPA 2006). Additional considerations for using a methylmercury criterion in fish residue were the difficulties in measuring methylmercury in the water column and relating the levels to concentrations in aquatic organisms.

## 3.3 LOCAL ANGLERS REGULARLY CATCH FISH IN PITTSBURGH'S RIVERS, CONSUME THEM AND ARE POTENTIALLY EXPOSED TO AS, HG AND SE

Fishing is a popular sport for recreational anglers and also an important protein source for semi-subsistence anglers in southwestern Pennsylvania. Based on a report of the Pennsylvania Fishing and Boat Commission, in 2006, 133,864 fishing licenses and permits were sold in our study area, anglers in Allegheny County bought nearly half of these fishing licenses (PFBC, 2007). Channel catfish is one of the popular fish that is often eaten by local anglers. Many low-income individuals rely on fish for their dietary needs, and native people in northwestern

Pennsylvania have cultural traditions of consuming large quantities of fish. Also recreational anglers have a strong preference for fish instead of meat or poultry. Furthermore, the semi-subsistence anglers consume greater amounts of self-caught fish than the general recreational angler population, due to their reliance on fishing as a major or sole source of dietary protein for their families. Most semi-subsistence anglers in southwestern Pennsylvania are African-American, Asian or Amish (Volz, C.D, 2007). Thus, local anglers are potentially exposed to high contaminants levels from eating catfish caught from southwestern Pennsylvania Rivers.

In this study, we collected fish samples directly from local anglers fishing with rod and reel because a study done by Joanna Burger showed that the sizes of fish that scientists caught are different (smaller) from what subsistence and recreational fishermen collected (Burger, Gochfeld et al. 2006). Literature support that scientists should either engage subsistence and/or recreational fishermen to collect fish or mimic local fishing methods to ensure that the fish collected are similar in size and weight to those being caught and consumed by the target population and to ensure accurate risk analysis.

## 3.4 HYPOTHESIS

We hypothesized there were differences in As, Hg, and Se levels in Channel Catfish caught at sites within the Pittsburgh Pool; at the Highland Park Dam, Monongahela River (Braddock Dam) and Point State Park. We anticipated the highest As, Hg and Se levels at Monongahela River (Braddock Dam) because of the legacy industrial iron and steel production at the Edgar Thompson Works. We also hypothesized that levels of As, Hg and Se would be higher at the Point State Park than the Highland Park Dam because of the extremely high densities of combined sewer overflows and major wastewater treatment plant effluent release at the Point State Park site. If the concentrations of As, Hg and Se from catfish in those locations were homogeneous, we apriori decided to group the fish samples together in a category called Pittsburgh Pool and compare them with the fish caught at the Kittanning Dam, the supposed cleaner water site. The Pittsburgh Pool is defined as the river (lake) system created by the Highland Park Dam on the Allegheny River, the Braddock Dam on Monongahela River and the Emsworth Dam on the Ohio River. We hypothesized that the As, Hg and Se concentrations in catfish fillet from the Pittsburgh Pool would be higher than the concentrations in catfish from the Kittanning Dam area because Kittanning Dam is located 40 miles upstream from Pittsburgh on the Allegheny River and is not as disturbed by iron and steel, foundry or other industrial facilities as Pittsburgh Pool and only receives combined sewer overflows from 9 effluent pipes over a 4 mile span below the Kittanning Dam. Moreover, we purchased channel catfish samples from local fish market for comparison purpose. We thus further hypothesize that store-bought fish will have lower Hg, As and Se fillet concentration than fish caught within the Pittsburgh Pool and those caught near Kittanning because of the lack of industrial and municipal waste in waters breeding farm raised fish.

## 3.5 OBJECTIVES

There are several objectives in this study. First we want to know if we can use catfish as sentinels to determine the environmental contaminant sources of As, Se and or Hg. Secondly, we want to determine if there are locational differences in As, Hg and Se levels in catfish flesh. Thirdly, we want to determine the safety of channel catfish consumption for local anglers and their families. Lastly, because this is a community-based participatory research project, we also strove to actively engage recreational and semi-subsistence anglers to become stewards of the local rivers.

# 4.0 METHODS

## 4.1 STUDY AREA

We chose 4 locations to collect fish: at Highland Park Dam on the Allegheny River, at the Braddock Dam on the Monongahela River near the Edgar Thompson Steel Works, at the Point State Park and at the Kittanning Dam on Allegheny River, located in Armstrong County, 45 miles away from Pittsburgh Metropolitan area. We chose the Highland Park, Point State Park and Kittanning locations based on information from local anglers in interviews and focus group meetings. Local anglers preferred these fishing sites for reasons that differ. The Point State Park area is convenient for recreational fishing during business hours and provides an outlet for semi-subsistence anglers to fish who live on the North Side of Pittsburgh and have no transportation to fish elsewhere, the Highland Park area on the Allegheny River is preferred by many semi-subsistence anglers living in the Pittsburgh area because waters in the area are highly oxygenated due to the dam and water flow thus providing excellent fishing for catfish, walleye, sauger and other prized game fish for table fare, the Kittanning site was chosen because all interviewed anglers said they would eat fish from this area because they considered the water quality to be much better than even that at the Highland Park Dam.

Figure 3, Study Area and Sampling Locations shows the counties of the study area in Southwestern Pennsylvania, sampling locations and the major power plants within the study area. The data were obtained from http://www.pasda.psu.edu/ (PASDA). PASDA is the official public geospatial data clearinghouse for Commonwealth of Pennsylvania and Pennsylvania's node on the National Spatial Data Infrastructure, Geospatial One-Stop, and National Biological Information Infrastructure.


Figure 3. **Study Area and Sampling Locations**

## 4.2 COMMUNITY BASED PARTICIPATORY RESEARCH

This study is a Community Based Participatory Research project, it was structured to include the non-academic partners Clean Water Action of Western Pennsylvania (an environmental action group), Venture outdoors (a local non-profit that promotes guided outdoor activities including fishing excursions) and local fishers and angling clubs. Academic partners are the University of Pittsburgh Cancer Institute – Center for Environmental Oncology, the Graduate School of Public Health and School of Medicine at the University of Pittsburgh.

## 4.3 SAMPLING PROCESS

Started from September 2005, all the samples were collected by three ways. 6 anglers are recruited to catch fish along the rivers where we wanted them. We also recruited other anglers who were found fishing on the rivers and asked them for what they caught. We asked fish from the Saturday recreational fishing activities Venture Outdoors organized. Venture Outdoors is a partner of this project. We also purchased catfish from local fish market for comparison purpose. Totally, 63 samples were collected with about 13 samples for each location.

## 4.4 ANALYTIC METHOD

Each fish was weighted, measured, dissected, wrapped and then frozen immediately at –80 ℃ freezer. Fish fillet were dissected at 0℃ and then frozen in dry ice and sent to authorized lab to do metal analysis. Approximately 0.5 g fish tissue (wet weight) was weighted on a five place balance into a tared microwave digestion vessel and 10 ml optima $HNO_3$ was added and the exact acid addition was recorded by weight. Samples were microwave digested following the general guidelines of EPA 3052 procedure; the vessels were heated to 180°C with a ramp time of 10 minutes and a hold time of 10 minutes in a MARS5 microwave digestion system (CEM Corporation, Matthews, NC). The samples were further diluted ten times with deionized water prior to analysis by ICP-MS. Digestions included blanks and reference materials (DORM2, CNRC, Ottowa, Canada) at a frequency of one blank and on reference material every 12 samples. All trace elements except Hg were analyzed by collision cell ICP-MS (7500c, Agilent, Santa Clara, CA) with calibration by the method of standard additions. Mercury was analyzed by isotope dilution cold vapor ICP-MS after spiking with a know mass of enriched isotopically enriched $^{199}Hg$.

The absolute detection limit for As is 0.006 mg/kg, for Hg is 0.001 mg/kg, for Se is 0.142 mg/kg. Quality control for the analysis included following: chain-of-custody documetation of all materials selected for analysis and archiving; the quality control samples were run every 10 analyses.

## 4.5 STATISTICAL METHOD

Statistical analysis is performed using SPSS 15.0 version. The assumption of normal distribution and equal variance were checked before doing analysis test. Because the data for metal levels in original scale is not normally distributed, we log 10 transformed the data and performed the ANOVA analysis. Using the Tukey Post Hoc multiple comparison, the results are converted back from log scale to original scale and interpreted as the ratio of medians. We also used Kruskal-Wallis test to compare the mean rank of metal or metalloid levels in original scale from different locations without assuming the normal distribution. The results from Kruskal-Wallis test are also showing the same results as the ANOVA test on log 10 scale data.

# 5.0 RESULTS

## 5.1 NO DIFFERENCES BETWEEN PITTSBURGH POOL CAUGHT CHANNEL CATFISH

We compared the As, Hg and Se levels in catfish from Highland Park Dam, Monongahela River and Point State Park and found no statistically significant difference between As, Hg and Se concentrations in catfish caught from those three locations. The multiple comparisons p-value for Hg comparison is 0.122, for As comparison is 0.806, for Se comparison is 0.766 (Shown in Table 3).

Thus, we combined those data together and compared them with the catfish caught from Kittanning Dam and store-bought. We want to compare the data with Kittanning Dam because local anglers thought that the water is cleaner and they continually said they would eat fish from this location. We also want to compare the data with fish from a local fish market, because from the fish consumption survey, the local fish market is a popular place for consumers including anglers to purchase fish, and the fish on sale there are from Georgia farm raised. We want to assess different risks people are exposed to by consuming fish either from local fish market or fishing in Pittsburgh Pool and Kittanning Dam.

Table 3. **Hg, As and Se Analysis for Catfish within Pittsburgh Pool**

| Metal/ Metalloid | Analysis | Catching Sites (Number of Samples) | | |
|---|---|---|---|---|
| | | Highland Park (12) | Point State Park (19) | Monongahela River (7) |
| Hg | Median Concentration (Range, mg/kg) | .088 (.040- .215) | .058 (.006 - .224) | .095 (.038 - .264) |
| | Mean Concentration (mg/kg) | 0.099 | 0.068 | 0.110 |
| | ANOVA Comparisons P value | 0.122 | | |
| As | Median Concentration (Range, mg/kg) | .016 (.003 - .044) | .014 (.003 - .119) | .020 (.006 - .046) |
| | Mean Concentration (mg/kg) | 0.018 | 0.020 | 0.023 |
| | ANOVA Comparisons P value | 0.806 | | |
| Se | Median Concentration ((Range, mg/kg) | .168 (.104 - .247) | .156 (.080 - .351) | .165 (.087 - .288) |
| | Mean Concentration (mg/kg) | 0.178 | 0.173 | 0.168 |
| | ANOVA Comparisons P value | 0.776 | | |

## 5.2 SIGNIFICANT DIFFERENCE BETWEEN PITTSBURGH POOL, KITTANNING AND LOCAL STORE BOUGHT FISH

We compared the data from Pittsburgh Pool with the data from Kittanning Dam and found significant difference of Hg and Se levels; the p-value is less than 0.0001 for both metals. We didn’t find significant difference of Arsenic levels in catfish caught from Pittsburgh Pool and Kittanning (as shown in Table 4 and Table 5).

When we compared the data from Pittsburgh Pool and local fish market, all three metal levels showed significant differences with P-value below 0.0001(as shown in Table 4 and Table 5).

According to the detection limits, all the metals levels in samples from Pittsburgh Pool and Kittanning Dam are above the detection limits. For arsenic, 8 of 11 samples from store-bought are below the detection limit.

Table 4. **Hg, As and Se analysis for Catfish Between Pittsburgh Pool, Kittanning Dam and Store-bought**

| Metal /Metalloid | Analysis | Catching Sites (Number of Samples) | | |
|---|---|---|---|---|
| | | Pittsburgh Pool (39) | Kittanning (13) | Store-Bought (11) |
| Hg | Median Concentration (Range, mg/kg) | .060 (.006 - .264) | .180 (.109 - .523) | .010 (.008 - .018) |
| | Mean Concentration (mg/kg) | 0.085 | 0.236 | 0.011 |
| | Number of Detects | 39 of 39 | 13 of 13 | 11 of 11 |
| As | Median Concentration (Range, mg/kg) | .015 (.003 - .119) | .022 (.006 - .032) | .003 (.003 - .059) |
| | Mean Concentration (mg/kg) | 0.020 | 0.019 | 0.009 |
| | Number of Detects | 39 of 39 | 13 of 13 | 3 of 11 |
| Se | Median Concentration ((Range, mg/kg) | .162 (.080 - .351) | .236 (.144 - .388) | .107 (.081 - .154) |
| | Mean Concentration (mg/kg) | 0.173 | 0.234 | 0.111 |
| | Number of Detects | 39 of 39 | 13 of 13 | 11 of 11 |

Table 5. **ANOVA Multiple Comparisons for As, Hg and Se**

| **Metal/Metalloid** | **ANOVA Multiple Comparisons (95% CI on the Ratio of Medians, mg/kg, P-value)** | | |
|---|---|---|---|
| | **Kittanning Vs Pittsburgh Pool** | **Kittanning Vs Store-Bought** | **Pittsburgh Pool Vs Store-Bought** |
| **Hg** | (1.91 - 4.95) P< 0.0001 | (10.3 - 34.7) P<0.0001 | (3.72 - 10.2) P<0.0001 |
| **As** | Non-significant | (1.83, - 8.09) P<0.0001 | (1.79 – 6.16) P<0.0001 |
| **Se** | (1.11 – 1.69) P< 0.002 | (1.58 – 2.71) P<0.0001 | (1.21 – 1.90) P<0.0001 |

For As, the median concentration in catfish from Pittsburgh Pool is 0.015 mg/kg (all units are in wet weight), from Kittanning is 0.022 mg/kg and from store-bought is 0.003 mg/kg. There is no statistically significant difference of As levels in catfish caught from Pittsburgh Pool and Kittanning Dam, but the samples from both locations contain significantly higher As level than those from store-bought. Comparing to the As level in samples from store-bought, the 95% confidence interval of median As ratio shows that the median As level in catfish from Kittanning is 1.83 to 8.09 times of the median As level in catfish from store bought. The median As level in catfish from Pittsburgh Pool is 1.79 to 6.16 times of the median As level in catfish from store bought.

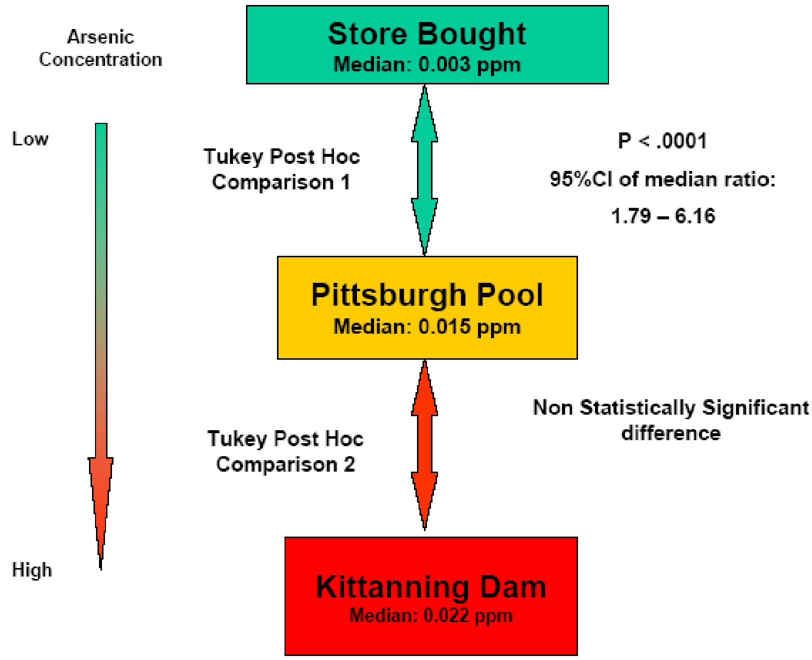


Figure 4. **Arsenic Comparisons Among 3 Locations**

For Hg, the median concentration in catfish from Pittsburgh Pool is 0.060 mg/kg (all units are in wet weight), from Kittanning is 0.180 mg/kg and from store-bought is 0.010 mg/kg. There is statistically significant difference among three locations. The 95% confidence interval of median Hg level in catfish from Kittanning is 10.3 to 34.7 times of the median Hg level in catfish from store bought. The median Hg level in catfish from Kittanning is 1.91 to 4.95 times of the median Hg level in catfish from Pittsburgh Pool. The median Hg level in catfish from Pittsburgh Pool is 3.72 to 10.2 times of the median Hg level in catfish from store bought. In other words, the Hg level in catfish from store bought is lowest, and from Kittanning Dam is highest among the store-bought, Pittsburgh Pool and Kittanning Dam caught catfish.

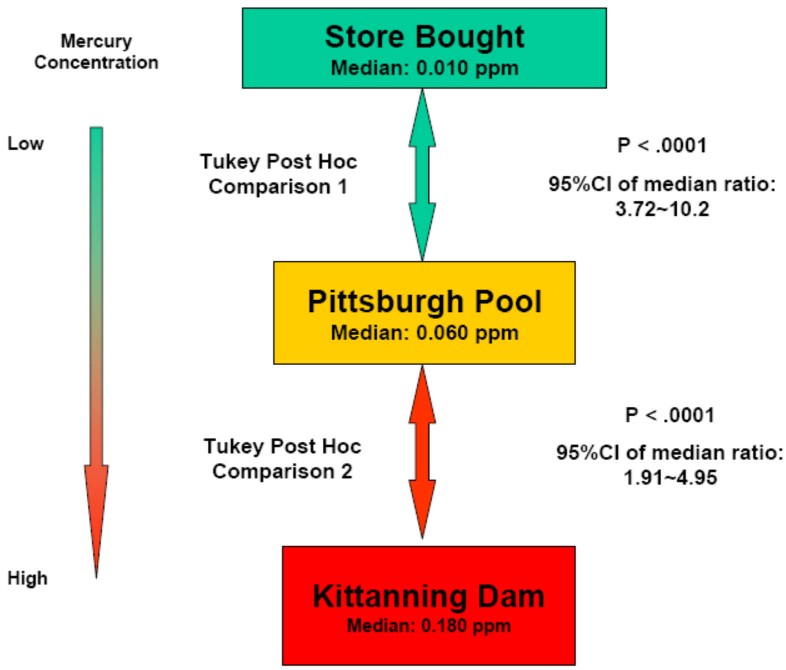


Figure 5. **Mercury Comparisons Among 3 Locations**

For Se, the median concentration in catfish from Pittsburgh Pool is 0.162 mg/kg (all units are in wet weight), from Kittanning is 0.236 mg/kg and from store-bought is 0.107 mg/kg. There is statistically significant difference between three locations. The 95% confidence interval of median Se level in catfish from Kittanning is 1.58 to 2.71 times of the median Se level in catfish from store bought. The median Se level in catfish from Kittanning is 1.11 to 1.69 times of the median Hg level in catfish from Pittsburgh Pool. The median Hg level in catfish from Pittsburgh Pool is 1.21 to 1.90 times of the median Hg level in catfish from store bought. This showed the same trend as Hg level in three locations, lowest Se level in store-bought catfish, but highest Se level in Kittanning Dam catfish among the store-bought, Pittsburgh Pool and Kittanning Dam caught catfish.

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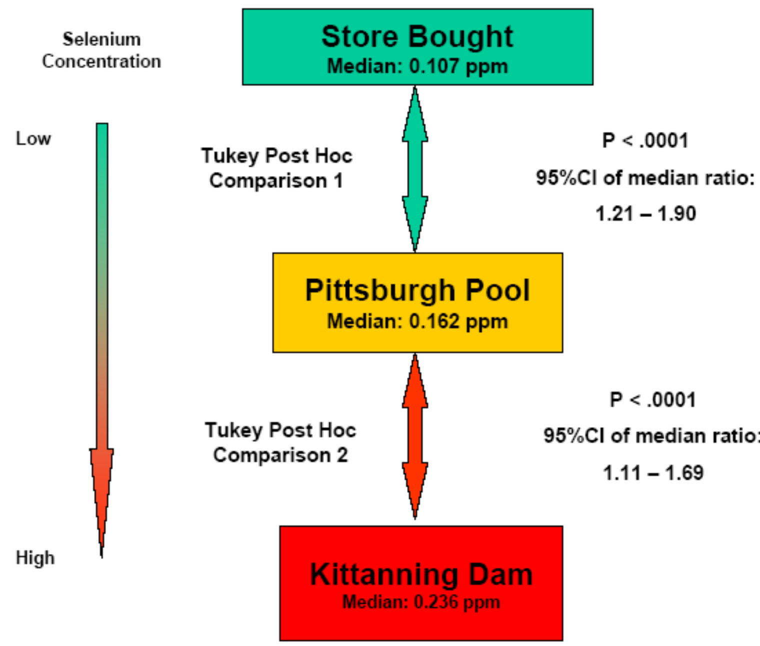


Figure 6. **Selenium Comparisons Among 3 Locations**

## 5.3 WEIGHT AND LENGTH COMPARISONS BY LOCATIONS

For some contaminants, particularly mercury, levels increase with the size of the fish (Lange, Royals et al. 1994; Bidone, Castilhos et al. 1997; Burger, Gaines et al. 2001; Burger, Gaines et al. 2001; Green and Knutzen 2003; Weis and Ashley 2007) because bigger fish tend to bioaccumulate more methyl mercury. However, this is not always the case (Stafford 2001), and at low contaminant levels, the size relationship may not hold (Park 1997). In this study, because of the highly significant location difference, we had expected that the fish size mattered in the metal level, and we compared the fish weight and length from different locations. Unexpectedly, the data showed that the catfish caught from Kittanning were significantly smaller than the catfish from the other locations. Table 6 presents the weight and length of catfish caught from different locations. We could only get the processed catfish fillet from the fish market so the weight and length data are not available for store-bought catfish.

As shown in Table 6, the size of the catfish caught from the Monongahela, Highland Park and Point sites are very close, with a mean value of 46 centimeters long and 1100 grams weight (Table 7). However, the size of catfish caught from Kittanning Dam is much smaller, with mean value of 37 centimeters long and 470 grams in weight.

When we combined the samples from the Pittsburgh Pool and compared them with the sample from Kittanning Dam again, we found significant differences in weight and length, as shown in figure 7 and figure 8. We used the t-test to test if there are mean differences in the weight and length for catfish samples from the two groups, assuming they are two independent groups. The p-values of two t-tests (one for mean difference of weight and one for mean difference of length) are both less than 0.0001.

Table 6. **Weight and Total Length of Channel Catfish Caught in Different locations**

| Description Characters | Locations | Mean | Range |
|---|---|---|---|
| Total Length (cm) | Monongahela | 46.1 | 32.0 – 50.5 |
| | Allegheny Highland Park | 48.5 | 39.5 – 54.5 |
| | Point | 45.9 | 36.4 – 57.0 |
| | Kittanning | 37.1 | 28.0 – 48.0 |
| Total Weight (g) | Monongahela | 1018.9 | 310.0 – 1450.0 |
| | Allegheny Highland Park | 1219.2 | 700.0 – 2230.0 |
| | Point | 1028.3 | 395.0 – 2000.0 |
| | Kittanning | 470.5 | 32.0 – 1125.0 |

Table 7. **T-test of Mean Difference of Length and Weight for Two Groups**

| Descriptive Characters | Locations | Mean | 95% CI of Mean Diff P-value |
|---|---|---|---|
| Total Length | Pittsburgh Pool | 46.5 cm | [5.4, 13.5] cm P< .0001 |
| | Kittanning | 37.1 cm | |
| Total Weight | Pittsburgh Pool | 1086.8 g | [343.8, 888.7] g P< .0001 |
| | Kittanning | 470.5 g | |

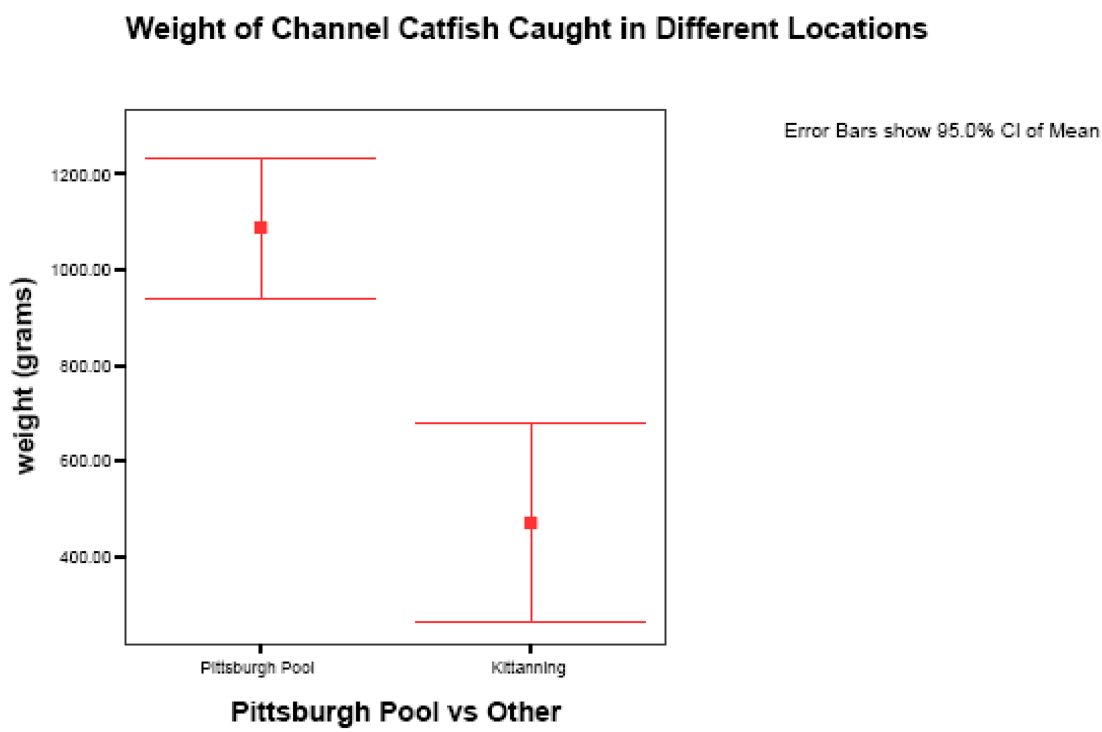


Figure 7. **Weight of Channel Catfish Caught in Different Locations**

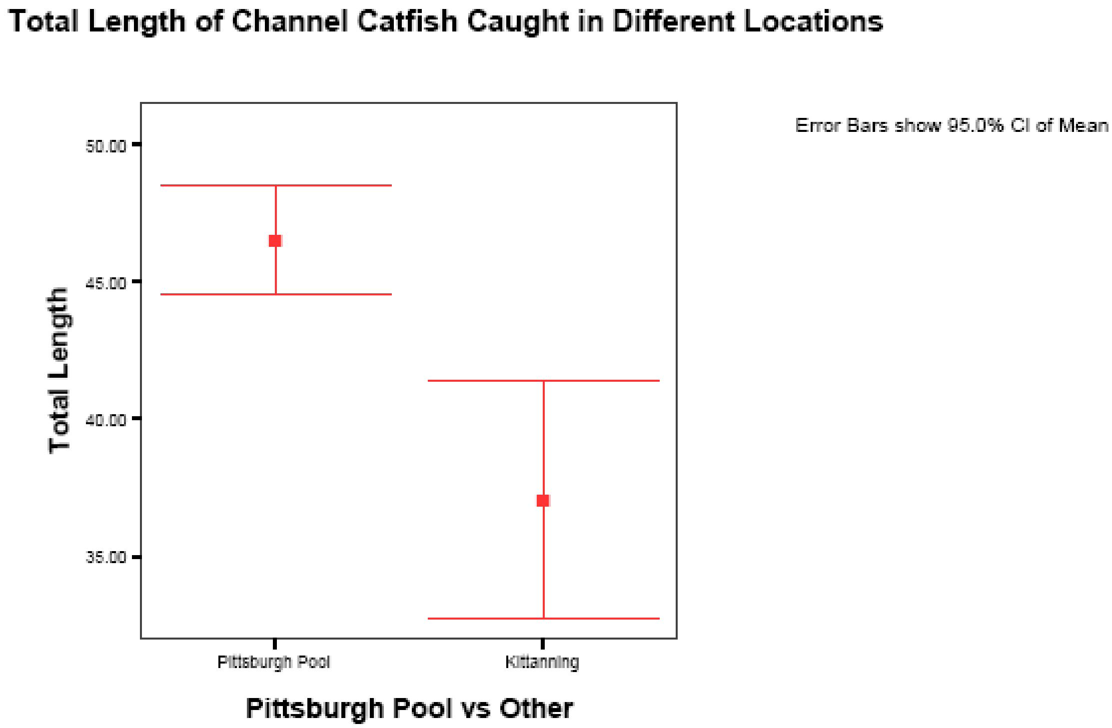


Figure 8. **Length of Channel Catfish Caught in Different Locations**

From our samples, the catfish caught from Kittanning dam were significantly smaller than the fish caught from other local locations (Figure 7, 8, Table 7); however, the mercury and selenium concentrations were highest in the catfish from Kittanning compare with other locations. This evidence further confirmed the results that the fish caught from Kittanning Dam have bioaccumulated more metals/metalloids than fish caught from Pittsburgh Pool.

## 5.4 MERCURY LEVEL IN CHANNEL CATFISH CAUGHT IN KITTANNING DAM

Additionally, 23% of Channel Catfish samples caught in Kittanning Dam had higher mercury levels than the EPA Methylmercury Fish Tissue Residue Criterion, which is 0.3 mg methylmercury/kg fish. This is the concentration in fish tissue that should not be exceeded based on a total fish and shellfish consumption-weighted rate of 0.0175 kg fish/day(USEPA 2006).

This is an unexpected result, since local anglers said that the water in this location is cleaner than other study locations and local anglers preferred to eat the fish caught from Kittanning Dam area than the fish from Pittsburgh Pool as the fishing interview meeting survey indicated.

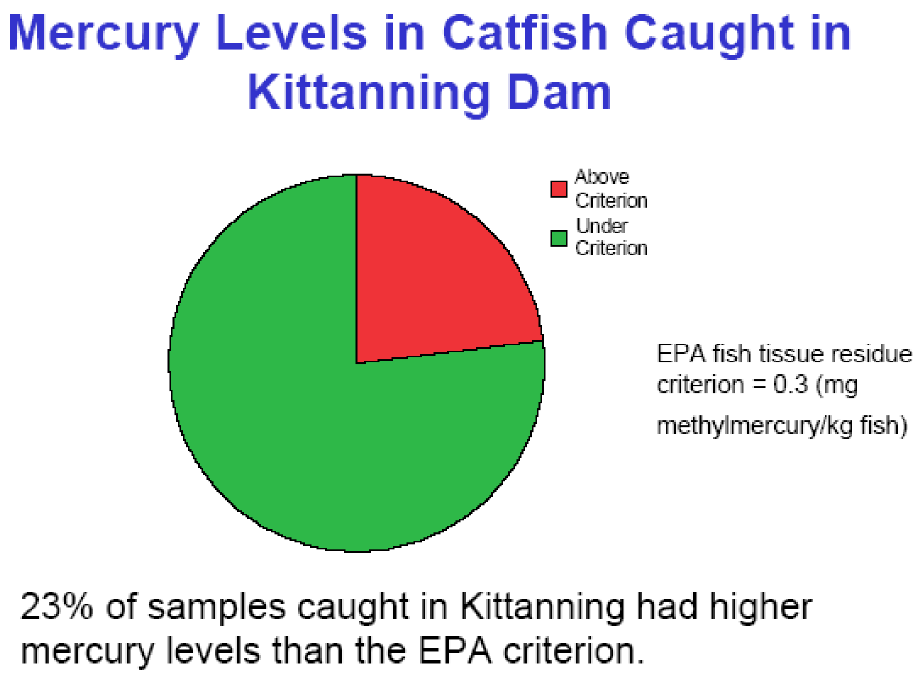


Figure 9. **Mercury Levels in Catfish Caught in Kittanning Dam**

### 5.5 CORRELATION OF SELENIUM AND MERCURY

Uptake of metals by fish is affected by both physical properties and the presence of other substances. In this study, we found significant positive correlation between selenium and mercury levels in catfish. As shown in table 8, the correlation coefficient for selenium and mercury is 0.504 at p value of 0.0001. The positive correlation between two elements in fish flesh were also stated by (Kuehl and Haebler 1995) and (Wagemann, Innes et al. 1996). Literatures showed that selenium has a protective effect on mercury toxicity (Ganther, Goudie et al. 1972; Satoh, Yasuda et al. 1985). At high concentrations, selenium has a protective effect on mercury toxicity in salmonid eggs (Klaverkamp, Macdonald et al. 1983), but at these high levels, selenium can cause behavioral abnormalities, reproductive deficits and ultimately mortality(Eisler 1985; Heinz 1996). Although mercury and selenium are correlated for catfish, the effects of selenium on mercury levels were not determined and the protective mechanism is unclear. But this may act as an additional evidence for our hypothesis that the contaminant sources are local coal-fired power plants because both Hg and Se can be released by coal-burning processes.

We didn't find significant correlation between As and other two elements levels in catfish.

Table 8. **Pearson Correlations Between As, Se and Hg**

| | **Arsenic Vs Selenium** | **Selenium Vs Mercury** | **Arsenic Vs Mercury** |
|---|---|---|---|
| **Correlation Coefficient** | 0.072 | 0.504 | .162 |
| **P-value** | 0.574 | 0.001 | .205 |

# 6.0 A RISK ASSESSMENT FOR SEMI-SUBSISTENCE ANGLERS AND THEIR FAMILIES' EXPOSURE TO MERCURY THROUGH INGESTION OF CATFISH FROM KITTANNING DAM

Because the mercury levels in catfish caught from Kittanning Dam are significantly higher than catfish caught from the Pittsburgh Pool and those purchased from the local fish market, and since almost 25% of the Kittanning samples contain mercury levels that exceeded the EPA criterion, local subsistence anglers and their families are at higher risk of health effects from eating fish caught from the Kittanning Dam area. Based on this finding, we want to assess the risk of non-carcinogenic health effects from mercury that the target group is exposed to. A conservative assumption was made that the total mercury we analyzed in fish tissue 100% exists in methyl mercury form (Bloom 1992; Akagi 1995; Becker 1995; Kim 1995; USEPA 2006). The average daily intake dose of exposed individuals was calculated and compared with the reference dose.

The population group of concern is adult subsistence anglers and their families who regularly eat catfish caught from Kittanning Dam area. The primary exposure pathway is ingestion of fish. Depending on different age and gender, 4 subpopulation groups are considered, including children from 3-8 years old, children from 9-15 years old, women of childbearing age and normal adults. In the exposure quantification, we use the exposure algorithm equation recommended by EPA (USEPA, Example Exposure Scenarios). The input parameters for use in risk are listed in Table 9. The 95% Confidence Interval of mean mercury level in catfish caught from Kittanning Dam is 0.154 mg/kg to 0.282 mg/kg wet weight. For risk based allowable monthly maximum fish consumption limit calculation, we use upper 95% Confidence Interval of the mean mercury level in Kittanning-caught catfish as a conservative method to assess the risk (USEPA, Example Exposure Scenarios). The oral reference dose for methyl mercury from IRIS is 0.0001 mg/kg-day, which is from the benchmark dose lower limit ($BMDL_{05}$) (the lower 95% confidence limit of the $BMD_{05}$). This number is based on the BMD analysis for the methyl mercury dose-response relationship (NRC 2000). A benchmark dose analysis was chosen as the most appropriate method of quantifying the dose effect relationship. The level chosen was a Benchmark Dose Lower Limit (BMDL); this was the lower 95% limit on a 5% effect level obtained by applying a K power model (K >= 1) to dose-response data based on mercury in cord blood. The BMDL was chosen as the functional equivalent of a no-adverse effect level for calculation of the RfD.

The RfD for methylmercury was not calculated to be a developmental RfD only. It is intended to serve as a level of exposure without expectation of adverse effects when that exposure is encountered on a daily basis for a lifetime. In the studies so far published on subtle neuropsychological effects in children, there has been no definitive separation of prenatal and postnatal exposure that would permit dose-response modeling. That is, there are currently no data that would support the derivation of a child (vs. general population) RfD (USEPA, 2001).

The assessment of methylmercury exposure from common media sources (e.g., diet, air) and relative source contribution (RSC) estimates follows the 2000 Human Health Methodology. The RSC is used to adjust the RfD to ensure that the water quality criterion is protective, given other anticipated sources of exposure. The exposure assessment characterizes the sources of methylmercury exposure in environmental media, providing estimates of intake from the relevant sources for children, women of childbearing age, and adults in the general population. Based on available data, human exposures to methylmercury from all media sources except freshwater/estuarine and marine fish are negligible, both in comparison with exposures from fish and compared with the RfD. Estimated exposure from ambient water, drinking water, nonfish dietary foods, air, and soil are all, on average, at least several orders of magnitude less than those from freshwater/estuarine fish intakes. Therefore, these exposures were not factored into the RSC. However, ingestion of marine fish is a significant contributor to total methylmercury exposure. But for our target population – the semi-subsistence anglers and their families, almost all of the fish consumption source are from freshwater caught fish.

We selected the basic demographic parameters' values from Exposure Factor Handbook (USEPA 1997), assuming all the groups eat 1 meal per day and 4 meals of fish every week.

We did a sensitivity analysis for each subgroup, meaning that we were calculating the range of average daily dose (ADD) and the range of Hazard Quotients for each specified subgroup based on the 95% CI of mean mercury level in Kittanning-caught catfish.

The average daily dose of ingestion fish based on methyl mercury's noncarcinogenic health effects is expressed in kilograms of fish per day.

$$\mathbf{ADD} = \frac{\mathbf{C_{fish} * IR_{fish} * EF * ED}}{\mathbf{BW * AT}} \qquad \textbf{(Equation 1)}$$

Where:

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

$\mathbf{C_{fish}}$ = Concentration of contaminants in fish (mg/kg fish)

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

**EF** = exposure frequency (meals/day)

**ED** = exposure duration (days)

**BW** = body weight (kg) and

**AT** = averaging time (days)

Table 9. **Input Parameters for Use in Risk Equations**

| **Equation parameter** | | **Values** |
|---|---|---|
| **Reference dose (RfD)** | | $10^{-4}$ mg/kg-d |
| **Body weight (BW)** | **3-8 yr** | 22 kg |
| | **9-15 yr** | 45 kg |
| | **Childbearing Aged Women** | 64 kg |
| | **Adults** | 70 kg |
| **Per capita intake rate of fish ($IR_{fish}$)** | **Less than 16 yr old** | 4 oz (0.114 kg/meal) |
| | **Adults** | 8 oz (0.228 kg/meal) |
| **Measured concentration of contaminants in fish ($C_{fish}$)** | | 95% CI: (.154 - .282) mg/kg fish |
| **Exposure Frequency (EF)** | | 1 meals/day |
| **Exposure Duration (ED)** | | 4 days |
| **Averaging time (AT)** | | 7 days |

Using the equation, we can calculate the range of ADD for children at 3-8 years old as:

$$\mathbf{ADD_{.05}} = \frac{\mathbf{0.154\ mg/kg * 0.114\ kg/meal * 1\ meal/day * 4\ days}}{\mathbf{22\ kg * 7\ days}}$$

$$= \mathbf{4.6 \times 10^{-4}\ mg/kg\text{-}day}$$

$$\mathbf{ADD_{.95} = \frac{0.282\ mg/kg * 0.114\ kg/meal * 1\ meal/day * 4\ days}{22\ kg * 7\ days}}$$

$$= \mathbf{8.3 \times 10^{-4} mg/kg\text{-}day}$$

Then the hazard quotient will be calculated by:

$$\mathbf{Hazard\ quotient = ADD/RfD}$$

The hazard quotient is greater than 1 means the population have excess non-carcinogenic health risk from the specified pathway and exposure frequency of the catfish. The hazard is less or equal to 1 means the study populations don't have excess non-carcinogenic health risk from the specified pathway and exposure frequency of the catfish.

For children at 3-8 years old, the hazard quotient range based on the 95% confidence interval of measured mercury concentrations in catfish is:

$$\mathbf{Hazard\ quotient_{.05} = 4.6 \times 10^{-4}\ mg/kg\text{-}day / 10^{-4}\ mg/kg\text{-}day \approx 5}$$

**To**

$$\mathbf{Hazard\ quotient_{.95} = 8.3 \times 10^{-4}\ mg/kg\text{-}day / 10^{-4}\ mg/kg\text{-}day \approx 8}$$

The ADD and Hazard Quotients for all the subgroups are calculated and listed in table 8.

Table 10. **The ADD and Risk for Each Subgroup**

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

Moreover, we can get the allowable number of fish meals of a specified meal size that may be consumed over a given time period based on the RfD. The consumption limit is determined in part by the size of the meal consumed. An 8-oz (0.228-kg) meal size was assumed for adults and 4-oz (0.114-kg) meal size was for children below 9 years old. Equations 2 and 3 can be used to convert daily consumption limits, the number of allowable kilograms per day (calculated using Equation 2), to the number of allowable meals per month:

$$\mathbf{CR_{lim} = \frac{RfD * BW}{C_{fish}}} \qquad \textbf{Equation 2}$$

Where

**$CR_{lim}$ = maximum allowable fish consumption rate (kg/d)**

**RfD = reference dose (mg/kg-day)**

**BW = consumer body weight (kg)**

**$C_{fish}$ = measured concentration of contaminants in catfish (mg/kg fish)**

Equation 3 was used to convert daily consumption limits, in kilograms, to meal consumption limits over a given time period (month) as a function of meal size.

$$\mathbf{CR_{mm} = \frac{CR_{lim} * AT}{IR_{fish}}} \qquad \textbf{Equation 3}$$

Where

**$CR_{mm}$** = maximum allowable fish consumption rate (meals/mo)

**$CR_{lim}$** = maximum allowable fish consumption rate (kg/d)

**AT** = average time (30 days/month)

**$IR_{fish}$** = Per capita intake rate of fish (kg fish/meal)

We are presenting the maximum allowable monthly consumption limits based on the upper 95% CI of mean mercury level in catfish from Kittanning Dam as a conservative method. Thus, the maximum allowable fish consumption daily rate for children at 3-8 years old can be calculated as:

$$\mathbf{CR_{lim} = \frac{10^{-4}\ mg/kg\text{-}day * 20\ kg}{0.282\ mg/kg} = 7.1 \times 10^{-3}\ kg/day}$$

and the maximum allowable fish consumption monthly rate for children at 3-8 years old is:

$$\mathbf{CR_{mm} = \frac{7.1 \times 10^{-3}\ kg/day * 30\ day}{0.114\ kg/meal} \approx 2\ meal}$$

The monthly fish consumption limits for all subgroups are calculated and listed in Table 11.

Table 11. **Monthly Fish Consumption Limits for Non-carcinogenic Health Endpoints – Methyl mercury**

| **Study Group** | **Fish meals/Month (Risk-Based Consumption Limit)** | **Fish Tissue Concentrations (upper 95% CI of mean mercury level)(mg/kg, wet weight)** |
|---|---|---|
| **3-8 yr** | **2** | .282 |
| **9-15 yr** | **2** | .282 |
| **Women of Childbearing Age** | **3** | .282 |
| **Adults** | **4** | .282 |

By calculation, the hazard quotients for all subgroups are greater than 1, which means all the subgroups are at greater risk of non-carcinogenic health effects by ingestion of catfish caught from Kittanning Dam. For each group, the range of hazard quotients is based on the 95%

confidence interval of mean mercury concentrations in catfish from Kittanning. Even with the left bound of the intervals, all the hazards are still significant. Expressed as the maximum monthly allowable fish consumption limits, the children below 16 years old can only eat at most 2 meals per month if the catfish is from Kittanning Dam Area. For women of childbearing age, the monthly maximum allowable consumption limit is 3 meals.

# 7.0 DISCUSSION

One pre-study hypothesis was that there should be differences in concentrations of contaminants within the Pittsburgh Pool between the area on the Monongahela River near at he Edger Thompson Steel Works, the Point State Park and the area furthest upstream on the Allegheny next to the Highland Park Dam. Fisherman in fact report feeling that fish from Highland Park are cleaner than other areas of the pool and many anglers eat catches from this area. However, there is no statistically significant difference among As, Hg and Se concentrations in catfish caught from all locations within Pittsburgh Pool. The possible explanation for non-statistically significant difference is because the Pittsburgh Pool is a locked water system within 3 locks and dams and thus all the industrial pollution discharged into the Pittsburgh Pool could become somewhat evenly distributed. Additionally, the fish may range throughout the pool. The other evidence supporting homogeneity of catfish in the Pittsburgh Pool is that the length and weight of the samples from Pittsburgh Pool are very similar and not significantly different.

Local anglers and regulators thought the water near Kittanning Dam is cleaner. But the analysis for mercury and selenium gave an opposite outcome for these particular contaminants. The catfish caught from Kittanning Dam is significantly smaller than those from Pittsburgh Pool but they contain significant higher concentrations of mercury and selenium. Because mercury and selenium can bioaccumulate in fish flesh, and their concentrations are generally positively correlated with fish size in the same living system, we assume that the Hg and Se levels in Kittanning Dam aquatic system are higher than that in Pittsburgh Pool. For arsenic, although there is no significant difference of arsenic level in our samples from Pittsburgh Pool and Kittanning, the small sample size from Kittanning Dam may limit the test power.

As, Hg and Se are known to be associated with the burning of coal for power production and fly-ash laden effluent. Southwestern Pennsylvania is a known fallout area for plants located in Ohio and other states and plants located within the area can deposit emissions within the area. Many fly-ash piles are located near area rivers. Area legacy smelting and other manufacturing can also result in emissions of these elements. There is a major specialty steel plant approximately 20 miles south of the Kittanning Dam located on the Allegheny River at Brackenridge. Although the Kittanning Dam is located 40 miles upstream on Allegheny River from Pittsburgh, it receives multiple pollution depositions, for example, the deposition of coal fire ash from Allegheny Energy INC. Armstrong Power Station and Cheswick Generating Station located in Springdale. The other possible reason for increased Hg and Se concentrations in the Kittanning aquatic system is because of the high frequency of upstream wind draft year around bringing emissions from the Cheswick Plant upstream to Kittanning for deposition. The metal levels in catfish from Pittsburgh Pool are significantly lower than those from Kittanning Dam. However, they are significantly higher than those from the local fish market, where the catfish is Georgia Farm-raised, indicating that the contamination level in Pittsburgh Pool is also significant. It is not as safe as consumption of catfish from store-bought. From the results, catfish caught from different sites can help pinpoint the location of pollution sources. A cause and effect relationship between fish consumption and Hg in blood levels is strongly supported by the correlations reported among fish consumers worldwide, including the large studies of U.S.

commercial fish consumers (WHO 1990; Brunne D 1991; Chang SB 1992). In our case, the subsistence anglers and their families are potentially at higher risk of health effects since they may have more fish consumption than the average fish consumers.

Some literatures point out that most arsenic in fish is in the form of organoarsenicals, most of which are poorly absorbed and metabolized by consumers. Thus, they are not considered to be toxic. However, this point of view is controversial, (Lehmann, Ebeling et al. 2001) indicated that the absorbed arsenic mainly as arsenonetaine due to ingestion of fish is not eliminated as fast as had been expected on the basis of published data. As long as it is not known what happens to arsenobetaine remaining for longer periods in the blood with a half-life of 63 hours, caution is advised regarding the general opinion that arsenobetaine is rapidly eliminated and non-toxic for human consumption. There are also abundant studies analyzing arsenic in fish tissue. An EPA report indicated that only 10% of arsenic in fish tissue exists in inorganic form (EPA 1998). Because our study area is historically anthropogenically contaminated and highly industrialized, we estimated that the inorganic arsenic form exists in fish tissue caught from local rives will be over 10%.

There are also some uncertainties in this study. For mercury analysis, we assumed all the mercury in collected fish samples exist in methylated form, however, (Kannan, Smith et al. 1998) studied total mercury and methyl mercury in water, sediment and fish from South Florida estuaries and found that, among the many fish species studied, the percentage of methylated Hg varied from 20% to 100%. Furthermore, methylmercury is associated more with the hypoxic interface of estuarine systems (Mason RP 1995). The US EPA methylmercury criterion document estimates 100% mercury exists in methylated form. In future studies, metal speciation for the tissue samples need to be done to assess the real methylmercury level in local catfish.

From our results, the selenium level is significantly positively correlated with mercury level in catfish, which is a further evidence for our hypothesis that the contaminant sources are from local power plants. For these two elements, although literature indicated that selenium might have protective effects on mercury toxicity in particular fish species, the mechanism is unclear and the effects are not determined. Moreover, the laboratory research is required to determine if the protective effects are equal in all the fish species.

Seasonal difference for metal levels in fish tissue is one of the concerns in our study. In (Weis and Ashley 2007), they found that the higher Hg levels tended occur in warmer weather, when more people are fishing. Thus, the probability of catching the more contaminated catfish would increase in the summer. The seasonal changes in metal bioaccumulation, some chemical-physical factors interactions and or/and food availability may also contribute to higher heavy metals levels in catfish and thus higher Hg consumption by anglers and their families in summer. We collected samples for this project in fall and found almost 25% of fish exceeded EPA mercury criterion in catfish from Kittanning. Because of the possible higher metal bioaccumulation factor and more fishing behaviors in summer, it is hypothesized that even a higher percentage of fish exceeding the mercury level and higher consumption risk would happen in summer. It would be preferred in future research that we collect fish from each sampling site year-around.

The risk to humans from contaminants in fish can be addressed by reducing contaminant levels in the aquatic environment and by reducing consumption of fish with high contaminant burdens, or both. To reduce contaminants in the aquatic system, emissions reduction can be accomplished by improving control devices in stack sources, improving the treatment of wastewater and implementing proper storage of the fly ash in concrete bunkers that are covered and positioned far from stream and river sources. Reducing the release of contaminants into the aquatic environment will ultimately reduces the levels in fish, but there is a lag time. Reducing contaminants in aquatic ecosystems requires a combination of regulatory effort and technical support in the region. It took 8 years for fish tissue to show evident declines of mercury in Everglades of Florida (SFWMD 2004), in other places decreases have been much slower. The other approach is to issue fish consumption advisories, and to assume that personal behavior will change accordingly. However, compliance to consumption advisories varies by ethnic, culture and economic status.

From the risk assessment, the semi-subsistence anglers and their families are at great health risk from ingestion of catfish from Kittanning Dam. Expressed as the maximum allowable fish consumption limits, the children below 16 years old can only eat at most 2 meals per month if the catfish is from Kittanning Dam Area. For women of childbearing age, they cannot eat more than 3 meals per month of the fish, for adults the limit is 4 fish meals per month. However, according to the transcript of the Pittsburgh Fish Consumption Study (Volz, C. D, 2007), most of anglers stated that they consumed fish at least twice every week with ingestion amount which usually were greater than 8 oz. In warm seasons, the effects of eating 30 fishmeals on 30 consecutive days need to be considered.

# 8.0 CONCLUSIONS

The Hg and Se concentrations in catfish do vary significantly by locations of catch in southwestern Pennsylvania. Hg and Se levels in Kittanning-caught catfish are significantly higher that catfish caught from Pittsburgh Pool.

Catfish can serve as a biomonitor for industrial pollution as the Kittanning Dam is a presumed deposition point for several local coal-fired power plants.

Local anglers were potentially exposed to higher mercury and selenium levels when they eat the catfish caught from near the Kittanning Dam and Pittsburgh Pool than catfish bought from local fish market. Local anglers, especially the semi-subsistence anglers and their families are the most sensitive group to Hg and Se exposures by ingestion of catfish caught from Kittanning Dam.

# 9.0 PUBLIC HEALTH IMPLICATIONS

Anglers and their families who consume fish from Kittanning are at higher risk of health effects from ingestion of Hg. Location-specific fish consumption advisories are needed for local fishers. Community Based Participatory Research approach performed beyond our expectations and energized the local fishing community to become stewards of the rivers. A metal monitoring program for sediments is recommended because the dry or wet deposition of emissions from coal fired plants and historically industrial pollution deposition takes decades to dissipate. 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 the multiple pollution sources.

# APPENDIX

# A RISK ASSESSMENT FOR SUBSISTENCE FISHERS' EXPOSURE TO METHYLMERCURY FROM CONSUMPTION OF CATFISH CAUGHT FROM KITTANNING DAM

Because the mercury level in catfish caught from Kittanning Dam is significantly higher than catfish caught from Pittsburgh Pool and purchased from local fish market, moreover, almost 25% of the samples contain the exceeded mercury levels than EPA criterion, local subsistence anglers and their families are at higher risk of health effects from eating fish caught from Kittanning Dam. Based on this finding, we want to assess the risk of non-carcinogenic health effects from mercury the target group is exposed to. A conservative assumption was made that the total mercury we analyzed in fish tissue 100% exists in methyl mercury form (Bloom 1992; Akagi 1995; Becker 1995; Kim 1995; USEPA 2006). Most chemical contaminants are not equally distributed throughout the fish. The portion of fish typically eaten may vary by fish species and/or the dietary habits of anglers. Most anglers in United States eat fish fillets. Therefore, the concentration measured in fish fillet for catfish is the exposure level chosen for our local anglers. The average daily intake dose of exposed individuals was calculated and compared with the reference dose.

## Hazard Identification

A commonly occuring form of methylmercury is methylmercuric chloride. Methylmercury is a highly toxic substance; a number of adverse health effects associated with exposure to it have been identified in humans and in animal studies. Most extensive are the data on neurotoxicity, particularly in developing organisms. The nervous system is considered to be the most sensitive target organ for which there are data suitable for derivation of an RfD (IRIS 2001). Methyl mercury is efficiently absorbed from the gastrointestinal tract following ingestion. Approximately 94% - 95% of methylmercury in fish ingested by volunteers was absorbed from the gastrointestinal tract (Aberg 1969). For fetuses, infants, and children, the primary health effect of methylmercury is impaired neurological development. Methylmercury exposure in the utero, which can result from a mother's consumption of fish and shellfish that contain methylmercury, can adversely affect a baby's growing brain and nervous system. Impacts on cognitive thinking, memory, attention, language, and fine motor and visual spatial skills have been seen in children exposed to methylmercury in the utero (USEPA 2006).

There is extensive studies documented the human methylmercury poisoning. The first documented widespread human methylmercury poisoning occurred in Minamata, Japan, between 1953 and 1960. Over time the source of the poisoning was traced to consumption of contaminated fish and seafood from Minamata Bay. Approximately 2,200 persons have Minamata disease. The most common clinical signs observed in adults were paresthesia, ataxia, sensory disturbances, tremors, impairment of hearing, and difficulty in walking (Harada 1995). In 1971, 90,000 metric tons of methylmercury-treated seed grain were imported through the southern seaport of Basra, Iraq, and distributed freely throughout the countryside. In late December 1971 the first case of methylmercury poisoning from this contaminated source was recorded. Within 2 months, 6530 hospital admissions and 459 hospital deaths were recorded from methylmercury ingestion. Children exposed in utero manifested severe sensory impairments such as blindness and deafness, general paralysis, hyperactive reflexes, cerebral palsy, and impaired mental development (Amin-Zaki 1974)

### Dose-response Assessment

There are three epidemiological studies for which quantitative analyses have become available since EPA's derivation of an RfD in 1995 (Council 2000). These longitudinal, developmental studies were conducted in the Seychelles Islands, the Faroe Islands, and New Zealand. The subjects of the Seychelles longitudinal prospective study were 779 mother-infant pairs from a fish-eating population (Davidson 1995; Myers 1995a; Myers 1995b; Myers 1995c; Myers 1997; Davidson 1998). Infants were followed from birth to 5.5 years of age, and assessed at various ages on a number of standardized neuropsychological endpoints. The independent variable was maternal-hair mercury levels. The Faroe Islands study was a longitudinal study of about 900 mother-infant pairs (Grandjean 1997). The main independent variable was cord-blood mercury; maternal-hair mercury was also measured. At 7 years of age, children were tested on a variety of tasks designed to assess function in specific behavioral domains. The New Zealand study was a prospective study in which 38 children of mothers with hair mercury levels during pregnancy greater than 6 mg/kg were matched with children whose mothers had lower hair mercury levels (Kjellstrom 1986; Kjellstrom 1989). At 6 years of age, a total of 237 children were assessed on a number of neuropsychological endpoints similar to those used in the Seychelles study (Kjellstrom 1989).

EPA chose BMD analysis as the most appropriate method of quantifying the dose-effect relationship in these studies, which was also the recommendation of the NRC (2000). A benchmark dose lower limit ($BMDL_{05}$) (the lower 95% confidence limit of the $BMD_{05}$) was calculated for each endpoint described above from the three studies. For Developmental neuropsychological impairment, the Benchmark Dose: $BMDL_{05}$ range of 46-79 ppb in maternal blood for different neuropsychological effects in the offspring at 7 years of age, corresponding to a range of maternal daily intakes of 0.857-1.472 μg/kg-day, the RfD is 0.0001 mg/kg-day.

**Exposure Assessment**

The population group of concern is adult subsistence anglers and their families who regularly eat catfish caught from Kittanning Dam area. The primary exposure pathway is ingestion of fish. Depending on different age and gender, 4 subpopulation groups are considered, including children from 3-8 years old, children from 9-15 years old, women of childbearing age and normal adults. In the exposure quantification, we use the exposure algorithm equation recommended by EPA (USEPA, Example Exposure Scenarios). The input parameters for use in risk are listed as Table 9. The 95% Confidence Interval of mean mercury level in catfish caught from Kittanning Dam is 0.154 mg/kg to 0.282 mg/kg wet weight. For risk based allowable monthly maximum fish consumption limit calculation, we use upper 95% Confidence Interval of the mean mercury level in Kittanning-caught catfish as a conservative method to assess the risk (USEPA, Example Exposure Scenarios). The oral reference dose for methyl mercury from IRIS is 0.0001 mg/kg-day, which is derived from the benchmark dose lower limit - $BMDL_{05,}$ meaning the lower 95% confidence limit of the $BMD_{05}$ based on the BMD analysis for methyl mercury dose-response relationship (NRC, 2000). A benchmark dose analysis was chosen as the most appropriate method of quantifying the dose effect relationship. The level chosen was a Benchmark Dose Lower Limit (BMDL); this was the lower 95% limit on a 5% effect level obtained by applying a K power model ($K >= 1$) to dose-response data based on mercury in cord blood. The BMDL was chosen as the functional equivalent of a no-adverse effect level for calculation of the RfD.

The RfD for methylmercury was not calculated to be a developmental RfD only. It is intended to serve as a level of exposure without expectation of adverse effects when that exposure is encountered on a daily basis for a lifetime. In the studies so far published on subtle neuropsychological effects in children, there has been no definitive separation of prenatal and postnatal exposure that would permit dose-response modeling. That is, there are currently no data that would support the derivation of a child (vs. general population) RfD (USEPA, 2001).

The assessment of methylmercury exposure from common media sources (e.g., diet, air) and relative source contribution (RSC) estimates follows the 2000 Human Health Methodology. The RSC is used to adjust the RfD to ensure that the water quality criterion is protective, given other anticipated sources of exposure. The exposure assessment characterizes the sources of methylmercury exposure in environmental media, providing estimates of intake from the relevant sources for children, women of childbearing age, and adults in the general population. Based on available data, human exposures to methylmercury from all media sources except freshwater/estuarine and marine fish are negligible, both in comparison with exposures from fish and compared with the RfD. Estimated exposure from ambient water, drinking water, nonfish dietary foods, air, and soil are all, on average, at least several orders of magnitude less than those from freshwater/estuarine fish intakes. Therefore, these exposures were not factored into the RSC. However, ingestion of marine fish is a significant contributor to total methylmercury exposure. But for our target population – the semi-subsistence anglers and their families, almost all of the fish consumption source are from freshwater caught fish.

We selected the basic demographic parameters' values from Exposure Factor Handbook (EPA 1997), assuming all the groups eat 1 meal per day and 4 meals of fish every week.

We did a sensitivity analysis for each subgroup, meaning that we were calculating the range of average daily dose (ADD) and the range of Hazard Quotients for each specified subgroup based on the 95% CI of mean mercury level in Kittanning-caught catfish.

The average daily dose of ingestion fish based on methyl mercury's noncarcinogenic health effects is expressed in kilograms of fish per day.

$$ADD = \frac{C_{fish} * IR_{fish} * EF * ED}{BW * AT} \qquad \text{(Equation 1)}$$

Where:

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

$C_{fish}$ = Concentration of contaminants in fish (mg/kg fish)

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

**EF** = exposure frequency (meals/day)

**ED** = exposure duration (days)

**BW** = body weight (kg) and

**AT** = averaging time (days)

Table 9. **Input Parameters for Use in Risk Equations**

| Equation parameter | | Values |
|---|---|---|
| **Reference dose (RfD)** | | $10^{-4}$ mg/kg-d |
| **Body weight (BW)** | **3-8 yr** | 22 kg |
| | **9-15 yr** | 45 kg |
| | **Childbearing Aged Women** | 64 kg |
| | **Adults** | 70 kg |
| **Per capita intake rate of fish ($IR_{fish}$)** | **Less than 16 yr old** | 4 oz (0.114 kg/meal) |
| | **Adults** | 8 oz (0.228 kg/meal) |
| **Measured concentration of contaminants in fish ($C_{fish}$)** | | 95% CI: (.154 - .282) mg/kg fish |
| **Exposure Frequency (EF)** | | 1 meals/day |
| **Exposure Duration (ED)** | | 4 days |
| **Averaging time (AT)** | | 7 days |

Using the equation, we can calculate the range of ADD for children at 3-8 years old as:

$$ADD_{.05} = \frac{0.154 \text{ mg/kg} * 0.114 \text{ kg/meal} * 1 \text{ meal/day} * 4 \text{ days}}{22 \text{ kg} * 7 \text{ days}}$$
$$= 4.6 \times 10^{-4} \text{ mg/kg-day}$$

$$ADD_{.95} = \frac{0.282 \text{ mg/kg} * 0.114 \text{ kg/meal} * 1 \text{ meal/day} * 4 \text{ days}}{22 \text{ kg} * 7 \text{ days}}$$
$$= 8.3 \times 10^{-4} \text{mg/kg-day}$$

Then the hazard quotient will be calculated by:

$$\textbf{Hazard quotient} = \textbf{ADD/RfD}$$

The hazard quotient is greater than 1 means the population have excess non-carcinogenic health risk from the specified pathway and exposure frequency of the catfish. The hazard is less or equal to 1 means the study populations don't have excess non-carcinogenic health risk from the specified pathway and exposure frequency of the catfish.

For children at 3-8 years old, the hazard quotient range based on the 95% confidence interval of measured mercury concentrations in catfish is:

$$\textbf{Hazard quotient}_{.05} = 4.6 \times 10^{-4} \text{ mg/kg-day} / 10^{-4} \text{ mg/kg-day} \approx 5$$

**To**

$$\textbf{Hazard quotient}_{.95} = 8.3 \times 10^{-4} \text{ mg/kg-day} / 10^{-4} \text{ mg/kg-day} \approx 8$$

The ADD and Hazard Quotients for all the subgroups are calculated and listed in table 8.

Table 10. **The ADD and Risk for Each Subgroup**

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

Moreover, we can get the allowable number of fish meals of a specified meal size that may be consumed over a given time period based on the RfD. The consumption limit is determined in part by the size of the meal consumed. An 8-oz (0.228-kg) meal size was assumed for adults and 4-oz (0.114-kg) meal size was for children below 9 years old. Equations 2 and 3 can be used to convert daily consumption limits, the number of allowable kilograms per day (calculated using Equation 2), to the number of allowable meals per month:

$$\mathbf{CR_{lim} = \frac{RfD * BW}{C_{fish}}} \qquad \textbf{Equation 2}$$

Where

**$CR_{lim}$ = maximum allowable fish consumption rate (kg/d)**

**RfD = reference dose (mg/kg-day)**

**BW = consumer body weight (kg)**

**$C_{fish}$ = measured concentration of contaminants in catfish (mg/kg fish)**

Equation 3 was used to convert daily consumption limits, in kilograms, to meal consumption limits over a given time period (month) as a function of meal size.

$$\mathbf{CR_{mm} = \frac{CR_{lim} * AT}{IR_{fish}}} \qquad \textbf{Equation 3}$$

Where

**$CR_{mm}$** = maximum allowable fish consumption rate (meals/mo)

**$CR_{lim}$** = maximum allowable fish consumption rate (kg/d)

**AT** = average time (30 days/month)

**$IR_{fish}$** = Per capita intake rate of fish (kg fish/meal)

We are presenting the maximum allowable monthly consumption limits based on the upper 95% CI of mean mercury level in catfish from Kittanning Dam as a conservative method. Thus, the maximum allowable fish consumption daily rate for children at 3-8 years old can be calculated as:

$$\mathbf{CR_{lim} = \frac{10^{-4}\ mg/kg\text{-}day * 20\ kg}{0.282\ mg/kg} = 7.1 \times 10^{-3}\ kg/day}$$

and the maximum allowable fish consumption monthly rate for children at 3-8 years old is:

$$\mathbf{CR_{mm} = \frac{7.1 \times 10^{-3}\ kg/day * 30\ day}{0.114\ kg/meal} \approx 2\ meal}$$

The monthly fish consumption limits for all subgroups are calculated and listed in Table 11.

Table 11. **Monthly Fish Consumption Limits for Non-carcinogenic Health Endpoints – Methyl mercury**

| Study Group | Fish meals/Month (Risk-Based Consumption Limit) | Fish Tissue Concentrations (upper 95% CI of mean mercury level)(mg/kg, wet weight) |
|---|---|---|
| **3-8 yr** | **2** | .282 |
| **9-15 yr** | **2** | .282 |
| **Women of Childbearing Age** | **3** | .282 |
| **Adults** | **4** | .282 |

## Risk Characterization

By calculation, the hazard quotients for all subgroups are greater than 1, which means all the subgroups are at greater risk of non-carcinogenic health effects by ingestion of catfish caught from Kittanning Dam. For each group, the range of hazard quotients are based on the 95%

confidence interval of measured mean mercury concentrations in catfish from Kittanning. Even with the left bound of the interval, all the hazards are still significant. Expressed as the maximum allowable fish consumption limits, the children below 16 years old can only eat at most 2 meals per month if the catfish is from Kittanning Dam Area. For women of childbearing age, they cannot eat more than 3 times of the fish, for adults it is 4 fish meals.

However, according to the transcript of the Pittsburgh Fish Consumption Study (Volz, C. D, 2007), most of anglers stated that they consumed fish at least twice every week with ingestion amount which usually great than 8 oz. In warm seasons, the effects of eating 30 fishmeals on 30 consecutive days need to be considered.

In this assessment, we didn't have the exact demographic and socioeconomical information about the study population. We made conservative assumption for total mercury in fish tissue and we used upper 95% confidence interval mercury concentration in fish. We also expected that in different seasons, the semi-subsistence anglers would have different fishing and consumption patterns. However, the significant difference between the fish consumption limit and the actual ingestion amount indicated from fish consumption study presented that the types of site-specific information including fish behavior, consumption advisories, contamination levels and knowledge are required for semi-subsistence anglers and their families. The World Health Organization recommends (WHO 1990) biological testing of women of child-bearing age – particularly pregnant women -- who consume large amounts of fish, i.e., greater than 100g per day. Biological testing is a more valid estimation of risk than self-reported consumption. Effective risk communication will have occurred when the target audience has been provided with sufficient site- and fish-specific information about the risks and benefits of consuming a given species of fish.

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Internet Resources (Figures and GIS Data):

http://www.epa.gov/mercury/exposure.htm

http://www.pasda.psu.edu/