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Technical Memorandum

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To: Peter Madden, Nalcor Energy
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**RE: Quantitative Measurement of Labile Carbon in Organic Soils of the
Lower Churchill River**

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1 Executive Summary

Six soil samples were randomly chosen from within the inundation zone of the Muskrat Falls Project on the Lower Churchill River (LCR) for analysis of labile carbon. Each sample had the litter and fermentation layers removed, to focus on the humic soil horizon, with measured total organic carbon (TOC) content ranging from 28% to 48%. “Labile” means the fraction of TOC that is easily decomposable by microorganisms. While there are several methods of estimating labile carbon, including by incubation under regimes of specific temperature, moisture content and time, the method employed for this study employed exhaustive distilled water extractions at ambient temperature to measure the progressive release of dissolved organic carbon (DOC) over time. Other published studies suggest this method gives results that are reasonably comparable to incubation studies. Results indicated that 0.8% or less of the total organic carbon was readily extracted and measured as DOC using this procedure. This suggests that only a very small fraction of the organic carbon in these soils is labile and capable of supporting growth of microorganisms that can methylate mercury. These results are not atypical and suggests that soil characteristics within the LCR are in good agreement with the labile portion of organic horizon soils found in boreal forests from other geographic regions.

2 Introduction and Objective

Labile carbon in soils is the fraction of total organic carbon (TOC %) that is readily decomposable by soil microorganisms. Labile carbon is the principle “fuel” that supports the early microbial conversion of inorganic mercury into methylmercury (MeHg) when soils are inundated under a water cover. Azimuth Consulting Group Partnership (Azimuth) quantified the labile portion of carbon in a subset (n=6) of previously-collected organic soil samples (AMEC 2016) from forested areas within the region forecast for inundation by the Muskrat Falls Reservoir along the Lower Churchill River. The objectives of this exercise were: 1) to provide a quantitative assessment of how much of the total organic carbon could be available to support mercury methylation; and 2) to provide a comparison of labile carbon in Lower Churchill River soils to organic soils from other boreal forest regions that have characterized this form of carbon.

3 Background

The ‘organic’ horizon of forest soils typically consists of three layers, the litter (L), fermentation (F) and humic (H) layers. This zonation is not always present due to the mixing activity of soil invertebrates (e.g., earthworms). The litter layer consists of relatively fresh organic residues with identifiable plant material such as needles, leaves and twigs resting on the surface. Just beneath this is the fermentation layer, where decomposing plant material is apparent and the origin of the material is still distinguishable. Roots can also be present here. The layer containing the bulk of the carbon (and mercury) in forest soils is the humic layer or topsoil that lies beneath the L / F layers and above the ‘mineralized’ soils that contain very little carbon and no distinguishable organic material. It takes many decades to form an established humic soil horizon. The organic carbon content of the L, F and H layers is not all the same with respect to its availability to be decomposed. Some is easily broken down, while a larger part is more recalcitrant or resistant to decomposition.

The portion of carbon in soil that is easily broken down is called ‘labile’ carbon. Typically, it is further defined by how much carbon is mineralized over a period of days to months, and not years. There are numerous analytical methods (e.g., Gregorich et al. 2003, McLauchlan and Hobie 2004, Landgraf et al. 2006, Guigue et al. 2014) to estimate the proportion of labile carbon in soil relative to the total amount of organic carbon – but all yield results that are “operational” – that is, results depend in part or wholly on the details of the measurement method. The more realistic methods employ incubation of samples under conditions simulating actual field conditions to measure release of gaseous and/or aqueous of carbon dioxide and methane.

4 Methods

To measure the labile proportion of carbon in forest soil of the Lower Churchill River, we selected six soil samples from the project area and tested these using an accepted analytical method. All were from the uppermost humic horizon (i.e., L and F layers

removed) with TOC concentrations ranging from 27.5% to 47.9% (Table1). Samples had previously been dried at <60 C and pulverized to pass a 2-mm screen. The method described by Landgraf et al. (2006) was generally followed and is briefly described:

- Ten grams of dry soil was placed in a flask containing 100 mL of room temperature deionized water.
- The flask was placed on a rotary mixing device and rotated (30 rpm) for 24 hours.
- After allowing suspensions to settle, the supernatant was decanted, filtered (0.4 μ m pore size) and analyzed for dissolved organic carbon (DOC).
- A fresh 100 ml aliquot of deionized water was added to the extraction vessel followed by another 24 hours of mixing.
- The same procedure was followed to recover the supernatant for DOC analysis and repeated a third time (i.e., three independent episodes of shaking and extraction).
- After the third iteration of this procedure the solids in each vessel were recovered, dried and re-analysed for total organic carbon (TOC).

Table 1. Properties of soil samples selected for analysis of labile carbon.

	Description	TOC-1 (%)	pH	Total Hg (μ g/g)	Methyl Hg (ng/g)
AP126A	Black spruce/feathermoss; 19 cm humic	40.1	3.4	0.112	<0.05
AZ132A	Fir white spruce; 2 cm humic	42.9	3.6	0.130	
CS79A	Black spruce/feathermoss; 14 cm humic	45.7	4.1	0.150	
BQ116A	Mixed wood forest; 8 cm humic	47.9	3.5	0.185	
BV86A	Mixed wood forest; 6 cm humic	28.0	4.2	0.127	
DV46A	Fir white spruce; 5 cm humic	41.8	3.5	0.194	

5 Results

Cumulative losses of carbon calculated from analyses of the three x 24 h aqueous extracts ranged from 0.46 to 0.77%. The fraction of carbon lost with each consecutive extraction decreased, with one exception (CS79A), in a geometric series. That is, successive DOC concentrations were about one-half of the previous concentration (Table 2). This leaching pattern suggests dissolution of a moderately soluble fraction that would continue to be extracted with additional iterations, albeit at decreasing mass per extraction. Plots of the cumulative fractions lost against extraction number best fit (r -square ≥ 0.99) log relationships (**Figure 1**) with projected maximum losses (e.g., at extraction number = 10) ranging up to 1.1%. By way of comparison, Landgraf et al (2006) performed only single cold-water extractions of deciduous (beech) in forest soils, with comparable TOC contents (34 to 48%) as Lower Churchill River soils. They found comparable fractions of TOC lost (0.27 to 0.40%) that were very similar to this study in our first extraction (Table 2, 0.20 to 0.40%). Hamkalo and Bedernichek (2014) reported somewhat higher cold water extractable organic carbon (1.5 to 3.9%) for single extractions of soil samples from multiple soil horizons beneath a deciduous forest. None

of the soil horizons sampled and tested in the Hamkalo and Bedernichek (2014) study were very high in TOC, with values ranging from 1 to 6% in the upper 30 cm. However, these authors found that cold water extractable organic carbon was moderately correlated ($r^2=0.55$) with TOC, and more so at TOC contents <3%. While Vasques et al. (2009) do not report results for cold water extractable carbon, they do report results for hot water extractable carbon for a suite of 141 soil samples with TOC concentrations ranging from 0.27 to 20.1%. In addition, they incubated all soils for 35 days and measured emitted CO₂ to assess mineralization rates. Hot water extractable carbon averaged only 5% of TOC while incubated samples lost an average of 0.75% of TOC.

Table 2. Fraction of TOC that is released as DOC in three consecutive 24 h extraction episodes.

	Extract #	AP126A	AZ132A	AZ132A-R	CS79A	BQ116A	BV86A	DY46A
DOC-1(mg/L)	1	105.9	103.9	87.8	112.5	120.6	111.2	89.5
DOC-2(mg/L)	2	58.5	71.4	55.5	60.8	88.6	55.6	62.8
DOC-3(mg/L)	3	35.0	45.2	31.6	61.5	40.1	46.1	41.7
TOC-1 (%)		40.1	42.9	42.9	45.7	47.9	27.5	41.8
TOC-1(grams)		4.01	4.29	4.29	4.57	4.79	2.75	4.18
DOC-1 (grams)	1	0.011	0.010	0.009	0.011	0.012	0.011	0.009
DOC-2 (grams)	2	0.006	0.007	0.006	0.006	0.009	0.006	0.006
DOC-3 (grams)	3	0.004	0.005	0.003	0.006	0.004	0.005	0.004
Total DOC(grams)		0.020	0.022	0.017	0.024	0.025	0.021	0.019
DOC-1 (%)	1	0.26	0.24	0.20	0.25	0.25	0.40	0.21
DOC-2 (%)	2	0.15	0.17	0.13	0.13	0.18	0.20	0.15
DOC-3 (%)	3	0.09	0.11	0.07	0.13	0.08	0.17	0.10
Total (%)		0.50	0.51	0.41	0.51	0.52	0.77	0.46

R = Laboratory replicate sample

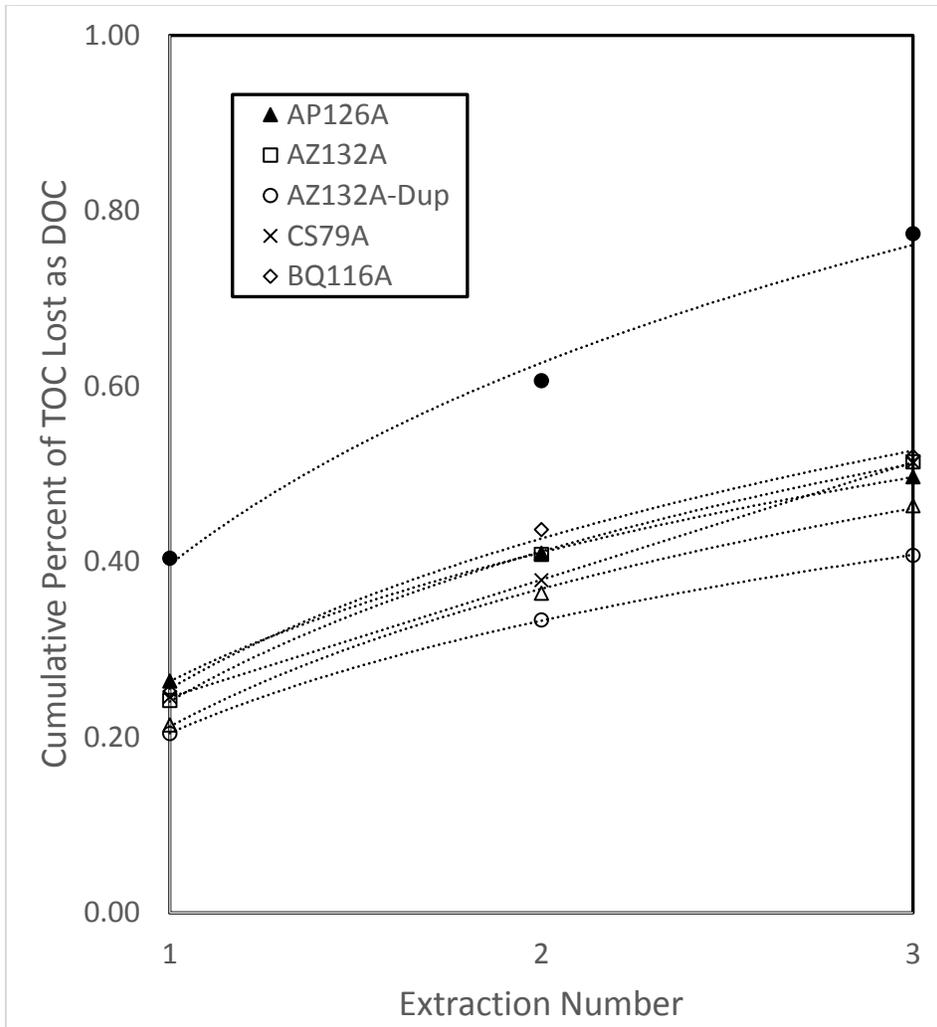


Figure 1. Cumulative percent of TOC lost as DOC. Dotted lines are logarithmic fits to data with exception of CS79A which best fit a linear function. All r-square values were ≥ 0.99 .

With respect to the amount TOC left over at the end of the three extractions, we saw some unusual results for some of the samples, with much lower TOC remaining than could be accounted for by the loss of DOC after the aqueous extractions (**Table 3**). This was not expected and may have occurred because solids were lost at each iteration of the procedure due to transfer to filters during decanting. If the solids transferred were representative of the bulk soil (i.e., no size or density fractionation due to differential settling rates) the concentration of TOC should not have changed by more than accounted for by the measured loss of dissolved organic carbon. Because TOC did change suggests fractionation occurred and resulted in loss of material that was richer in TOC (had a higher concentration) than material retained in the vessel. The analytical laboratory is investigating possible reasons for this.

Table 3. Results of pre- (TOC-1) and post-analysis (TOC-2) of soils for total organic carbon.

	TOC-1 (%)	TOC-2 (%)	TOC loss (%)	%change
AP126A	40.1	27.7	-12.4	-30.9
AZ132A	42.9	23.3	-19.6	-45.7
AZ132A-R	Insufficient sample			
CS79A	45.7	46	0.3	0.7
BQ116A	47.9	41.2	-6.7	-14.0
BV86A	27.5	21.3	-6.2	-22.5
DY46A	41.8	44.1	2.3	5.5

6 Discussion and Conclusions

Overall the estimates of “labile” carbon measured in this study using an “exhaustive” extraction procedure agree very well with results from other studies where similar soils from boreal regions were characterized for the “labile” or “easily decomposable” fraction of total organic carbon using water extraction, incubation, density separation or spectroscopic methods. As noted in the introduction, the more realistic estimates of labile carbon are derived when samples are incubated, especially for long periods of time. Where water extractable carbon has been compared to carbon losses by sample incubation (e.g., Vasques et al. 2009, Guigue et al. 2014) hot water extractable carbon was only slightly higher than carbon lost by incubation. Unfortunately, no published studies were found where cold water extractable carbon was compared to carbon lost by incubation. Where hot water extractable carbon has been compared to carbon lost by incubation the hot water extraction method has typically overestimated carbon lost by incubation. Possibly better agreement would be achieved if longer incubation times were involved. Nevertheless, the cold-water extraction used here better approximates ambient cold-water conditions found on the Lower Churchill River.

For current mercury modeling purposes, where soil is considered to have two carbon fractions with fast and slow mineralization rates, respectively, the fraction of total carbon that is labile is important to the extent that: 1) it provides an estimate of the maximum possible extent of mineralization by the faster decomposition rate; and 2) the rate of mineralization may be proportional to the quantity of mineralizable organic matter (e.g. Stanford and Smith 1972). The results of this investigation suggest that labile carbon comprises a very small fraction (~1%) of the total organic carbon in Churchill River soils. This agrees with other published studies at other sites with similar organic soil horizons. Thus the “typical” nature of our low measured labile carbon concentrations are not expected to provide a greater “fuel source” for methylating bacteria than other soils, and thus no greater rate or prolonged duration of mercury methylation should be expected at the Lower Churchill River project compared to other locations.

7 References

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