Development of an Ohio River Site-Specific Methyl Mercury Bioaccumulation Factor

Ohio River Mile 126 · Hannibal Locks and Dam

ORSANCO

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Abstract

The report describes a methyl mercury bioaccumulation study that was conducted over one year near Hannibal Locks and Dam at mile 126 on the Ohio River near Moundsville, West Virginia. The study area was in the vicinity of a facility with a large mercury discharge that was granted a variance from the Ohio River Valley Water Sanitation Commission (ORSANCO) prohibition of mixing zones for Bioaccumulative Chemicals of Concern (BCCs) in 2012. The study shows bioaccumulation factors higher than those USEPA presented as Draft National Bioaccumulation Factors in 2001. The higher bioaccumulation factors indicate a risk for mercury concentrations in fish tissue to exceed the 0.3 mg/kg water quality criterion at aqueous concentrations of total mercury below ORSANCO's current criterion of 0.012 ug/L. Directly measured methyl mercury concentrations in water and fish tissue proved comparable to earlier Commission work with total mercury measured in water and hybrid striped bass tissue. The information may be used to evaluate whether the Commission's current 0.012 ug/L water quality criterion for total mercury is protective of the 0.3 mg/kg methyl mercury tissue criterion.

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Introduction

The Ohio River is a multiple-use waterway with protected uses for drinking and industrial water, recreation, aquatic life use, and safe consumption of fish. The Ohio River Valley Water Sanitation Commission (ORSANCO, the Commission) has documented in Ohio River Biennial Assessments from 2002-2014 (encompassing data from 2001-2014) the existence of mercury contamination in aqueous form and resultant bioaccumulation in fish tissue. Violations of the 0.012 ug/L total mercury (THg) Water Quality Criterion (WQC) (ORSANCO, 2013) occur on a regular basis at all monitoring stations on the Ohio River and with greater frequency in the lower third of the 981-mile river (see Figure 1).

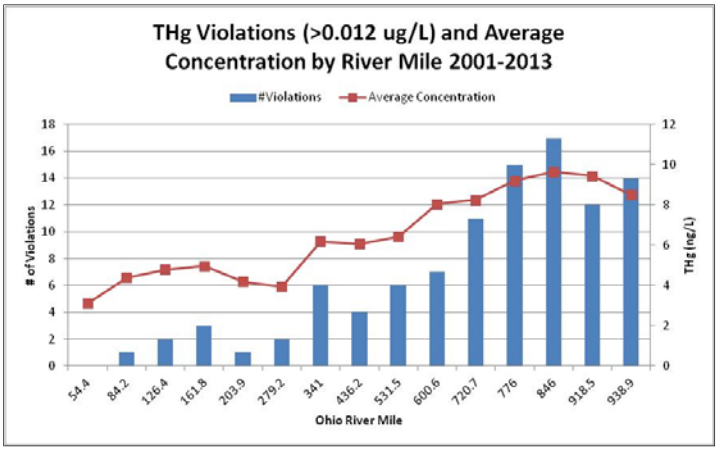

Figure 1: Total Mercury WQC Violations and Average Concentration

ORSANCO monitoring of total mercury in Ohio River fish tissue to support human health consumption advisories has been routine since 1989. ORSANCO adopted a USEPA fish tissue criterion of 0.3 mg/kg methyl mercury (USEPA, 2001) for the protection of human health in 2003. In 2009, to satisfy assessments of the tissue criterion, ORSANCO began directly measuring methyl mercury in fish tissue.

Monitoring of the dual human health criteria for total mercury in water and methyl mercury in fish tissue has created conflicts in Ohio River Biennial Assessments which must be approved by the Commission's eight Compact states. Assessments of Ohio River uses based on the individual criteria often disagree, in such cases the Commission has elected to follow a "weight-of-evidence" approach which allowed the frequently violated water column criterion to be reported alongside a lack of evidence of fish tissue impairment. The conflicting measurements have resulted in a determination of "unassessed" (ORSANCO 2008, 2012) or "supporting" (ORSANCO, 2014).

Site-Specific Methyl Mercury Bioaccumulation Factor

An impending October 2013 prohibition on mixing zones[1] for bioaccumulative chemicals of concern (BCCs) threatened to create end-of-pipe discharge permit limits for total mercury at the 0.012 ug/L concentration. A request for a discharge variance from the mixing zone prohibition was received by the Commission from a facility near Hannibal Locks and Dam at Ohio River mile 126 in 2011. The need to resolve conflicting mercury assessments and the variance request spurred the proposal to develop a single site-specific Bioaccumulation Factor (BAF) for methyl mercury in fish tissue as it related to methyl mercury and total mercury in the water column.

Methyl Mercury in the Ohio River

Inorganic and organic mercury exists in the environment through both anthropogenic and

[1] "an area where an effluent discharge undergoes initial dilution" (USEPA, 1991)

natural sources. Once released to the atmosphere, elemental mercury (Hg^o), which is volatile, will remain in a gaseous state. Some elemental mercury is oxidized in the atmosphere and will return to ground level chiefly in the form of dissolved Hg (II) with precipitation (Morel et al., 1998). Mercury becomes highly bioavailable after conversion to the organic form, methyl mercury, by the addition of a single carbon methyl group, which can then be taken up by plankton and zooplankton (Mason, et al., 1995). The methyl mercury form then biomagnifies in the food web resulting in the highest concentrations occurring in the top predators, such as Hybrid Striped Bass, a commonly consumed sport fish in the Ohio River. Methyl mercury is toxic to humans and is of particular concern; because it is able to cross blood-brain and placental barriers more easily than inorganic mercury (USDHHS, 1999).

The Ohio River main channel is not likely to be a site for the net transformation of inorganic mercury to the more bioavailable form methyl mercury. Methyl mercury has been shown to be most effectively produced in anoxic conditions and sediment pore water with available sulfate-reducing bacteria (Glimour, 1992, Ekstrom, E.B., et al., 2003). De-methylation likely overtakes methylation in the water column due to aerobic conditions and light transmission (Korthals, E.T. and Winfrey, M.R., 1987, Tsz Ki Tsui, M. et al., 2013). In addition, studies have shown regulated rivers like the Ohio River show less methyl mercury accumulation in tissue due to infrequently inundated floodplains and directly connected wetlands (Rypel, 2008).

ORSANCO Monitoring of Aqueous Methyl Mercury

In 2010, ORSANCO first measured concentrations of aqueous methyl mercury in the Ohio River as part of a cooperative effort with the United States Geological Survey Indiana Water Science Center (USGS IN). In that project, three sample events were conducted at six locations on the Ohio River (Risch, 2011). Samples were collected by USGS and ORSANCO personnel using USEPA Method 1669 clean techniques and the Equal Discharge Increment (EDI) method (see Monitoring Methods, pg 9) with concurrent grab samples by ORSANCO sampling staff at adjacent fixed monitoring stations. Laboratory analysis of mercury and methyl mercury was performed by the USGS Mercury Research Laboratory in Middleton, Wisconsin. The reporting limit (RL)for mercury and methyl mercury in that study was 0.05 ng/L with a method detection level (MDL) of 0.04 ng/L.

An important finding of that investigation was that unfiltered surface grab samples for methyl mercury showed very poor correlation with concentrations measured from the entire river channel by the multiple vertically integrated and composited samples of the EDI method. Methyl mercury was only detectable during the high flow sampling events in May when suspended mean solids were elevated (arithmetic mean 155 mg/L, geometric mean 118 mg/L).

In summary, 18 composite samples were analyzed for aqueous methyl mercury, resulting in 9 detections in unfiltered samples with a maximum concentration of 0.13 ng/L, a Kaplan-Maier (a survival function that can be used to estimate summary statistics of censored environmental data, see Helsel, 2005)

estimated median of 0.04 ng/L, and minimum values below detectable concentrations.

Further measurements of aqueous methyl mercury were made by ORSANCO in a separate study of power plant discharges from 2012-2013 (ORSANCO, 2013b). That study included sampling of raw Ohio River intake water and generated 15 unfiltered methyl mercury results from four different locations. Raw intake water was collected from running taps directly connected to intake pumps. The large volumes and high velocities of the intake pumps minimize alterations of the sample water from the pump system (USEPA, 1975). Power generation facility intakes draw from mid-depth, bankside locations and are less impacted by photo degradation of methyl mercury than can occur in the light permeated zone of surface grab samples (Tsz Ki Tsui, M. et al. 2013). These samples are included in the body of knowledge about aqueous methyl mercury in the Ohio River because there are so few samples overall (Figure 2). The current bioaccumulation study adds 12 more methyl mercury results. Each of the later two studies benefitted from a lower reporting level of 0.04 ng/L with a MDL of 0.02 ng/L.

Combining the data gathered from all Ohio River methyl mercury measurements results in 45 samples, with 26 measured values above the reporting limits of the two different laboratories (0.05 ng/L and 0.04 ng/L). Of the 26 measured values, 9 were qualified by the laboratory as "J-values," meaning estimated from results below the reporting level but above the detection level. There were 19 non-detects reported below the RLs (denoted < RL EDI Sample and <RL Intake Sample in Figure 2). The Kaplan-Maier estimated median for all Ohio River methyl mercury samples is 0.35 ng/L. Individual results used to calculate this median are presented in Appendix B.

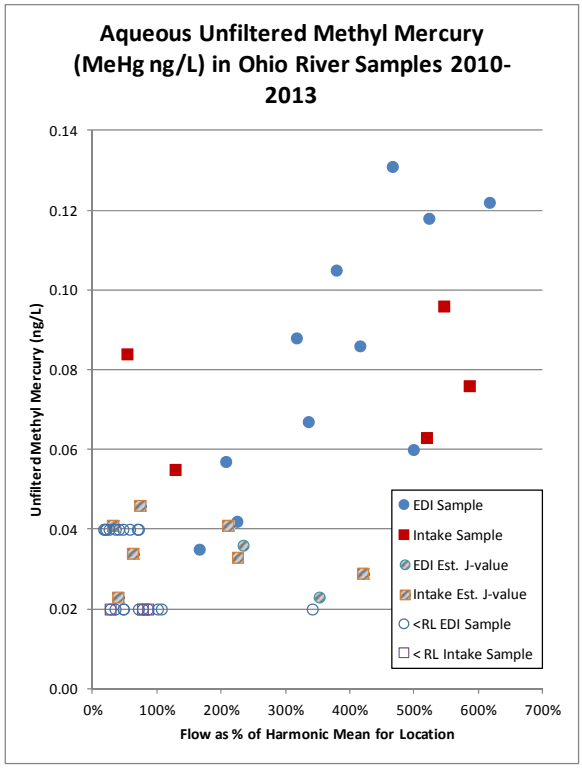

Figure 2: Ohio River Methyl Mercury Samples vs. Flow

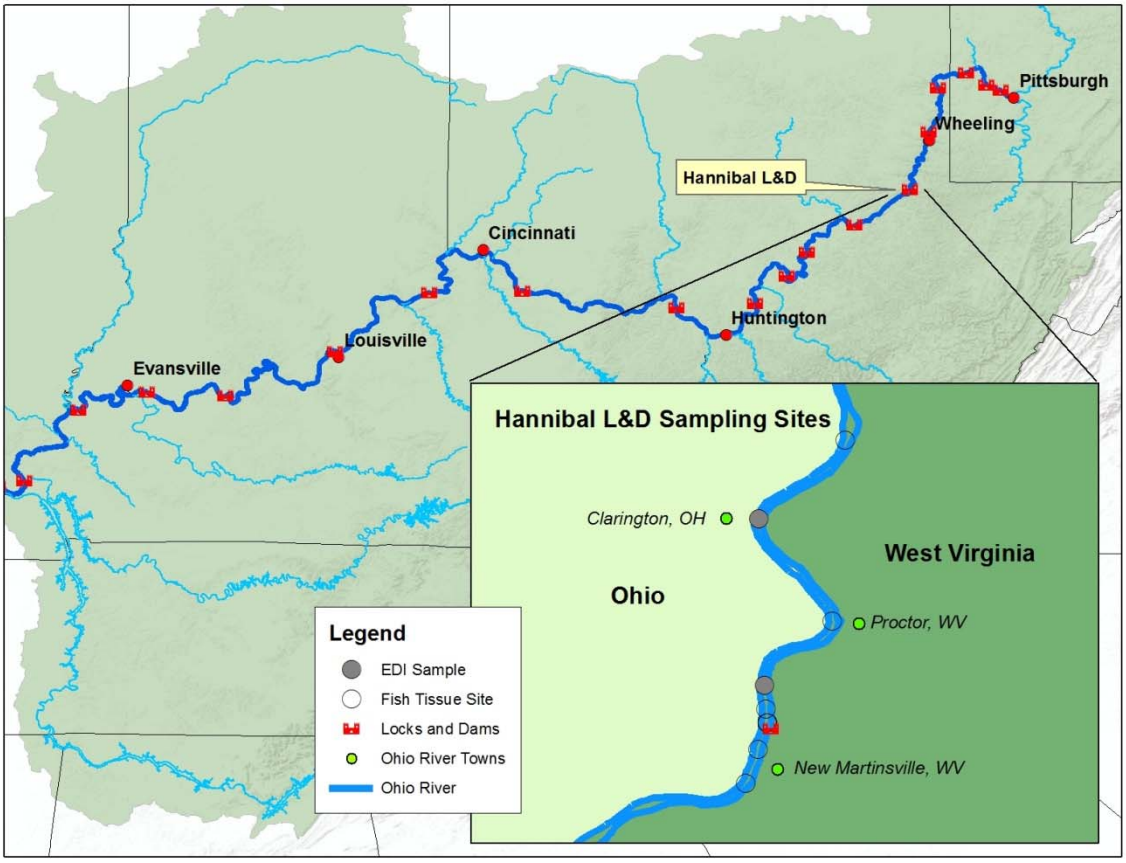

Figure 3: Location Map for Site-Specific Methyl Mercury BAF
(EDI Samples are collected by Equal Discharge Increment methods, see Monitoring Methods section)

Bioaccumulation Factor Study Design: Aqueous and Tissue Sampling

A one-year project was planned to develop a site-specific bioaccumulation factor at Ohio River mile 126 in the region of the mercury discharge variance request. Aqueous methyl mercury concentrations were measured with monthly sample events a mile upstream from Hannibal Locks and Dam. Fish tissue methyl mercury concentrations were measured in 17 tissue composites of commonly consumed trophic level 3 and trophic level 4 species.

Water was sampled by the Equal Discharge Increment method for the period July 2012 through June 2013. Monthly sampling was intended to capture wide conditions of seasonal variation in filtered methyl mercury that have been reported in unregulated smaller streams (Bradley, P.M., et al., 2011) and could persist in the highly regulated and large Ohio River system. Samples were gathered over that year at river flows ranging from 3,900 cubic feet per second (cfs) to 102,000 cfs. Those event flows represent a range on the 15-year flow duration

curve from the 1st percentile to the 93rd percentile flow. Sample events are shown in thousand cubic feet per second (kcfs) on the 15-year flow duration curve (Figure 4).

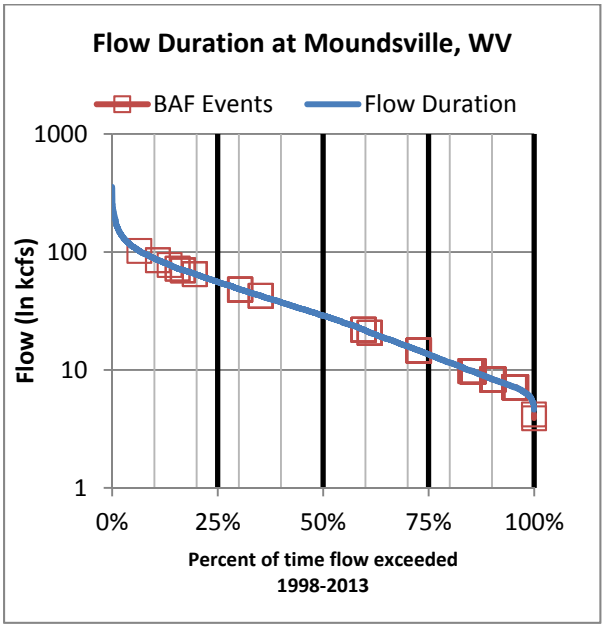

Figure 4: Flows Sampled for BAF Methyl Mercury Data

Fish tissue samples were composites of filets from three individual fish and were taken from fish species thought to be commonly encountered and caught by anglers or commercial fishermen. Composites were harvested from fish of consumable size and of commonly consumed species to satisfy the intent of the bioaccumulation factor to assess risk to human health from fish consumed by people in the Ohio River Basin. Tissue collection was planned for two time periods to account for possible seasonality in tissue mercury concentrations (Greenfield, B.K., et al., 2012) due to growth of yearly young or change of seasonal forage.

Monitoring Methods

Tissue Accumulated Mercury

ORSANCO has developed a protocol for sampling of fish tissue (Emery, et. al., 2003) that closely relates to common fish consumption practices. In keeping with the preparation used by most fishermen, a single left-side fillet is collected from each individual fish. Fillets are descaled but kept skin-on in keeping with common practices for fish preparation and consumption. The collected fillets are frozen and shipped to the analyzing laboratory. Tissue composite samples consist of three individual fish of the same species of which the total length of smallest individual in the composite must be at least 75% of the length of the largest individual in that same sample. An arithmetic mean length is recorded for each composite tissue sample. Fish are collected as part of specific tissue surveys and as bycatch from other fish population surveys.

Aqueous Mercury

The Equal Discharge Increment (EDI) method was used to collect water samples to be analyzed in both unfiltered and filtered forms for methyl mercury concentrations. The EDI method for collection of isokinetic, depth-integrated samples was selected because it is important for methyl mercury, a photosensitive parameter, which may be reduced in the surface grab sampling zone by the transmission of sunlight. It is also known that particulate-bound pollutants, like elemental mercury, are not always as well-distributed in the water column as dissolved constituents, a finding supported by an earlier ORSANCO assessment of sampling methods (ORSANCO, 2009).

Equal Discharge Increment Method

The EDI method, described in the USGS manual Techniques for Water Resource Investigations (TWRI) (USGS, 2006), is a product of the Federal Interagency Sedimentation Program and was devised to accurately assess suspended sediment loads in rivers. The EDI method requires accurate measurement of river velocities across the channel at the sample location. The optimum instrument for that measurement is the Acoustic Doppler Current Profiler (ADCP) which will calculate water velocities from the surface to the river bottom in a series of "bins" or square segments (Figure 5). Using the comprehensive velocity information, five verticals are calculated representing 10, 30, 50, 70, and 90% of the accumulating discharge from one side of the river to the opposite bank. Samples are collected from the five verticals, each at the center of segments representing 20% of the river discharge.

Isokinetic Sample Collection

The D-96-A-1 collapsible bag sampling device uses interchangeable intake nozzles that are sized to match water velocities ensuring no change in velocity at the intake, thus the sample is collected isokineticly. Changes to the velocity of collected water at the intake could skew the capture of suspended particles (USGS, 1999). The sampler is lowered from the surface to the channel bottom and back to the surface at a calculated transit rate, creating the depth-integrated sample. The transit rate is calculated for each vertical sample to ensure equivalent volumes are collected regardless of the total depth travelled. The five verticals are composited for a sample representing the entire discharge of the river. A complete description of the EDI method is found in the USGS TWRI (USGS, 2006).

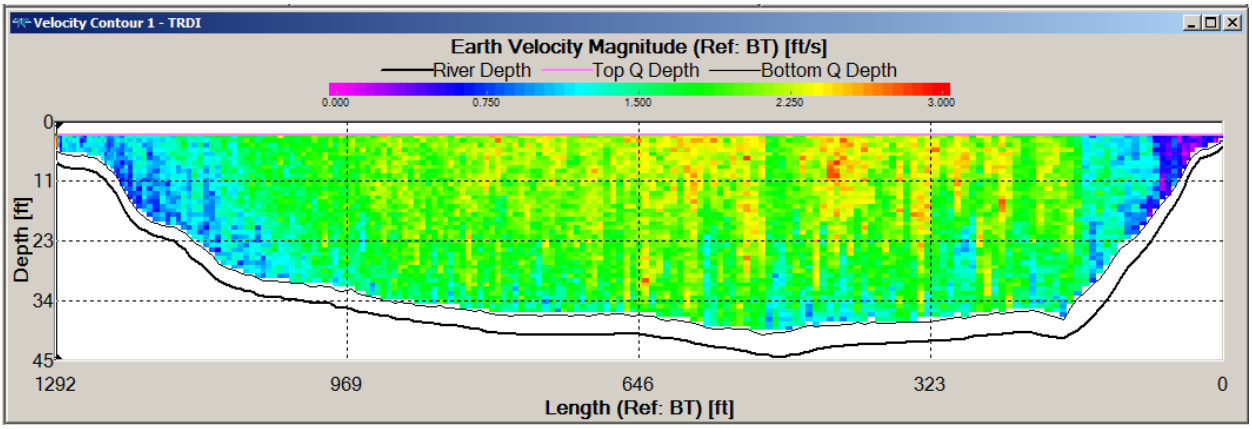

Figure 5: ADCP Measurement at Ohio River Mile 126 on March 19, 2013, Total Discharge 72,268 cfs

Clean methods (i.e. clean hands/dirty hands) from USEPA Method 1669 (USEPA, 1996) were used along with lint-free outer clothing as measures to prevent sample contamination. Fluoropolymer bags were used in the D96-A-1 with fluoropolymer intake nozzles in the as shown in Figure 6.

Figure 6: Clean Techniques Employed for BAF Sampling

The sample was composited in a fluoropolymer churn splitter and decanted into specific sample containers off the boat in the ORSANCO Mobile Laboratory on a clean plastic-covered surface. All samples collected were sent to the laboratory in unfiltered, whole-water form. For determination of dissolved mercury fractions samples were filtered by the contract laboratory.

Equipment decontamination procedures came from USGS TWRI (USGS, 2004) and included cleaning with anionic detergent and subsequent rinses with tap water, 5% hydrochloric acid, Type II deionized water, and ambient sample water at the site and time of the next event. Fluoropolymer bags were not reused. New bags were rinsed with acid and deionized water and then rinsed with ambient sample water at the site prior to use.

Mercury and Methyl Mercury Analysis

Analytical work for the bioaccumulation factor project was performed by Brooks Rand Laboratories (BRL) of Seattle, Washington. BRL employed USEPA Method 1631 for aqueous total mercury and 1631E for aqueous methyl mercury, obtaining method limits of 0.15 ng/L for total mercury and 0.02 ng/L for methyl mercury. Filtered and unfiltered aliquots of the samples were prepared by BRL in their environmentally-controlled laboratory for determination of dissolved and total recoverable mercury and methyl mercury.

BRL performed fish tissue analysis on a wet weight basis using USEPA Method 1631 (USEPA, 2002) for total mercury and USEPA Method 1630 (USEPA, 1998) for methyl mercury. Brooks Rand Laboratories achieved method detection limits of 0.6 ng/g (ppb) for Method 1631 and 1.0 ng/g for Method 1630.

Quality Assurance Sample

One field blank was collected as part of the 12 monthly events of the bioaccumulation factor monitoring plan. The field blank was collected using all the equipment for the water sample collection and compositing. Results of the mercury and methyl mercury analysis for the field blank were less than the laboratory method detection limit (MDL) of 0.15 for total mercury and 0.02 ng/L for methyl mercury (Table 1, Appendix A).

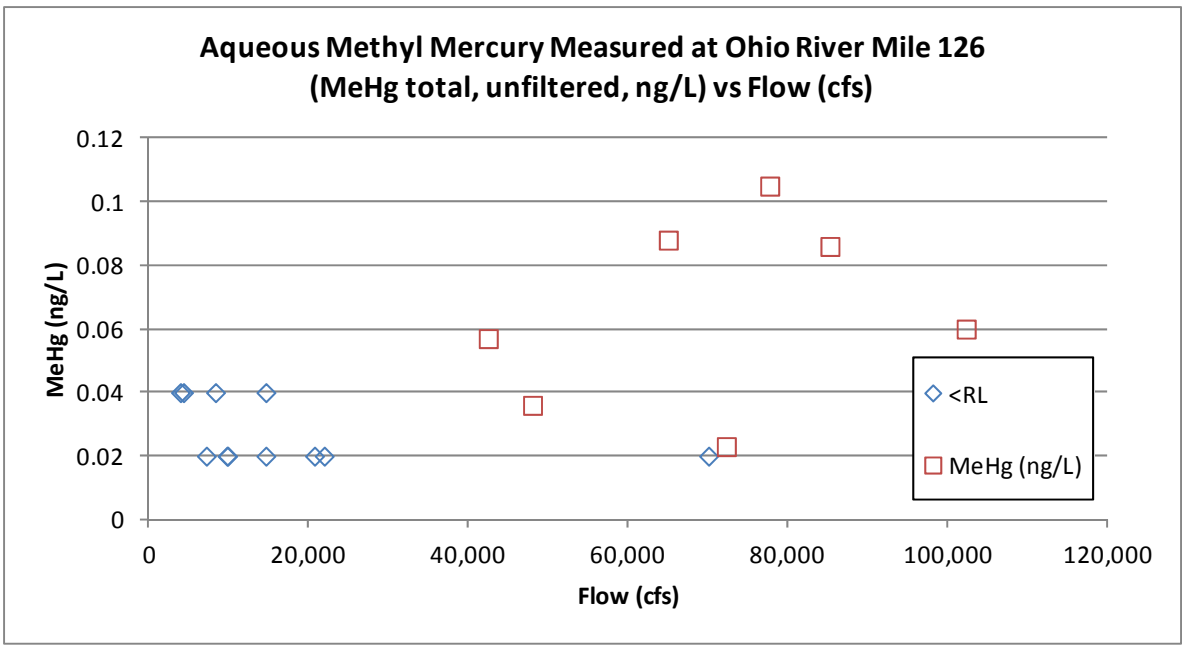

Figure 7: Aqueous Methyl Mercury Data Collected for BAF

Additional Data Available for Bioaccumulation Factor Calculation

Monthly samples collected specifically for the BAF (12) and 6 samples collected in 2010 (as part of the earlier study) were combined to yield a set of 18 composite water samples. The year of water sampling for the BAF development began in July 2012 and finished in June of 2013. Water methyl mercury analysis results are plotted against flow conditions in Figure 7 and presented with the total mercury data in Appendix A.

Tissue samples were gathered from Mile 113, 13 miles upstream of Hannibal Locks and Dam, to Mile 129.3, three miles downstream of the navigation dam. The majority of the tissue, 12 composite samples, was collected in the immediate tailwaters of the dam at mile 127.

Tissue used in the BAF calculation was collected from 2010 to 2013. Tissue specifically for the BAF project was collected in November 2012, April 2013, and July 2013 during the year of water sampling. In addition to the 12 composite samples gathered for the project, five composites from earlier tissue sampling in April and June of 2010 were included to match the period of water data used in the study. The available tissue data for the bioaccumulation factor included 12 trophic level 3 (TL3) species specific composites: two collected in 2010, five in the fall of 2012, and five in the spring of 2013. Five trophic level 4 (TL4) composites were analyzed: two collected in 2010, one in November 2012 and one each in April and July 2013. Methyl mercury tissue results are presented with average length of the composite samples ($r = 0.756$, $p < 0.005$) and the tissue criterion in Figure 8, and in tabular form in Appendix A.

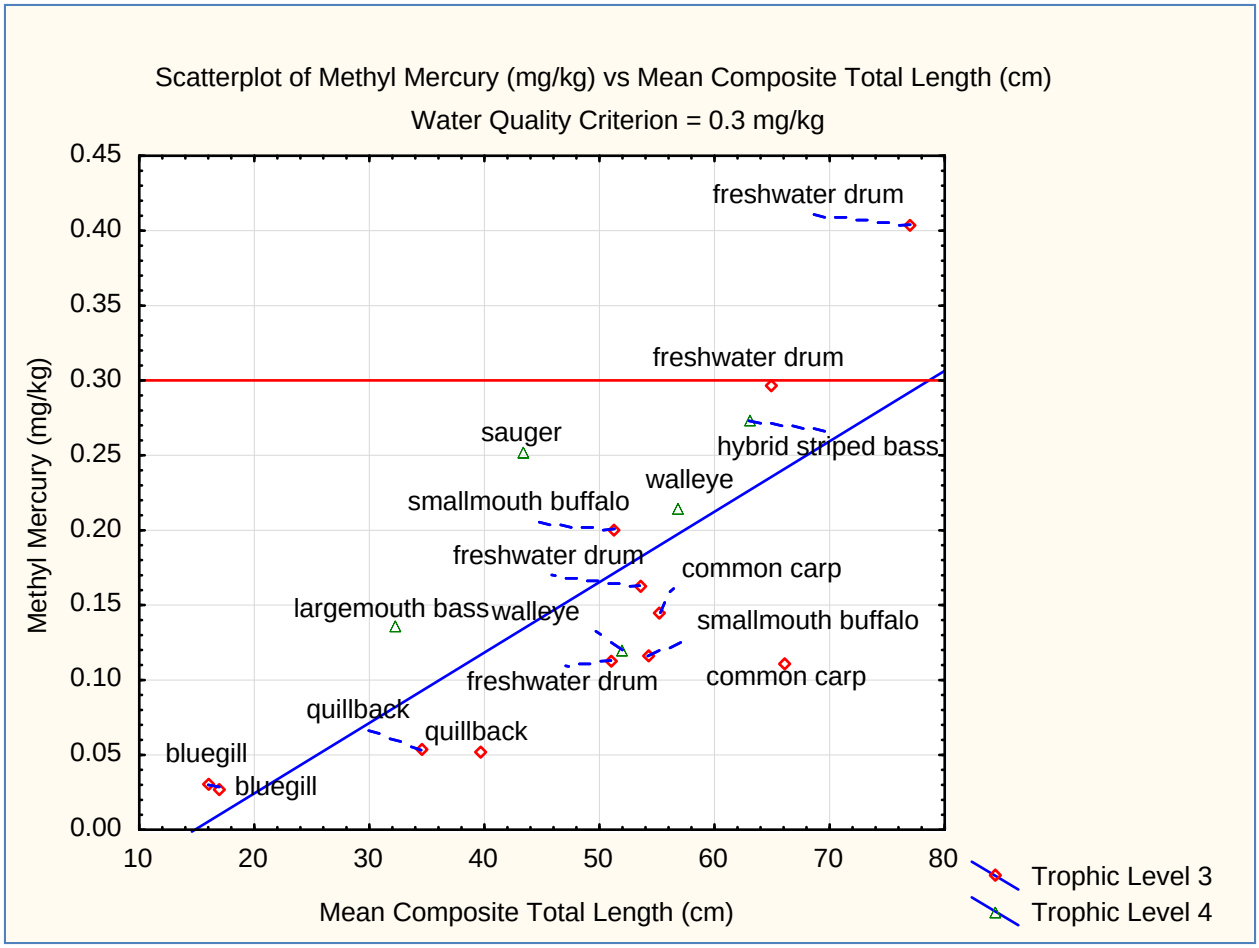

Figure 8: Tissue Methyl Mercury Data Collected for BAF

Bioaccumulation Factor Calculation

The bioaccumulation factor (BAF) is intended to be calculated directly from the tissue concentrations and the water concentrations of a given pollutant. A bioaccumulation factor is "a ratio (in L/kg) which relates the concentration of a chemical in water to its expected concentration in commonly consumed aquatic organisms in a specified trophic level." (USEPA, 2001) When the pollutant water concentrations are directly measured, the BAF can be termed "direct." If concentrations are estimated, rather than measured, the resulting BAF is termed "converted." A converted BAF for methyl mercury was published by USEPA in 2001 as the Draft National Bioaccumulation Factor for Methyl Mercury (USEPA, 2001) referred to in the following discussion as the Draft National BAF. Previous efforts have established methyl mercury to be superior to total mercury as a predictor of fish tissue methyl mercury contamination (Riva-Murray, K. et al., 2013).

The effort in this project was to quantify for the first time in the Ohio River the dissolved methyl mercury concentration in the water with direct measurement of methyl mercury in fish tissue from the same location, and therefore calculate a direct BAF for methyl mercury at a single location in the Ohio River. Standardization of tissue concentrations by size/age has been

recommended by USEPA (USEPA, 2010), although that approach is intended to mitigate variability due to size and age when combining tissue data from multiple locations. Size standardization has not been performed as part of this single site-specific BAF: however, it is necessary if data from this location were to be compared to same species data from another location in the future.

Water sampling for this project did not produce enough measured values of filtered methyl mercury to use that metric directly. For that reason, the resulting BAF is based partially on estimated dissolved methyl mercury values and becomes a "converted" BAF like the USEPA Draft National BAF. Equation 1 describes the BAF calculation (Watras, C.J., and Bloom N.S., 1992).

Equation 1: BAF Calculation

$$BAF_{(L/kg)} = \frac{CT_{MeHg(mg/kg)}}{CW_{Est.FMeHg(mg/L)}}$$

Where:

CT_{MeHg} = concentration of methyl mercury in fish tissue, wet weight basis

$CW_{EstFMeHg}$ = geometric mean concentration of estimated filtered methyl mercury in water

Partition of Methyl Mercury and Total Mercury in the Ohio River at mile 126

For the site-specific BAF, unmeasured concentrations of methyl mercury were estimated by utilizing the geometric mean of percent methyl mercury observed in all Ohio River samples (1.3%, N=25, SD 0.007) and the total mercury detected in each sample. Combining all paired total and methyl mercury detections from the 2010 study and the current BAF study yields an estimate of the percent of aqueous mercury that is methylated at Ohio River Mile 126. The geometric mean percent methyl mercury of each paired detection in the BAF study area is 1.2% (N=11, SD=0.005) and appears to be stable at that level through the normal range of concentrations of total mercury found in the Ohio River. At very low levels of total mercury, where methyl mercury detections are estimated, designated as "j-values," the percentages appear higher, but analytical noise may account for this variation (Figure 9).

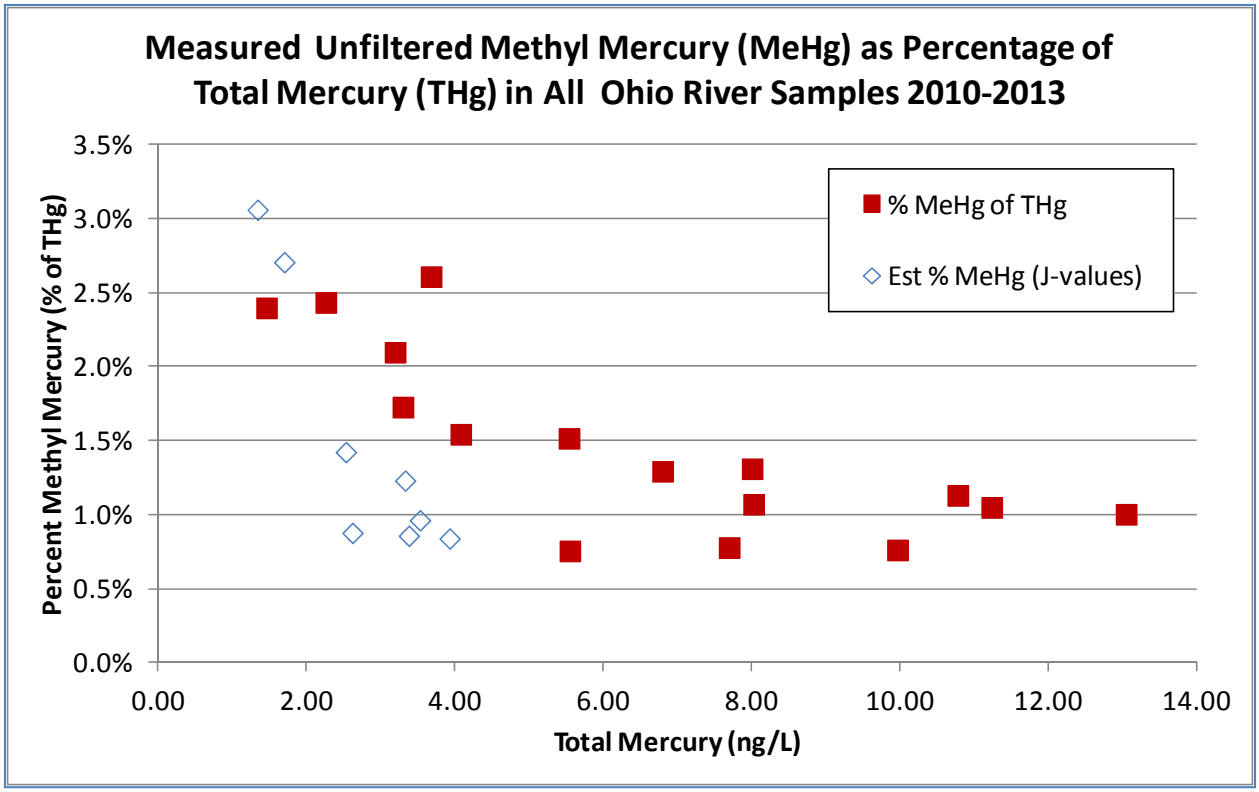

Figure 9: Percent methy mercury at varying total mercury concentrations

The percent unfiltered methyl mercury observed in the Ohio River (1.3%) was further reduced to estimate only the filtered portion of the methyl mercury using the USEPA translation factor for dissolved methyl mercury from total methyl mercury: 0.49 (USEPA, 2001). This translator indicates half of the methyl mercury in water is in the dissolved phase. The USEPA translation factor is consistent with the average of the only two measured concentrations of filtered methyl mercury at this location which indicated 57% and 38% of methyl mercury was in the dissolved phase. Studies in other water bodies have shown consistently higher percentages of filtered methyl mercury (Riva-Murray, K. et al., 2013) although other measured filtered methyl mercury fractions (Appendix B) in the Ohio River support the 0.49 translator suggested by USEPA.

Where measured values of methyl mercury are available the estimated filtered methyl mercury uses only the translator offered by USEPA. The two measured filtered methyl mercury concentrations have been used without modification in calculation of the BAF. See Appendix A, Table 3, for the estimation method and methyl mercury value used for each sample event. This combination of measured and estimated concentrations was also used in calculation of the Draft National BAF values. The geometric mean of the estimated filtered methyl mercury in water is 0.014 ng/L.

BAFs can be calculated on an individual sample basis using the concentration in a single fish tissue composite vs. the geometric mean of the water concentrations or generalized by trophic level using the geometric mean concentration of all tissue samples gathered. Individual BAFs calculated for fish tissue composites are plotted

in Figure 10 which also shows the geometric mean for each trophic level plotted as a larger marker. The geometric mean of trophic level 3 tissue samples collected for the BAF is 0.105 ng/g while the geometric mean of trophic level 4 samples is 0.189 ng/g. The final site-specific BAFs are the geometric means for each trophic level: 7.4E+06 for trophic level 3 and 1.3E+07 for trophic level 4.

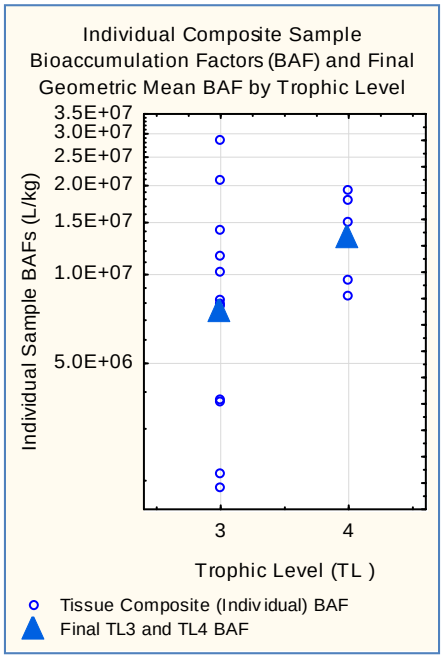

Figure 10: Range of individual calculated BAFs

The site specific BAFs are compared to the similarly calculated Draft National Bioaccumulation factors in Table 1. The calculated Ohio River BAFs are one order of magnitude higher than those calculated nationally; however, the National BAFs are calculated from both lentic and lotic data and "the lotic BAFs are primarily based on data from canals of the Everglades (assumed to act as flowing aquatic ecosystems) and a point-source contaminated stream in Tennessee." (USEPA, 2001).

The Ohio River site specific BAFs for trophic level 3 are higher than the 95th percentile of BAFs (6.2E+06) calculated for the draft national values while the trophic level 4 BAF is lower than the 95th percentile BAF (2.8E+07) reported in the national study.

Table 1: Site Specific BAF vs Draft National BAF

ORSANCO MeHg BAF vs. Draft National BAFs			
TL	ORSANCO BAF	National BAF	Nat. Lotic BAF
TL3	7.4E+06	6.8E+05	5.2E+05
TL4	1.3E+07	2.7E+06	1.2E+06

Relating Methyl Mercury BAFs to Total Mercury Concentrations and Discharges

The bioaccumulation of methyl mercury in fish tissue can be related to total mercury in the Ohio River and discharges using the translators previously used to estimate dissolved methyl mercury. Total mercury is historically the parameter of interest because National Pollutant Discharge Elimination System (NPDES) discharges to the Ohio River are frequently regulated based on their total mercury concentration. Permits based on the more bioavailable methyl mercury concentrations remain unlikely because the concentrations of methyl mercury are very small and the analysis is expensive.

By transforming the BAF equation and using the 0.3mg/kg total mercury fish tissue criterion as shown in Equation 2, one can arrive at a water concentration of methyl mercury that is protective of the tissue criterion. The resulting aqueous methyl mercury concentration corresponds to the geometric mean used in the equation as representative of the long-term conditions of mercury exposure. That "critical value" can be transformed to the assumed corresponding total mercury concentration using the partition of dissolved methyl mercury and partition of methyl mercury to total mercury. With this information, the BAF can be

compared to the existing total mercury water criterion of 12ng/L. The current BAF can also be compared with earlier total mercury BAF work completed in 2009.

Equation 2: Conversion of BAF equation to calculate critical aqueous total mercury concentration

$$\frac{\left(\frac{CT_{MeHg(mg/kg)}}{BAF_{(L/kg)}}\right)}{F_{dMeHg/tHg(\%)}} = CW_{THg(ng/L)}$$

Where:
BAF = bioaccumulation factor
CT_{MeHg} = concentration of methyl mercury in fish tissue
$F_{dMeHg/THg}$=fraction of total mercury as dissolved methyl mercury
CW_{THg} = concentration of total mercury in water (geometric mean)

Table 2 shows the critical values of total mercury indicated by the site specific BAFs for trophic level 3 and 4 species and combines those two BAFs as an arithmetic mean and as a consumption-weighted mean using the National fish tissue consumption weights given by USEPA for each trophic level Shown in Equation 3. The consumption calculation is based on apportioning the 17.5 g/day national default consumption rate for freshwater fish by trophic level (USEPA, 2000). The same weighting is applied to the trophic level 3 and 4 tissue concentrations to arrive at a single bioaccumulation factor to relate tissue concentrations to total mercury water concentrations.

Equation 3: Consumption Weighting of Ohio River Trophic levels

$$C_{avg} = \frac{8.0 * C_3 + 5.7 * C_4}{(8.0 + 5.7)}$$

Where:
C_{avg}= average mercury concentration across applicable trophic levels
C_3 = average mercury concentration for trophic level 3
C_4 = average mercury concentration for trophic level 4

Table 2 shows the translator in the calculation from the BAF to a water concentration of total mercury as 0.0064 for the ORSANCO data and 0.014 for the USPA study. The different translators come from the 2001 methyl mercury criterion document (USEPA, 2001) that offers the 0.49 translator from unfiltered methyl mercury to filtered methyl mercury and also reports a 0.014 translator from total mercury to filtered methyl mercury.

Table 2 also shows critical values calculated for each TL3 in the ORSANCO study and in the USEPA National Study. Consumption weighted critical values are calculated for the draft national BAFs using all trophic levels and using only trophic level 3 and 4 as in the ORSANCO study. The ORSANCO consumption-weighted BAF indicates the critical value of total mercury at Ohio River mile 126 is a long-term mean concentration of 4.8 ng/L. See Appendix C for a test of the BAF-generated consumption weighted critical value against existing background concentrations of total mercury in the Ohio River at Hannibal Locks and Dam.

Table 2: Values of aqueous mercury critical values based on 0.3 mg/kg tissue criterion

BAF	BAF value (L/kg)	Critical Value (ng/L MeHg)	Translator (1.3%x49%)	Critical Value (ng/L THg)
ORSANCO TL3 BAF	7.4E+06	0.04	0.0064	6.3
ORSANCO TL4 BAF	1.3E+07	0.02	0.0064	3.5
Draft Natl. TL3 BAF	6.8E+05	0.44	0.014	31.5
Draft Natl. TL4 BAF	2.7E+06	0.11	0.014	7.9
Draft Natl. Average BAF	1.7E+06	0.18	0.014	12.7
ORSANCO Average BAF	1.0E+07	0.03	0.0064	4.5
Consumption Weighted (CW) Average				
Draft Natl. CW BAF	1.2E+06	0.25	0.014	17.6
Draft Natl. BAF TL3&4 only	1.5E+06	0.20	0.0140	14.1
ORSANCO CW BAF	9.9E+06	0.03	0.0064	4.8

Comparison to Total Mercury Bioaccumulation Factors

In 2010, prior to collection of any methyl mercury data on the Ohio River, ORSANCO produced a bioaccumulation study (Emery, E.B., Spaeth, J.P., 2011) based on total mercury concentrations in water and fish tissue. No data was collected in the vicinity of the current BAF project or the Hannibal Locks and Dam navigation pool. This data is included here as a means to estimate the BAF variability along the length of the Ohio River.

The 2010 study focused on large (>55 cm) hybrid striped bass (*Morone chrysops x M. saxatilis*) [2], a top predator at high risk for methyl mercury bioaccumulation. Composite tissue samples of three individuals each from 12 Ohio River navigation pools were compared to ORSANCO's long-term fixed monitoring station data for total mercury. The BAFs produced by that study ranged from $8.4x10^4$ to $4.1x10^4$ L/kg.

These much lower BAFs are indicative of the higher concentration averages in aqueous total mercury versus the very low concentrations of dissolved methyl mercury that produce BAFs several orders of magnitude larger (i.e. 10^6 - 10^7 L/kg).

The same process of transformation was used on the 2010 study data to calculate a "critical value" for the long-term concentrations of total mercury that indicate risk for tissue contamination above the water quality criterion of 0.3 mg/kg methyl mercury. To compare the total mercury analyses to the methyl mercury tissue criteria, the equation uses 0.4 mg/kg to reflect the 75% methyl vs. total mercury found in current study trophic level 4 species. Table 3 shows the BAF values calculated in the earlier study and displays a recent calculation of the critical value associated with each navigation pool. The bioaccumulation factors given in the study generate critical values from 4.8 ng/L to 9.7 ng/L.

[2] All harvested fish were >55cm in total length and at least 75% of the of the largest fish captured in the project

Table 3: Previous total mercury BAF calculations and associated critical values

Location	Mile	Avg Length (cm)	Tissue THg (mg/kg)	Geometric Mean Aqueous THg (ng/L)	BAF (L/kg)	Critical Value* (ng/L THg)
Pike Island	84.2	61.4	0.23	3.89	5.91E+04	6.8
Willow Island	161.8	59.8	0.28	4.43	6.32E+04	6.3
Belleville	203.9	60.3	0.28	3.33	8.41E+04	4.8
RC Byrd	279.2	55.1	0.2	2.83	7.07E+04	5.7
Greenup	341.1	57	0.26	3.99	6.52E+04	6.1
Meldahl	436.2	61	0.29	4.1	7.07E+04	5.7
Markland	531.5	56.8	0.2	4.71	4.25E+04	9.4
McAlpine	606.8	61.9	0.4	5.32	7.52E+04	5.3
Cannelton	720.7	56.5	0.33	7.08	4.66E+04	8.6
Newburgh	776	58.6	0.33	7.82	4.22E+04	9.5
JT Myers	846	57.8	0.3	7.25	4.14E+04	9.7
Smithland	918.5	59.9	0.34	6.78	5.01E+04	8.0

* Critical value based on 0.4 mg/kg using 75% MeHg in tissue from current study TL4 composites

Conclusion

The site-specific methyl mercury BAF project produced information about mean concentrations of methyl mercury in the Ohio River at mile 126. This project also used a wide range of fish species from trophic levels 3 and 4. The final BAF developed is within the range of values calculated by USEPA in their national study. It was also comparable to earlier work completed by ORSANCO to develop BAFs for total mercury. The site-specific consumption-weighted BAF for mile 126 of the Ohio River, $9.9x10^6$ L/kg, indicates long-term average concentrations of total mercury in the Ohio River above 4.8 ng/L risk contamination of fish tissue greater than the tissue-based water quality criterion for methyl mercury.

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Appendix A: Monitoring Data

Table 1. Total and Methyl Mercury Data Collected for the BAF

Project (Mile Point)	Date	Flow (kcfs)	Unfilterd Total Hg (ng/L)	Unfiltered Methy Hg (ng/L)	Filterd Total Hg (ng/L)	Filtered MeHg (ng/L)
BAF Project (126)	24-Jul-12	7.1	1.04	<0.02	0.16	<0.02
	30-Aug-12	9.8	2.15	<0.02	0.22	<0.02
	27-Sep-12	14.6	1.95	<0.02	0.27	<0.02
	25-Oct-12	9.7	1.31	<0.02	<0.15	<0.02
	19-Nov-12	20.7	1.06	<0.02	0.55	<0.02
	17-Dec-12	48.0	2.53	0.036	0.65	<0.21
	14-Jan-13	102.3	7.7	0.060	0.49	<0.02
	14-Feb-13	70.1	1.91	<0.02	0.69	<0.02
	19-Mar-13	72.3	2.62	0.023	0.55	<0.02
	15-Apr-13	85.2	8.03	0.086	0.89	<0.02
	21-May-13	21.9	1.97	<0.02	0.36	<0.02
	17-Jun-13	42.5	3.3	0.057	0.39	<0.02
BAF Field Blank	21-May-13	-	<0.15	<0.02	-	-
USGS Coop (118)	18-May-10	65.0	6.802	0.088	0.58	0.050
	20-Jul-10	8.3	1.246	<0.04	0.28	<0.04
	15-Sep-10	3.9	1.362	<0.04	0.23	<0.04
USGS Coop (126)	19-May-10	77.7	8.009	0.105	0.73	0.040
	21-Jul-10	14.6	1.296	<0.04	0.34	<0.04
	14-Sep-10	4.3	1.59	<0.04	0.26	<0.04

Table 2 Fish Tissue Composite Samples Collected for the BAF

Trophic Level	Sample Mile	Date Collected	Common Name	Scientific Name	avg length (cm)	Hg (mg/kg)	MeHg (mg/kg)	% MeHg
TL3	113.8	22-Apr-10	Freshwater Drum	*Aplodinotus grunniens*	64.8	0.464	0.297	64%
	129.3	22-Apr-10	Freshwater Drum	*Aplodinotus grunniens*	77.0	0.431	0.404	94%
	127.0	7-Nov-12	Freshwater Drum	*Aplodinotus grunniens*	51.0	0.229	0.113	49%
	127.0	7-Nov-12	Bluegill	*Lepomis macrochirus*	16.9	0.053	0.027	51%
	127.0	7-Nov-12	Quillback	*Carpiodes cyprinus*	34.5	0.084	0.053	63%
	127.0	7-Nov-12	Common Carp	*Cyprinus carpio*	66.0	0.173	0.111	64%
	127.0	7-Nov-12	Smallmouth Buffalo	*Ictiobus bubalus*	54.2	0.172	0.116	67%
	127.0	2-Apr-13	Bluegill	*Lepomis macrochirus*	16.0	0.049	0.030	61%
	127.0	2-Apr-13	Quillback	*Carpiodes cyprinus*	39.7	0.083	0.052	63%
	127.0	2-Apr-13	Freshwater Drum	*Aplodinotus grunniens*	53.5	0.226	0.163	72%
	127.0	2-Apr-13	Smallmouth Buffalo	*Ictiobus bubalus*	51.3	0.261	0.201	77%
	127.0	2-Apr-13	Common Carp	*Cyprinus carpio*	55.3	0.163	0.145	89%
TL4	128.0	12-May-10	Hybrid Striped Bass	*Morone chrysops x M. saxatillis*	63.0	0.496	0.273	55%
	126.5	1-Jun-10	largemouth Bass	*Micropterus salmoides*	32.3	0.149	0.135	91%
	127.0	7-Nov-12	Walleye	*Sander vitreus*	56.8	0.309	0.214	69%
	127.0	2-Apr-13	Walleye	*Sander vitreus*	52.0	0.162	0.120	74%
	122.2	17-Jul-13	Sauger	*Sander canadensis*	43.3	0.300	0.252	84%

Table 3 Methyl Mercury Estimation Methods and Values for Each Sample Event

Project (Mile Point)	Date	Total Hg (ng/L)	Methyl Hg (ng/L)	FMeHg (ng/L)	Estimated FMeHg (ng/L)	FMeHg Estimate Type
BAF Project (126)	24-Jul-12	1.04	<0.02	<0.02	0.007	Est. from THg
	30-Aug-12	2.15	<0.02	<0.02	0.014	Est. from THg
	27-Sep-12	1.95	<0.02	<0.02	0.012	Est. from THg
	25-Oct-12	1.31	<0.02	<0.02	0.008	Est. from THg
	19-Nov-12	1.06	<0.02	<0.02	0.007	Est. from THg
	17-Dec-12	2.53	0.036	<0.02	0.018	Est. from MeHg
	14-Jan-13	7.70	0.060	<0.02	0.029	Est. from MeHg
	14-Feb-13	1.91	<0.02	<0.02	0.012	Est. from THg
	19-Mar-13	2.62	0.023	<0.02	0.011	Est. from MeHg
	15-Apr-13	8.03	0.086	<0.02	0.042	Est. from MeHg
	21-May-13	1.97	<0.02	<0.02	0.013	Est. from THg
	17-Jun-13	3.30	0.057	<0.02	0.028	Est. from MeHg
USGS Coop (118)	18-May-10	6.80	0.088	0.05	0.050	Measured DMeHg
	20-Jul-10	1.25	<0.04	<0.04	0.005	Est. from MeHg
	15-Sep-10	1.36	<0.04	<0.04	0.009	Est. from MeHg
USGS Coop (126)	19-May-10	8.01	0.105	0.04	0.040	Measured DMeHg
	21-Jul-10	1.30	<0.04	<0.04	0.008	Est. from THg
	14-Sep-10	1.59	<0.04	<0.04	0.010	Est. from THg

Appendix B: All Available Ohio River Methyl Mercury Data

Project	River Mile	Date	Flow (kcfs)	Total Hg (ng/L)	Total Hg Filtered (ng/L)	Methyl Hg (ng/L)	Methyl Hg Filtered (ng/L)	MeHg Qualifier	MeHg RL (ng/L)
USGS Coop	118.0	May-10	65.0	6.80	0.58	0.09	0.05		0.04
USGS Coop	118.0	Jul-10	8.3	1.25	0.28		<0.04	ND	0.04
USGS Coop	118.0	Sep-10	3.9	1.36	0.23		<0.04	ND	0.04
USGS Coop	125.6	May-10	77.7	8.01	0.73	0.11	0.04		0.04
USGS Coop	125.6	Jul-10	14.6	1.30	0.34		<0.04	ND	0.04
USGS Coop	125.6	Sep-10	4.3	1.59	0.26		<0.04	ND	0.04
USGS Coop	606.6	May-10	237.0	11.24	0.65	0.12	<0.04		0.04
USGS Coop	606.6	Jul-10	152.0	3.19	0.38	0.07	<0.04		0.04
USGS Coop	606.6	Sep-10	16.0	1.23	0.38		<0.04	ND	0.04
USGS Coop	720.0	May-10	110.0	5.55	1.61	0.04	<0.04		0.04
USGS Coop	720.0	Jul-10	23.1	0.87	0.28		<0.04	ND	0.04
USGS Coop	720.0	Sep-10	8.4	1.17	0.57		<0.04	ND	0.04
USGS Coop	845.0	May-10	284.0	13.05	1.31	0.13	<0.04		0.04
USGS Coop	845.0	Jul-10	42.4	1.29	0.5		<0.04	ND	0.04
USGS Coop	845.0	Sep-10	15.6	1.05	0.33		<0.04	ND	0.04
USGS Coop	916.0	May-10	376.0	10.78	1.23	0.12	<0.04		0.04
USGS Coop	916.0	Jul-10	101.0	1.46	0.38	0.04	<0.04		0.04
USGS Coop	916.0	Sep-10	35.0	1.36	0.37		<0.04	ND	0.04
FGD Mont Raw Water Intake	76.5	Mar-12	43.1	3.33	0.39	0.041	<0.02	Est	0.02
FGD Mont Raw Water Intake	76.5	Jun-12	8.0		0.25	0.023	<0.02	Est	0.02
FGD Mont Raw Water Intake	76.5	Sep-12	6.3	1.34		0.041	<0.02	Est	0.02
FGD Mont Raw Water Intake	76.5	Dec-12	106.5	4.08		0.063	<0.02		0.02
FGD Mont Raw Water Intake	112.5	Mar-12	46.2	3.93	0.42	0.033	<0.02	Est	0.02
FGD Mont Raw Water Intake	112.5	Jun-12	12.7	3.53	0.4	0.034	<0.02	Est	0.02
FGD Mont Raw Water Intake	112.5	Sep-12	5.6	1.56	0.18		<0.02	ND	0.02
FGD Mont Raw Water Intake	112.5	Dec-12	112.0	3.68		0.096	<0.02		0.02
FGD Mont Raw Water Intake	242.5	May-12	109.2	3.38	0.3	0.029	<0.02	Est	0.02
FGD Mont Raw Water Intake	242.5	Aug-12	13.9	5.54	1.65	0.084	<0.02		0.02
FGD Mont Raw Water Intake	242.5	Nov-12	22.3	0.92	0.42		<0.02	ND	0.02
FGD Mont Raw Water Intake	560.0	May-12	58.1	2.26	0.47	0.055	0.022		0.02
FGD Mont Raw Water Intake	560.0	Aug-12	33.2	1.70	0.24	0.046	<0.02	Est	0.02
FGD Mont Raw Water Intake	560.0	Nov-12	35.1	0.76	0.27		<0.02	ND	0.02
FGD Mont Raw Water Intake	560.0	Feb-13	265.5	9.97	1.33	0.076	0.02		0.02
BAF Project	125.6	Jul-12	7.1	1.04	0.16		<0.02	ND	0.02
BAF Project	125.6	Aug-12	9.8	2.15	0.22		<0.02	ND	0.02
BAF Project	125.6	Sep-12	14.6	1.95	0.27		<0.02	ND	0.02
BAF Project	125.6	Oct-12	9.7	1.31	<0.15		<0.02	ND	0.02
BAF Project	125.6	Nov-12	20.7	1.06	0.55		<0.02	ND	0.02
BAF Project	125.6	Dec-12	48.0	2.53	0.65	0.036	<0.21	Est	0.02
BAF Project	125.6	Jan-13	102.3	7.70	0.49	0.060	<0.02		0.02
BAF Project	125.6	Feb-13	70.1	1.91	0.69		<0.02	ND	0.02
BAF Project	125.6	Mar-13	72.3	2.62	0.55	0.023	<0.02	Est	0.02
BAF Project	125.6	Apr-13	85.2	8.03	0.89	0.086	<0.02		0.02
BAF Project	125.6	May-13	21.9	1.97	0.36		<0.02	ND	0.02
BAF Project	125.6	Jun-13	42.5	3.30	0.39	0.057	<0.02		0.02

Appendix C: Testing the BAF-Generated Critical Value Against Background Conditions

The applicability of the "critical value" was tested by comparing a three-year geometric mean of estimated total mercury concentrations to the consumption-weighted average of trophic levels 3 and 4 tissue concentrations. A simple least squares linear regression model was employed using National Weather Service, Ohio River Forecast Center daily flow values for Hannibal Locks and Dam, and the measured unfiltered total mercury data from this project.

The regression equation: estimated THg (ng/L) = 0.0649(Flow)+0.6587 shows a correlation coefficient of r^2= 0.69. A three-year geometric mean of daily concentrations estimated by the regression equation is 2.7 ng/L (max. 18.7, min 1.0, S.D=2.54,). The daily estimations are shown in Figure 1 alongside the measured values.

Comparing the estimated daily total mercury values to the methyl mercury BAF-generated "critical value" based on the tissue methyl mercury criterion shows mean concentrations (2.7 ng/L THg) are about half (56%) of the 4.8 ng/L total mercury "critical value". Comparing the tissue methyl mercury concentrations to the tissue criterion also shows that the mean tissue concentrations from the BAF project (0.14 mg/kg) are also nearly half (46%) of the methyl mercury criterion of 0.3 mg/kg (Figure 2).

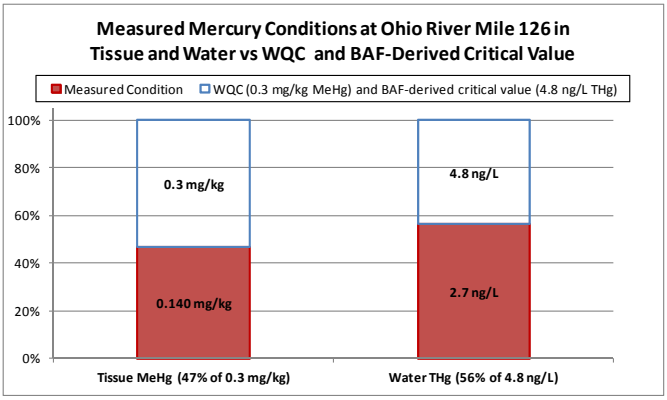

Figure 2: Measured Conditions vs Criterion and "Critical value"

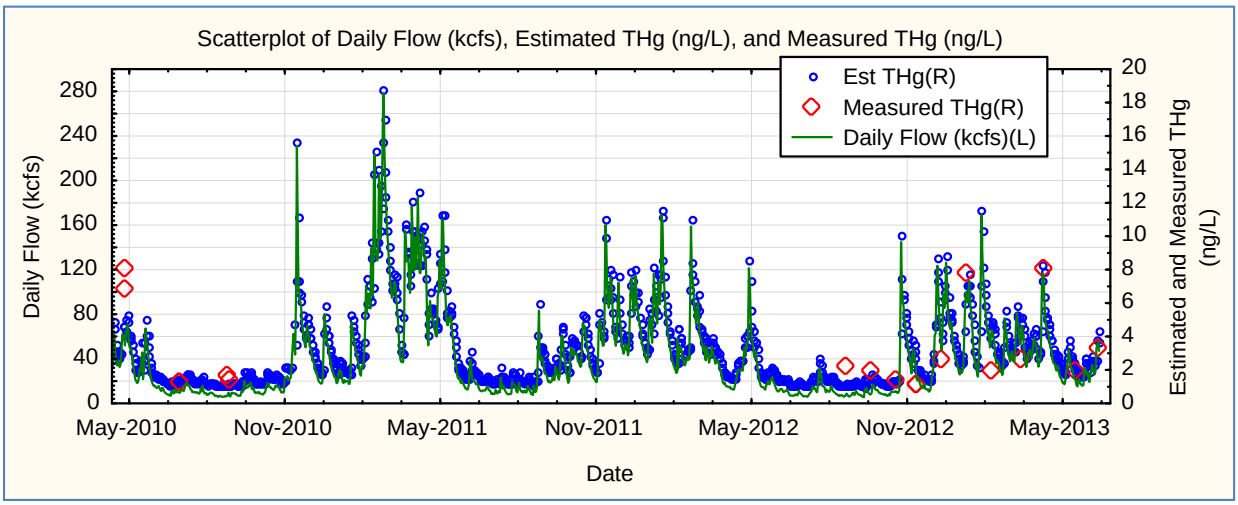

Figure 11 - Estimated Daily Unfiltered Total Mercury Concentrations (ng/L)