COMMONWEALTH OF PENNSYLVANIA
DEPARTMENT OF ENVIRONMENTAL PROTECTION
BUREAU OF CLEAN WATER

Development of a Site-Specific Methylmercury Water Quality Criterion for Ebaughs Creek

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Introduction

The York County Solid Waste and Refuse Authority (YCSWRA) operates the York County Sanitary Landfill (YCSL), located in Hopewell Township, York County. Department staff from the Clean Water Program, Southcentral Regional Office (SCRO) identified the presence of mercury in the YCSWRA's permitted landfill leachate discharge. YCWRA requested development of site-specific criteria for methylmercury. SCRO requested the assistance of Central Office staff in developing ambient water quality criteria (AWQC) for methylmercury for the unnamed tributary (UNT) to Ebaughs Creek.

The YCSL is a 306-acre site owned by the YCSWRA. Between 1974 and 1997, the landfill received municipal and industrial waste, which was placed into lined and unlined cells. The site contains approximately 135 acres of unlined landfill. Detection of volatile organic compounds associated with the unlined cells was discovered in 1983. A pump and treat system was installed and began operation in 1985. The system consisted of 17 extraction wells and air stripping towers. The air stripping towers discharge treated groundwater from two outfalls under NPDES permit number PA0081744. Outfall 002 discharges into a UNT to Ebaughs Creek. This outfall discharges to the headwaters of a small first-order tributary with limited watershed area and comprises a significant portion of the stream flow (effluent dominated) at the point discharge. Ebaughs Creek is designated as a Cold Water Fishes, Migratory Fishes (CWF, MF) stream. The outfall has documented total mercury (THg) concentrations consistently above the Commonwealth's current human health criterion of 0.05 µg/L, but below the aquatic life criteria continuous concentration (CCC) of 0.77 µg/L and the criteria maximum concentration (CMC) of 1.4 µg/L.

Background

Mercury is a naturally occurring, widely distributed element that cycles in the environment through natural processes and human activities. However, the source of mercury to the receiving streams is not naturally occurring. It comes from an anthropogenic source originating from effluent at the landfill operated by YCSWRA. Various forms of mercury exist in the environment with some forms being more toxic to people than others. Toxicity is also related to exposure amount, exposure pathway and individual susceptibility. The most toxic form currently known is methylmercury (MeHg), which is an organic form of mercury. Relevant organic forms in the environment are dimethyl- and monomethylmercury. Acidic conditions will increase the shift to this more toxic form (Harte et al., 1991). Human exposure to MeHg primarily occurs through the consumption of contaminated fish tissue. MeHg is highly fat soluble and has a high affinity for sulfhydryl proteins (Hong et al., 2012). Therefore, it tends to accumulate in the fatty tissue of the central nervous system, but it may also cause negative effects on nearly every system within the body including cardiovascular, pulmonary, renal, immunological, neurological, endocrine, hematological and reproductive (Rice et al., 2014). Given its high fat solubility, MeHg can easily cross cell membranes, the blood-brain barrier, and the placenta. Fetal exposure tends to be significantly increased when compared to the maternal burden and leads to impaired neurological development (ATSDR, 2013, Rice et al., 2014, Myers and Davidson, 1998). In contrast, inorganic mercury is poorly absorbed through the digestive tract (Hong et al., 2012) and does not readily cross the body's blood-brain barrier or placenta (Harte et al., 1991). As such, it is generally regarded as less toxic.

MeHg is formed in the environment when bacteria capable of methylation are exposed to a source of inorganic mercury and convert it to an organic (methylated) form. MeHg is both a bioaccumulating and a biomagnifying substance. As previously stated, fish serve as the primary source of human exposure. Fish exposure to MeHg can occur through their interactions with the water column, the sediment and food sources (i.e. epiphytes, macrophytes, macroinvertebrates and lower trophic level fish). Freshwater species are known to be more sensitive to the effects of mercury than marine species (Harte et al., 1991).

YCSWRA Site-Specific Mercury and Metals Translator Studies

YCSWRA performed a site-specific study for the collection of data necessary to develop a site-specific AWQC for MeHg ($AWQC_{MeHg}$) that is protective of human health for Ebaughs Creek. YCSWRA also performed a study to develop site-specific translator factor, which, when applied to the site-specific $AWQC_{MeHg}$, would establish the THg permit effluent limitation necessary to achieve the $AWQC_{MeHg}$ in the receiving water. On September 23, 2015, YCSWRA submitted their Site-Specific Methylmercury Water Quality Criterion Stream Study Plan (hereafter referred to as "the Plan"). The Plan contained both the criterion study and the translator study. YCSWRA agreed to collect fish tissue samples and surface water samples at a location on Ebaughs Creek for the calculation of site-specific bioaccumulation factor (BAF).

The site-specific BAF, along with USEPA's revised national human health inputs (USEPA, n.d., USEPA, 2000b, USEPA, 2002a, USEPA, 2010), and 25 Pa. Code Chapters 93 and 16 (as noted in the following section titled *Development of Ambient Water Quality Criteria for Methylmercury Criteria*) were used to translate and update USEPA's 2001 fish tissue-based $AWQC_{MeHg}$ criterion of 0.3 mg/kg (USEPA, 2001) into site-specific water column-based $AWQC_{MeHg}$ for the receiving stream.

A separate, but concurrent, study was proposed for the development of a metals translator factor for the receiving stream. For that study, water column samples were collected from the well-mixed effluent and receiving water (approximately 25 feet downstream from the discharge outfall). Since NPDES discharge permit limitations must be developed as THg, a conversion factor was needed to establish appropriate water column-based effluent limitation for the facility. The factors were used to translate the final $AWQC_{MeHg}$ back to $AWQC_{THg}$. The final Plan was approved by DEP on October 6, 2016. Sampling began in October 2016 and ended in September

2017. On behalf of YCSWRA, AECOM (YCSWRA's consultant) submitted a Site-Specific Methylmercury Water Quality Criterion Stream Study Report (the Report) in December 2017.

Fish Tissue Sampling

Site Selection

The fish tissue collection sites were determined through a qualitative fish survey of Ebaughs Creek conducted by AECOM in March 2016. The fish tissue sampling sites for the MeHg study were selected based on sufficient densities of apex predatory fish and proximity to the discharge (i.e. nearest downstream location from the discharge containing legal-sized gamefish). Survey collection methods were consistent with the DEP's *Pennsylvania Wadeable Semi-Quantitative Fish Sampling Protocol for Streams* (DEP, 2013). Results of the qualitative survey identified brown trout and American eel as the only target species for Ebaughs Creek. Three composite fish tissue samples made up of two to five individual fish per composite would be targeted for collection at a single location on the tributary. AECOM selected the Ebaughs Creek EC-02 station as the fish tissue collection site for the study. This site is located nearly 2 miles downstream of the outfall.

Sample Collection

Fish tissue was collected at EC-02 in October 2016 and September 2017 (Table 1). Sufficient quantities of fish allowed for three composite samples to be collected at each site for each target species as described above. However, one composite sample was determined to be an outlier and removed from the final BAF calculation. The MeHg fish tissue result for Composite II (brown trout) collected on October 18, 2016 from Ebaughs Creek was extremely low. This value was extremely out of range when compared to all other composite results collected during both sampling events. As this value would appear to be an outlier, DEP has removed it from the final data set used in calculating a BAF for Ebaughs Creek (See Table 6).

<u>Table 1.</u> Summary of Composite Fish Tissue Sample Results for Mercury.

Sample #	Species	Location	Result	Unit	Date Collected
Comp 1	American Eel	EC -02	76.8	ng/g	10/18/16
Comp 2	American Eel	EC -02	87.7	ng/g	10/18/16
Comp 3	American Eel	EC -02	64.8	ng/g	10/18/16
Comp 1	Brown Trout	EC -02	45.2	ng/g	10/18/16
Comp 2	Brown Trout	EC -02	3.27	ng/g	10/18/16
Comp 3	Brown Trout	EC -02	55.2	ng/g	10/18/16
Comp 1	American Eel	EC -02	110	ng/g	9/12/2017
Comp 2	American Eel	EC -02	119	ng/g	9/12/2017
Comp 3	American Eel	EC -02	83.6	ng/g	9/12/2017
Comp 1	Brown Trout	EC -02	41.3	ng/g	9/12/2017
Comp 2	Brown Trout	EC -02	28.1	ng/g	9/12/2017
Comp 3	Brown Trout	EC -02	21.1	ng/g	9/12/2017

Surface Water Sampling

Surface water samples were collected at EC-02 (Table 2). Water samples were collected by YCSWRA staff and AECOM staff in accordance with the approved work plan and sampling method following USEPA's *Method 1669: Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels*. Water samples were collected monthly for the duration of the study. The MeHg criterion-related samples were collected at the fish tissue sample locations (EC-02), and the THg translator-related samples were collected approximately 25 feet downstream from the outfall, which is a location representative of well-mixed effluent and receiving water. Samples were analyzed for THg and dissolved MeHg in accordance with USEPA's *Method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry* (USEPA, 2002b) and *Method 1630: Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry* (USEPA, 1998).

Table 2. Summary of the monthly water column sample results (dissolved MeHg) collected at the fish tissue site on Ebaughs Creek. One-half of the method detection limit (MDL) (0.01 ng/L) was used for any values reported as <0.02 ng/L.

Date	Location	MeHg result	MDL	Unit
Oct-16	EC-02	<0.02	0.020	ng/L
Nov-16	EC-02	<0.02	0.020	ng/L
Dec-16	EC-02	<0.02	0.020	ng/L
Jan-17	EC-02	<0.02	0.020	ng/L
Feb-17	EC-02	<0.02	0.020	ng/L
Mar-17	EC-02	<0.02	0.022	ng/L
Apr-17	EC-02	<0.02	0.020	ng/L
May-17	EC-02	<0.02	0.020	ng/L
Jun-17	EC-02	<0.02	0.020	ng/L
Jul-17	EC-02	<0.02	0.020	ng/L
Aug-17	EC-02	<0.02	0.020	ng/L
Sep-17	EC-02	<0.02	0.020	ng/L

Development of Ambient Water Quality Criteria for Methylmercury

In accordance with 25 Pa. Code Chapter 93, Water Quality Standards, and Chapter 16, Statement of Policy, the human health ambient water quality criterion was developed using the provisions in §§ 93.8d (relating to development of site-specific water quality criteria) and 16.32 (relating to threshold level toxic effects) and the USEPA *Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion* (USEPA, 2010). The inputs for body weight (80 kg), drinking water intake (2.4 L) and fish consumption (22 g/day) were updated to reflect the most current data available from USEPA and were used in the development of this criterion.

The data sets resulting from these studies contained a significant number of water column MeHg results that were reported as less than the method detection limit (MDL). The Plan did not discuss how the consultant, or DEP, would handle non-detect values. Furthermore, non-detect values were not expected since highly sensitive USEPA methods were used to analyze the samples. DEP contacted USEPA for additional guidance and consultation on the non-detect values, and DEP was referred to USEPA's *Guidance for Implementing the January 2001 Methylmercury Water Quality Criterion* (USEPA, 2010). Section 4.3.1 of the guidance references the USEPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories* (USEPA, 2000a), which recommends using one-half of the MDL for non-detects in calculating mean values.

Site-specific BAF, site-specific metals translation factor, and SSC for MeHg were developed for the purpose of developing THg effluent limitations for the YCSWRA NPDES permit (PA0081744) for discharging to the UNT to Ebaughs Creek. The equations used for this process are as follows.

Equations for Water Quality Criteria Development and Metals Translation Factors

Individual Bioaccumulation Factor (BAF) — Eq.

$$BAF = Ct/Cw \quad (1)$$

where: BAF = bioaccumulation factor in L/kg

Ct = concentration of total mercury in fish tissue in mg/kg, wet tissue weight

Cw = concentration of dissolved methylmercury in water in mg/L

Final Bioaccumulation Factor (Final BAF)

$$\text{Final BAF} = \text{geometric mean of BAF} \quad (2)$$

Methylmercury Threshold Human Health Ambient Water Quality Criterion ($AWQC_{MeHg}$)

$$AWQC_{MeHg} = [BW \times (RfD\text{-}RSC)]/[DI + (FI \times BAF)] \quad (3)$$

where: $AWQC_{MeHg}$ = methylmercury ambient water quality criteria

BW = human body weight, 80 kg

RfD = reference dose, (0.0001 mg/kg-d)

RSC = relative source contribution, (0.000027 mg/kg-d)

DI = drinking water intake, 2.4L/day

FI = fish intake, current USEPA recommended value, 0.022 kg/day

BAF = bioaccumulation factor L/kg, tropic level 4

Individual Metals Translation Factor (f_d)

$$f_d = Cd_{MeHg}/Ct_{Hg} \quad (4)$$

where: f_d = site-specific water column metals translation factor

Cd_{MeHg} = the dissolved concentration of methylmercury

Ct_{Hg} = the total recoverable concentration of mercury

Final Metals Translation Factor (Final f_d)

$$\text{Final } f_d = \text{geometric mean of the site-specific individual metals translation factors} \quad (5)$$

Specific Water Quality Criteria Development for Ebaughs Creek

BAFs for Ebaughs Creek

Eq. (1) was used to calculate the individual BAFs for each sample at Ebaughs Creek (Table 6), and Eq. (2) was used to calculate the Final BAF(Ebaughs) (Final $BAF_{(Ebaughs)}$), which is 5.882398 x 10^6 L/kg.

Table 3. Summary of the individual BAF calculations for Ebaughs Creek.

Sample #	Species	Location	Result	Unit	Date Collected	BAF (L/g)	BAF (L/kg)
Comp 1	American Eel	EC-02	76.8	ng/g	10/18/16	7680	7680000
Comp 2	American Eel	EC-02	87.7	ng/g	10/18/16	8770	8770000
Comp 3	American Eel	EC-02	64.8	ng/g	10/18/16	6480	6480000
Comp 1	Brown Trout	EC-02	45.2	ng/g	10/18/16	4520	4520000
Comp 2	Brown Trout	EC-02	(Outlier)	ng/g	10/18/16	--	--
Comp 3	Brown Trout	EC-02	55.2	ng/g	10/18/16	5520	5520000
Comp 1	American Eel	EC-02	110	ng/g	9/12/2017	11000	11000000
Comp 2	American Eel	EC-02	119	ng/g	9/12/2017	11900	11900000
Comp 3	American Eel	EC-02	83.6	ng/g	9/12/2017	8360	8360000
Comp 1	Brown Trout	EC-02	41.3	ng/g	9/12/2017	4130	4130000
Comp 2	Brown Trout	EC-02	28.1	ng/g	9/12/2017	2810	2810000
Comp 3	Brown Trout	EC-02	21.1	ng/g	9/12/2017	2110	2110000

Final $BAF_{(Ebaughs)}$ = geometric mean of individual BAFs for Ebaughs Creek

= 5,882,398 L/kg

= 5.882398 x 10^6 L/kg

Methylmercury - $AWQC_{MeHg}$ for Ebaughs Creek

Eq. (3) was used to calculate the $AWQC_{MeHg}$ for Ebaughs Creek ($AWQC_{MeHg\ (Ebaughs)}$), which is 4 x 10^{-5} µg/L.

$AWQC_{MeHg(Ebaughs)}$ = [80 kg x (0.0001mg/kg-d-0.000027 mg/kg-d)]/[2.4 L + (0.022 kg x 5882398 L/kg)]

= [0.00584 mg]/[129415 L]

= 0.000000045 mg/L

= 4 x 10^{-8} mg/L

= 4 x 10^{-5} µg/L

Metals Translation Factors for Ebaughs Creek

Eq. (4) was used to calculate the individual f_d for Ebaughs Creek (Table 7), and Eq. (5) was used to calculate the Final f_d for Ebaughs Creek (Final $f_{d\ (Ebaughs)}$), which is 5.88 x 10^{-5}.

Table 4. Summary of the individual translation factors calculated from the monthly sample results for Ebaughs Creek. One-half of the MDL (0.01 ng/L) was used for any values reported as <0.02 ng/L.

Sample Date	Ebaughs Down	Analyte	Report matrix	Unit	$F_{d\ (Ebaughs)}$
Oct-16	171	Hg	TR	ng/L	5.55556E-05
	0.0095	MeHg	D	ng/L	
Nov-16	302	Hg	TR	ng/L	3.31126E-05
	0.01	MeHg	D	ng/L	
Dec-16	164	Hg	TR	ng/L	6.09756E-05
	0.01	MeHg	D	ng/L	
Jan-17	165	Hg	TR	ng/L	6.06061E-05
	0.01	MeHg	D	ng/L	
Feb-17	178	Hg	TR	ng/L	5.61798E-05
	0.01	MeHg	D	ng/L	
Mar-17	160	Hg	TR	ng/L	6.25000E-05
	0.01	MeHg	D	ng/L	
Apr-17	224	Hg	TR	ng/L	1.25000E-05
	0.028	MeHg	D	ng/L	
May-17	168	Hg	TR	ng/L	6.25000E-05
	0.0105	MeHg	D	ng/L	
Jun-17	189	Hg	TR	ng/L	5.02646E-05
	0.0095	MeHg	D	ng/L	
Jul-17	169	Hg	TR	ng/L	5.91716E-05
	0.01	MeHg	D	ng/L	
Aug-17	143	Hg	TR	ng/L	6.99301E-05
	0.01	MeHg	D	ng/L	
Sep-17	228	Hg	TR	ng/L	4.38596E-05
	0.01	MeHg	D	ng/L	

Final $f_{d(Ebaughs)}$ = geometric mean of the individual f_d for Ebaughs Creek

= 0.00005877

= 5.88 x 10^{-5}

NPDES Permit and Water Quality Standards Considerations

A study was conducted and submitted to DEP by YCWSRA for DEP to develop site-specific $AWQC_{MeHg}$ and metals translation factor for the UNT to Ebaughs Creek, York County. The site-specific $AWQC_{MeHg}$ for the UNT to Ebaughs Creek was determined to be 4 x 10^{-5} µg/L (0.00004 µg/L), and the metals translation factor was determined to be 5.88 x 10^{-5} (0.0000588).

Once the site-specific $AWQC_{MeHg}$ has been incorporated into Chapter 93 and approved by USEPA, it will be used by NPDES staff to develop THg effluent discharge limitation for the UNT to Ebaughs Creek, based on application of the metals translator factor (Final f_d) developed for the receiving water.

Waterbody	BAF	$AWQC_{MeHg}$	Translator Factor (f_d)
Ebaughs Creek	5.882398 x 10^6 L/kg	0.00004 µg/L	5.88 x 10^{-5}

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