REED HARRIS Environmental Ltd.

February 21, 2018

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Chair, Independent Expert Advisory Committee
Happy Valley – Goose Bay, NL

Re: Comments on the relationship between carbon and methylmercury in flooded soils

This memo provides comments on the relationship between carbon and methylmercury in flooded soils, further to your request. The memo includes general information on the carbon-methylmercury relationship in flooded soils and some specific comments on the approach used by Calder *et al.* (2016).

1) How does carbon affect methylmercury in flooded soils?

Methylmercury is produced by bacteria in aquatic environments. The reaction needs two basic ingredients: (1) inorganic Hg(II) in a form available to the microbes and (2) activity by methylating microbes. Changes to either of these factors affects the reaction. There are many examples showing elevated methylmercury levels at sites locally contaminated with inorganic mercury (*e.g.* see Munthe *et al.*, 2007). The creation of new reservoirs does not however add mercury to the local environment. Instead, it increases the efficiency of the microbial conversion of existing stores of inorganic mercury to methylmercury. This occurs primarily via increased activity of the microbes that methylate. Harris *et al*. (2009) also found that simulations to predict methylmercury increases in flooded upland experiments (FLUDEX) improved when decomposition increased porewater DOC concentrations, which increased the concentration of inorganic Hg(II) available to methylate in the model.

Newly flooded terrain often contains large stores of organic matter. This results in a period of years where decomposition rates are elevated relative to typical aquatic sediments. While overall decomposition rates may be viewed as a relative indicator of the activity of methylating microbes, it is well established that microbes that produce methylmercury are specifically adapted for anaerobic conditions, *e.g.* sulfate reducing bacteria (Gilmour *et al*., 2011 and others). Increased supply of organic matter could increase the activity of methylating microbes and/or could shift anaerobic zones where methylation occurs to locations that are more relevant to bioaccumulation. For example, increased overall decomposition in flooded soils could shift the depth of anaerobic activity and methylation closer to the sediment/water interface. In some cases anoxic conditions and methylation can occur in the water column but Muskrat Falls reservoir is predicted to remain vertically well mixed and oxygenated (Nalcor, 2009).

Carbon content is an indicator of the fraction of the soil that is organic. It follows that reservoirs with greater stores of carbon, particularly carbon that is readily decomposed, should have higher methylmercury production rates in locations ultimately relevant to bioaccumulation, all else being equal.

Positive relationships between carbon content and methylmercury can also occur for reasons other than carbon affecting methylmercury production. For example, sand will typically have lower methylmercury concentrations than organic solids in the same waterbody, simply because sand is less able to bind methylmercury (and inorganic mercury) than organic matter. Differences in partitioning of methylmercury between solids and the dissolved phase cannot however explain the fact that flood zone solids have much higher concentrations of methylmercury than pre-flood soils. This requires additional production of methylmercury.

2) Comments on flooded areas for Muskrat Falls Reservoir

The total flooded terrestrial area for Muskrat Falls Reservoir at full elevation (39 m asl) is 43.9 km^2, representing 43% of the total reservoir area of 101.5 km^2 (Table 1). Within this flooded area, 6.9 km^2 are gravel bars, which have minimal organic carbon and would not be expected to be a source of elevated methylmercury production. A further 6.6 km^2 of the flooded terrain consists of riparian soils. Limited data for these soils indicates very low organic carbon content (n=3, average = 3%, compare to 30%+ for organic soil). Litter was removed from samples prior to analysis. If gravel bars are excluded from the area effectively contributing methylmercury to the reservoir, the relevant area is 36.98 km^2. If the riparian flooded area is also excluded, the relevant area is 30.42 km^2. We are therefore examining a range of effective flooded areas (30.42 to 36.98 km^2) in our model simulations. Calder *et al.* (2016) used an estimate of 41 km^2 in their analysis, which was reasonable given the data available at the time.

Table 1. Muskrat Falls Reservoir flooded terrain at full elevation (39 m asl). Data from AMEC (2018)

ELC type	Area (km^2)	% of reservoir area	% of flooded area
Black Spruce / Feathermoss Forest	8.59	8.5	19.6
Fir - White Spruce Forest	8.14	8.0	18.6
Black Spruce / Lichen Woodland	0.91	0.9	2.1
Hardwood Forest	2.20	2.2	5.0
Mixedwood Forest	6.96	6.9	15.9
Spruce Fir / Feathermoss Forest	1.16	1.1	2.6
Bl. Spruce/Sphagnum Woodland	0.20	0.2	0.5
Unvegetated	0.04	0.04	0.1
Wetland	2.18	2.2	5.0
Riparian	6.56	6.5	15.0
Gravel Bar	6.92	6.8	15.8
All flooded forest	28.18	27.8	64.2
All flooded forest + wetland	30.38	29.9	69.2
Total flooded area	43.91	43.3	100.0
Total flooded area minus gravel bar	36.98	36.4	84.2
Total flooded area minus gravel bar and riparian	30.42	30.0	69.3
Water	57.59	56.7	
Total	101.51	100.0	

3) Comments on Figure 1 from Calder *et al.* (2016)

Calder *et al.* (2016) presented a figure indicating a positive relationship between carbon content and methylmercury concentrations in flooded soils using data from different reservoirs (**Figure *1***).

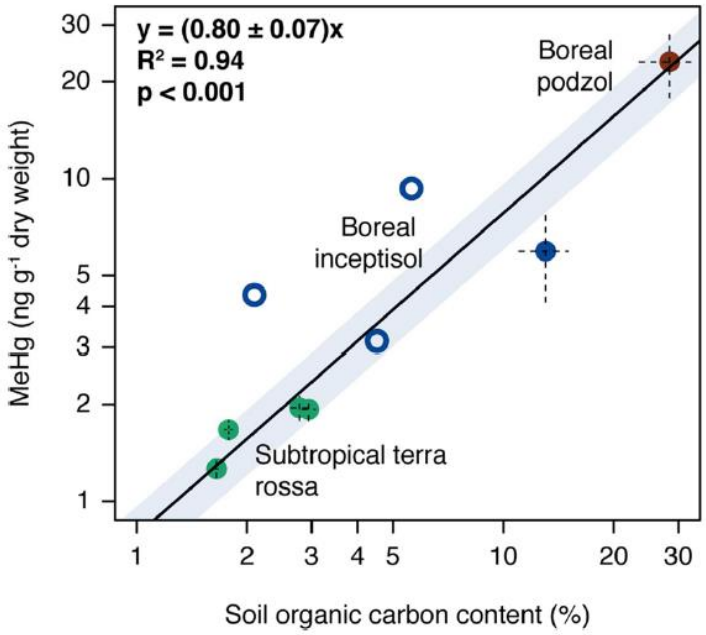

Figure 1. Relationship between soil organic carbon content and MeHg concentrations (ng g^{-1} dry weight) of flooded soils. Each data point represents an individual sampling location. Hatched lines indicate standard errors around the mean. Soil cores are from the Wujiangu reservoir, China (subtropical terra rossa),[28] the Experimental Lakes Area (ELA, boreal inceptisol) in Northern Ontario, Canada,[7,26] and La Grande-2 (Robert Bourassa) Reservoir in Quebec, Canada.[27] ELA data indicate the site-wide peak in MeHg (1−2 years postflood) except for the filled circle, which represents 9-years post flooding.

Figure 1. Relationship between methylmercury concentration and percent carbon in soils from a variety of ecosystems. From Calder *et al* (2016).

While I agree with a positive relationship between carbon content and methylmercury in flooded soils, several aspects of Figure 1 from Calder *et al.* (2016) warrant comment:

i. The estimates of carbon content reported in Figure 1 from Calder *et al.* (2016) for three upland sites at the Experimental Lakes Area are very low, ranging from about 2-6 percent. I believe this is because:
   a. Some of the published values that Calder *et al* used to estimate carbon pools at ELA sites, shown in Figure 1, may be incorrect and too low. There appears to be an error in the published values, which Calder *et al* could not have known. Using raw data from the FLUDEX experiment, I could not match published values for carbon pools from Hall *et al*. (2005). This was discussed with two FLUDEX researchers who published papers on the FLUDEX experiments. Britt Hall did not find (yet) the origin of the published values for carbon pools for the fungal/humic layer, expressed as kg C/ha, but did find estimates that were higher. Unless the origin of the published values is found and verified, Britt Hall suggested using the higher, unpublished values in the current analysis. Updating the FLUDEX values could change the relationship between methylmercury and carbon in Figure 1. The change may or may not be significant, but the update should be done to determine this. I informed Ryan Calder of this issue on February 7, 2018, with permission from B. Hall. Updated estimates of carbon pools were sent to Ryan Calder today.

   b. Calder *et al* included the mineral soil layer when estimating the carbon content for the ELA upland sites (FLUDEX experiment) shown in Figure 1. This would significantly lower the depth-averaged percent carbon if compared to just using the organic horizons, because mineral layers have very low carbon content. While it is debatable what depth should be used when estimating carbon and methylmercury concentrations in flooded soils, we assume that the top few cm (*e.g.* 3-5 cm) are most influential for the MeHg flux to overlying waters. Additional discussion is provided below. The depth selected has a important effect on estimates of carbon content and differences among sites. For example, including the mineral layer for the ELA sites, but not Muskrat Falls, would increase the difference in carbon content between the two areas, compared to comparing the carbon content in the top few cm of the organic horizons. For context, the average depths of the litter and fungal/humic layers at the FLUDEX medium carbon site were 1 and 3 cm, based on my analysis of raw data. At Muskrat Falls, the fungal humic horizon in uplands had an average depth of 8-9 cm (derived from AMEC Foster Wheeler, 2017).

ii. It is not clear what sample depths were involved for non-ELA sites in Figure 1. This would be useful to know. Did carbon estimates from other sites include mineral layers for example?

iii. Calder's supplemental memo states that wetlands were excluded from the analysis because methylation in wetlands may be sulfate limited. I am guessing however that a wetland site is included in Figure 1 (solid blue dot). If so, the carbon content is about 12% in the figure, which would be low for a wetland, and it is lower than the carbon content shown for a podzol soil, which is unexpected. It would be useful to know if that point in Figure 1 is indeed a wetland site. Also, is Calder suggesting that the wetlands are sulfate limited but the uplands are carbon limited? If so, what is the conceptual model to support that?

Overall, the relationship between methylmercury and percent carbon Figure 1 should at a minimum be updated to adjust for updated information from the ELA experiments.

4) What depth of soil should be used?

The question of what depth of flooded soils to use is important when a key goal of the overall analysis is to estimate the flux of methylmercury from flooded soils to overlying water. We assume this is the top few cm. This is the zone in direct contact with overlying waters. Methylmercury concentrations in sediments are also often greatest in the top few cm, and the transition to anoxic conditions likely occurs well within the top few cm in organic sediments underlying oxygenated water. It is also likely that the organic matter in the top few cm of the soils is more labile because it is "younger" and has not already been partially decomposed. Also, methylmercury production in deeper sediments has limited connectivity with overlying surface sediments and fluxes to the water column because diffusion in sediments is slow.

Our mechanistic model is set up with two sediment layers, the first of which is typically 1-3 cm thick. The 2nd layer typically represents the remainder of the organic horizon. Below those two layers, a boundary layer is assumed to be mineral soil.

As an example of the implications of the soil depth chosen, consider one site with a shallow organic horizon, *e.g.* 5 cm, while another site has a 20 cm organic horizon (Figure 2). Would the methylmercury fluxes to overlying waters be similar or very different for these two sites? This is relevant when comparing ELA upland sites, which have thin organic horizons, with many other reservoir locations. ELA had an intense fire in 1980 that could partly explain the thinner organic layers for the FLUDEX sites.

While our model assumption is that the primary zone influencing peak methylmercury fluxes to overlying waters is the top few cm, organic material below the top few cm may still be important, affecting how long elevated methylmercury supply occurs to overlying waters. As decomposition consumes the original surface layer, underlying organic matter becomes closer to the new sediment-water interface, and could sustain methylation longer if it serves as a source of carbon to the surface layer. A related consideration is whether bank erosion and sedimentation rates in the new reservoir will cover organic matter, and if so, with what type of material (organic/inorganic)?

While my expectation is that methylmercury production in flood zones is usually greatest near the sediment surface, methylation can occur deeper than a few cm. Transport by diffusion from these depths toward the surface sediments would be slow.

Some insights into this issue may be available by comparing wetland and uplands. Wetlands have much greater carbon stores than uplands. Net methylmercury loads to the water column for the ELARP wetland were no greater than for the flooded uplands (Figure 3). While there are certainly differences between the characteristics of wetland and flooded uplands, the similar fluxes shown in Figure 3 from the two types of terrain could be partly explained if it is only the top layer of flooded soil that controls the flux to overlying waters.

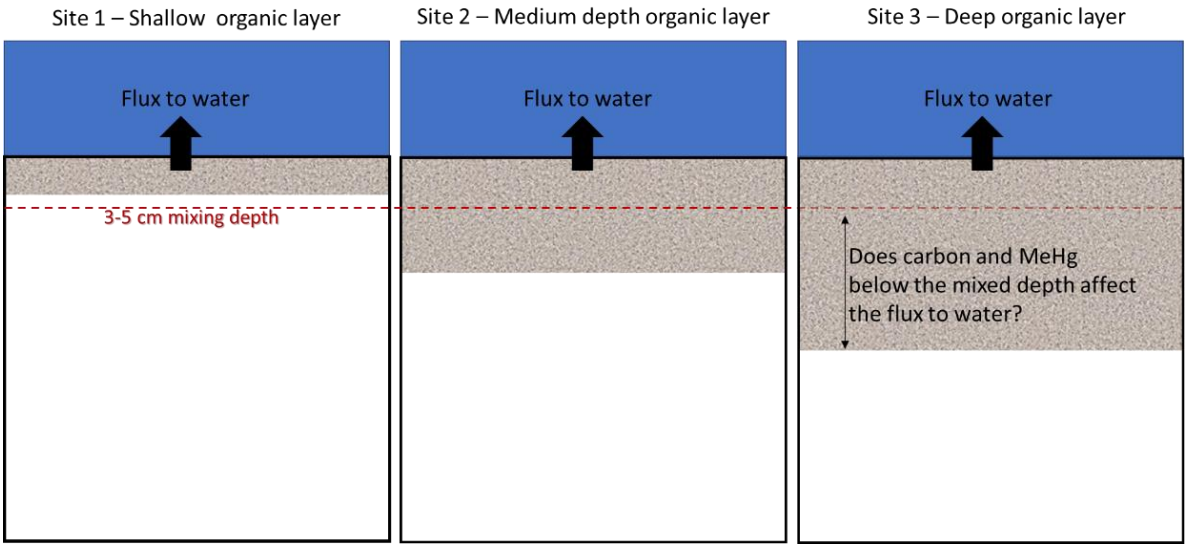

Figure 2. Conceptual diagram showing three sites with different depths of organic soils

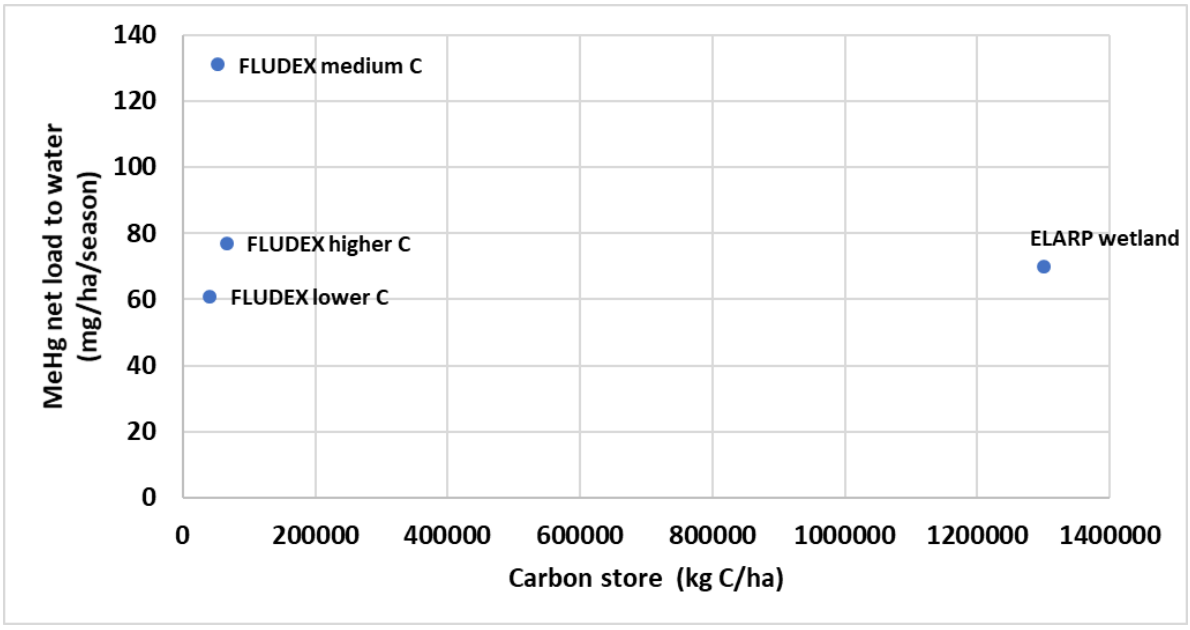

Figure 3. Net MeHg flux increases from inflow to outflow for the FLUDEX upland and ELARP wetland experiments. Carbon stores for FLUDEX from Hall (2018). Carbon stores for ELARP from Bodaly et al. (2004). MeHg fluxes for FLUDEX from Hall *et al.* (2005). MeHg flux for ELARP is for 1st year after flooding, and is from St. Louis *et al* (2004). FLUDEX MeHg fluxes are maximum seasonal averages from the first three seasons.

Overall I agree with the concept that more labile carbon in flood zones should lead to increased methylmercury production at depths relevant to bioaccumulation. However, it is important in my view to consider the depth of soil that is most influential in determining methylmercury fluxes to overlying waters. Finally, updated information characterizing the flood zone indicates that the effective area loading methylmercury to overlying waters should be less than previously assumed, between 30.42-36.98 km^2.

I hope these comments are helpful. Contact me at your convenience if you have any comments or questions.

Sincerely,

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