Site C Technical Memorandum

Mercury Data Review and Planning Considerations

Prepared for

BC Hydro
Site C Fisheries and Aquatics
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TABLE OF CONTENTS

TABLE OF CONTENTS

LIST OF TABLES

APPENDICES

ACKNOWLEDGEMENTS

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EXECUTIVE SUMMARY

Azimuth Consulting Group (Azimuth) was retained by BC Hydro to develop a strategy to address the issue of mercury related to the potential Site C hydroelectric development. This planning document addressed three tasks:

- Review documents for status of metals and mercury in environmental media with respect to their amenability as data input parameters for mercury modeling.

- Evaluate existing models to predict changes in mercury concentrations in environmental media of new reservoirs and identify key data gaps to support modeling. This task also includes a communications strategy.

- Summarize field data requirements for 2010 to support modeling and develop Standard Operating Procedures to collect mercury data in environmental media.

Task 1 – Review of Existing Data

The main documents reviewed included TEM (Keystone Wildlife Research), water quality, sediment, soil and vegetation data (Golder) from Peace River and Dinosaur Reservoir and Peace River fish mercury data (Mainstream Aquatics).

Key results are as follows:

- Total suspended solids (TSS) concentrations are orders of magnitude higher during freshet and are closely related to total metals concentrations. Dissolved metals concentrations are always low.
- Mercury was not detected in water samples in 2007 or 2008 because of the high detection limit used (50 ng/L). Mercury in water from Williston is <1.5 ng/L.
- Williston and Dinosaur are have well oxygenated hypolimnia with moderate DOC and sulphate concentrations and high pH that do not favor methylation.
- Sediment mercury concentrations of Peace River are poorly characterized and available data are not useful as model input parameters.
- Soil mercury concentrations are not well characterized and more data, stratified by soil horizon (i.e., vertically) and according to soil/habitat type are required for modeling. In the few soil samples collected, mercury is low (<0.05 ppm).
- TEM information reviewed indicates that there are few terrestrial habitats with the potential of contributing methyl mercury to the new reservoir. Although there are few data for mercury in vegetation, we expect concentrations to be low. Further data, stratified by dominant vegetation type, are required for modeling purposes.
- Tissue data from 25 bull trout and 61 mountain whitefish within the Peace River along the Site C corridor revealed very low concentrations for both species (0.09 ppm and 0.04 ppm respectively. These are 'size adjusted' concentrations assuming a 550 mm bull trout and a 300 mm mountain whitefish.
- Stable isotope data have not been collected to date. We recommend that stable carbon and nitrogen data be collected from benthic invertebrates, zooplankton and fish from different trophic levels to facilitate our understanding of mercury dynamics in the food web of the Peace River and Dinosaur Reservoir.

Task 2 – Review of Mercury Models

This chapter begins with a review of the relationship between reservoir creation and mercury and recent developments in our understanding of mercury dynamics in reservoirs, based primarily on research conducted at the Experimental Lakes area in northwestern Ontario related to the ELARP (Experimental Lakes Area Reservoir Project) and FLUDEX (Flooded Upland Dynamics Experiment) projects. This is followed by perspective on the current status of mercury in Williston Reservoir relative to what is known about other large Canadian reservoirs. Very low mercury concentrations were found in all environmental media in 2001 except bull trout from Finlay Reach. Given the relatively old age of Williston Reservoir it is very likely that mercury concentrations observed are 'background'.

Four models have been developed to predict fish mercury concentrations in central and eastern Canadian hydroelectric reservoirs; two simple regression based models and two multi-dimensional complex models. The simple models require a minimum of input data (i.e., flooded area, mean annual flow, total reservoir area, and baseline values for mercury in fish in the area to be flooded, which are known) but only predict maximum mercury concentrations in fish with no timelines. The complex models require a considerable amount of detailed input parameters, some of which are not currently available and will have to be collected. The complex models provide estimates of mercury concentrations in all environmental media over time.

We recommend that a staged approach be carried out beginning with the Harris and Hutchinson (2008) simple linear model to provide first order approximations of predicted mercury concentrations of candidate fish species. Given the expected level of scrutiny targeted at this proposed development, we advise that BCH consider application of the Manitoba Hydro model developed by Reed Harris (which was adapted for Williston in 2002). A sophisticated model will allow for a more quantitative approach to explore the effectiveness (from a cost-benefit analysis perspective) of various management options for limiting mercury accumulation.

Task 3 – Field Data Requirements and SOPs

Based on a comparison of available information and critical input parameters to conduct sophisticated mercury modeling, the following data are required:

- Total and methyl mercury (total and dissolved phase) in mainstream and tributary streams
- Phytoplankton and zooplankton biomass (mg/m^3)
- Zooplankton mercury concentration
- Fish diet
- Fish growth and bioenergetics of key species (i.e., benthic herbivore, benthic omnivore, planktivore, piscivore)
- Stable isotope analysis of zooplankton, benthos and candidate fish species stratified by trophic level

There are well established protocols for sampling of mercury and methyl mercury in environmental media. Standard methods, including quality assurance/quality control (QA/QC) procedures must be followed to avoid the risk of inadvertent contamination.

Detailed methodologies and QA/QC procedures for the collection of total and methyl mercury in water, sediment and soil are provided in Appendix 1. General methodologies for the collection of biota tissues (vegetation, plankton and fish) are described in the body of this document in less detail because the risk of contamination is much lower.

Conclusion

This strategy document is intended to provide a foundation from which to build a cohesive body of information to support informed management decisions and communications regarding mercury and Site C. While this document has a strong focus on the use of literature and models as a tool to explore the issue quantitatively, the strategy also includes a more holistic approach to improving our understanding of the factors likely to affect mercury dynamics at Site C.

Prior to moving towards implementation, this strategy should be reviewed against BC Hydro's management options and objectives and revised as necessary. Finally, the strategy to address mercury at Site C needs to be flexible to adapt to changing understanding of the issue and to recognize the perspective and concerns of First Nations, local residents and stakeholders.

1. OBJECTIVE AND SCOPE OF WORK

BC Hydro is presently considering the Peace River Site C hydroelectric project (Site C) in north eastern British Columbia as a potential resource option to help meet BC's future electricity needs. Azimuth Consulting Group (Azimuth) was retained by BC Hydro to develop a strategy to address the issue of mercury within the potential Site C hydroelectric development project on the Peace River, BC. We undertook four major tasks as follows:

1. Reviewed technical documents provided by BCH to Azimuth and assess suitability of data to support mercury modeling

2. Developed an overall strategy for addressing mercury as it relates to Site C development including a literature review, review of mercury models, and identification of key data gaps

3. Summarized field data input requirements to satisfy basic requirements of potential future modeling scenarios and provide Standard Operating Procedures (SOPs) for the collection of mercury in various environmental media.

4. Reviewed and provided recommendations on a public information piece intended to educate readers on the relationship between hydroelectric projects and mercury and the context of Site C. This has been included as an Appendix at the end of this report.

For readers unfamiliar with the issue of mercury and mercury in reservoirs, we refer you to Section 3.1 of this document. This section provides an overview of historic research about the relationship between reservoir creation and mercury and a discussion of recent advances in the science. Reading this section first may facilitate a better understanding of this topic.

This report provides a detailed strategy and supporting rationale for addressing the issue of mercury accumulation in aquatic biota related to the proposed development of the Site C Reservoir. While we examine the use of predictive models as a tool to explore the issue quantitatively, we are advising a strategy that takes a holistic approach to improving our understanding of the factors likely to affect mercury dynamics at Site C. We believe that careful implementation of this integrated strategy will provide BC Hydro with essential information to manage this issue.

While this strategy is intended to provide a foundation from which to build a cohesive body of information to support informed management decisions, prior to moving towards implementation, this strategy will need to be reviewed against BC Hydro's management options and objectives and revised as necessary. The strategy can then be translated into a more formal Sampling and Analysis Plan (SAP) to guide data collection and data analysis.

2. REVIEW OF EXISTING PEACE RIVER INFORMATION FROM BC HYDRO

BC Hydro provided Azimuth Consulting Group (Azimuth) with the following reports or information / data sources for review:

- Terrestrial Ecosystem Mapping (TEM) project pdf maps and report by Keystone Wildlife Research Ltd. (2007)
- Golder (2009a) report entitled Water Quality, River Sediment, Soil and Vegetation Samples from the Peace River Watershed – 2007. Baseline Data Collection.
- Golder (2009b) report entitled Peace River Watershed Water Quality and Dinosaur Lake Limnology Sampling – 2008.
- Mainstream Aquatics Ltd (2009) report entitled Site C Fisheries Studies Mercury Levels in Peace River Fish Tissue Data Report. June, 2009.
- Five reports documenting the status of recent mercury studies as part of the Environmental Impact Statement for the proposed Lower Churchill River Hydroelectric Generation Project in Labrador by Nalcor Energy.

The following text provides our technical review of the scope and quality of the data provided and its utility for addressing the issue of mercury within the proposed reservoir from the perspective of employing a quantitative 'mercury model'. Gaps in data are identified by comparing model input parameters with the extent and quality of data in hand.

2.1. Data Review

Golder Associates (2009a, 2009b) conducted extensive seasonal limnology and water quality sampling along the Peace River downstream of the Peace Canyon Dam near Hudson's Hope, BC towards the BC / Alberta border at Clayhurst during spring, summer and winter seasons of 2007 and 2008. Five primary stations were sampled (Peace 1 – Peace 5), with Peace 1 – 3 situated between Peace Canyon and Site C; Peace 4 and Peace 5 are downstream. Along the mainstem, the 2007 study also included synoptic sampling of upland soil and vegetation from five locations adjacent to the Peace River, three within the proposed flood zone, as well as one additional station where only soil was collected and two stations where vegetation was collected. Water quality monitoring in 2007 also included tributary streams entering the Peace River upstream of Site C namely: Lynx, Farrell, Boudreau, Halfway, Cache and Moberly. These are the largest tributary streams discharging to the proposed reservoir and provide inputs of suspended solids (with adhered metals including mercury) and nutrients. Depending on mineral sources, erosion, upstream logging activities, or mines, tributary inputs can be direct contributors of organic carbon and mercury, which can contribute to the process of

mercury methylation within the proposed reservoir. Water quality was also measured from three large tributaries downstream of Site C including Pine, Beatton and Kiskatinaw rivers.

In 2008, seasonal water samples (six events) were collected from the Peace 1 – Peace 5 stations as well as Farrell and Cache creeks and Halfway, Boudreau, and Moberly rivers. In addition there was a focus on water quality and limnological parameters of Dinosaur Reservoir upstream of Peace Canyon Dam. Sampling within the reservoir included vertical temperature and oxygen profiles, hydrology, gas pressure and water chemistry. This information will be useful in determining temperature regimes and stratification patterns, if any, within the potential Site C Reservoir.

Our review of recent water, soil and sediment chemistry data from the Peace River is limited, for the most part, to those parameters that have the potential to affect mercury transport, cycling and methylation within the proposed reservoir. We do not make specific comment on other parameters except where the general understanding of chemical conditions in the river might contribute to our understanding of mercury. For example, although there is an extensive database on total and dissolved metals where there are clear temporal and spatial patterns in concentrations, these data have a minor influence on our understanding of mercury dynamics. The exception is the general pattern of the magnitude of increases in metals that are seasonally related to freshet. For example, total suspended solids (TSS) concentrations increased by orders of magnitude during freshet (timing differs between tributary and mainstem patterns) and was closely related to total metals concentrations. However, dissolved metals concentrations were nearly always below detection limits, and were unrelated to total metals concentrations and TSS. The data provided by Golder (2008) indicate that metals are primarily particulate bound and related to the high sediment load contained within the tributaries and mainstem flow during freshet.

Mercury was not detected in water samples by Golder in 2007 or 2008 because of the high detection limit used (i.e., >50 ng/L). However, a very similar pattern in seasonal tributary inputs of TSS and metals (including mercury) in Williston Reservoir was found in August 2000 and June 2001 by Baker et al. (2002). Total metals concentrations were elevated in all tributary streams during freshet relative to concentrations in summer. However, concentrations of the dissolved phase of select metals were below detection limits during spring. Total mercury concentrations were also significantly higher in spring, ranging from 4 – 28 ng/L in tributary streams and were correlated with total suspended solids concentrations (TSS). August concentrations of total mercury were much reduced and ranged from 0.3 – 1.0 ng/L. Dissolved mercury concentrations were relatively low in June (1.3 – 3.2 ng/L) but only slightly lower in August (0.4 – 0.9 ng/L). These results suggest that mercury inputs to Williston Reservoir were predominantly associated with particulate matter during freshet in June and predominantly in the dissolved phase in August.

2.1.1. Water Quality / Chemistry

Important water quality / chemistry parameters that influence mercury methylation potential (and hence food chain bioaccumulation of mercury) include pH, temperature, oxygen, nutrients and productivity, total suspended solids (as transport media for mercury), dissolved organic carbon (DOC), and sulphate. Data from the Peace River downstream of the Peace Canyon dam gathered by Golder in 2007 and 2008 for the above parameters are evaluated with respect to sufficiency in characterizing conditions within the proposed reservoir area and on their likely influence on methylation potential, based on our understanding of the literature and professional judgment.

- **Temperature / Oxygen** – Thermal conditions within the proposed reservoir are very well documented seasonally, as well as spatially and no further characterization is necessary. The temperature/oxygen conditions within Dinosaur Reservoir and Peace River will not likely favor methylation. Mean annual water temperature is cold. Dinosaur Reservoir, although shorter in length (23 km), does not stratify and is highly oxygenated, thus no hypolimnion is likely to be formed. Methylation is greater under anoxic conditions in the hypolimnion of lakes (Eckley and Hintlemen, 2005), which are not found here. Although Williston Reservoir is stratified, the hypolimnion is well oxygenated, despite the huge reservoir of organic material that still exists within the flooded terrain.

- **Nutrients and productivity** – Nitrogen and phosphorus nutrient concentrations from Peace1 – Peace 3 are also well characterized by Golder and no further data are necessary to support a mercury modeling exercise. Nutrients are in the low to moderate range and are reflected in low to moderate concentrations of chlorophyll a. These data indicate that productivity of the Peace River in this reach is low and moderately oligotrophic. These conditions are less favorable for methylation than highly productive systems.

- **pH** – pH of the Peace River is stable, well characterized and ranged from 7.5 to 8.2 with a mean around 8.0, which is slightly basic. Conditions do not change spatially down the river. Methylation is favoured in slightly acidic (pH~6) waters and the range of pH found in the Peace River will likely not favour methylation.

- **Dissolved organic carbon** – DOC concentrations varied between 2 and 2.8 mg/L, which are in the low to moderately low range. Current conditions are well characterized with little variability down through the system. However, DOC concentrations will likely increase in the newly formed reservoir. Elevated DOC is known to stimulate or facilitate the production of methyl mercury. Krabbenhoft et al. (2003) found that additions of DOC alone stimulated the production of additional methyl mercury from "old" mercury (i.e., existing mercury in the environment and not newly introduced mercury from atmospheric or other point

sources). Additions of DOC and mercury in mesocosm experiments caused greatly elevated methylation than when mercury alone was added. These results suggest that DOC is directly involved in the methylation process, rather than the common assumption that DOC is simply an attractive ligand for mercury in aqueous solution. This result has implications in new reservoirs where large pools of "old" mercury exist and can be methylated after flooding. DOC concentrations in excess of 5 mg/L are associated with greater methyl mercury production. Reservoir development planning should include careful consideration of management options for controlling organic carbon sources.

- **Sulphate** – Sulphate reducing bacteria are well known to be responsible for methyl mercury production in aquatic systems and there is a positive correlation between methylation rate and sulphate over environmentally relevant concentrations (5 – 30 mg/L). Concentrations in Peace River (12 – 15 mg/L) are in the moderate range (Golder, 2009a). Given the relatively remote geography of the area inputs of sulphates from industrial activities are presumed to be low not likely to exacerbate methylation.

Total mercury concentrations measured in surface waters of the Peace River and its tributaries were reported by Golder as largely non-detectable, with one exception. No analysis for methyl mercury was conducted so concentrations are not known. Typical concentrations of mercury in remote, non-industrial areas range from <1 – 5 ng/L (parts per trillion) or 0.001 – 0.005 µg/L (parts per billion). Total mercury concentration of Finlay Reach of Williston Reservoir in 2000/2001 was < 1.5 ng/L (Baker et al., 2002).

The detection limit for mercury stated in the Golder reports is 0.00005 mg/L or 0.05 µg/L (i.e., 50 ng/L), which is at least an order of magnitude greater than what would be expected for the Peace River, so the lack of detection is not surprising. However, concentrations of 120 and 130 ng/L were observed on 8 and 9 May 2008 respectively from Peace 5 (Golder, 2009a). Total suspended solids (TSS) concentrations on these dates were also very high (1,110 and 738 mg/L) and it is likely that this is a plausible result because of inorganic mercury adhered to sediment particles introduced during freshet, possibly from large tributary streams. For these two samples the mercury content of suspended solids (mg/kg dw) can be estimated from the mercury and TSS concentrations as 0.11 and 0.18 mg/kg, respectively, i.e., comparable to background. However, no tributary stream had mercury concentrations in excess of the detection limit (50 ng/L), so the origin may be from within the mainstem. Several other metals that are also typically particulate-bound (e.g., arsenic, cadmium, copper, nickel, zinc) were also at least two orders of magnitude higher in concentration at the same location in February 2008 (Golder, 2009b). Dissolved mercury concentrations are typically very low, even in events where total mercury is elevated. This is because mercury tends to be strongly bound to sediment particles and do not dissolve easily into water.

In Appendix G of Golder (2009a) the stated guideline concentration for mercury to protect aquatic life in BC is 0.00001 mg/L or 0.1 µg/L. This is the outdated 1987 guideline concentration that was updated by the province in 2001. The BC WLAP (2001) and Canadian Council of Ministers of the Environment (CCME, 2002) guideline concentration for mercury in drinking water is 1 µg/L (parts per billion) or 1,000 ng/L. The CCME guideline for the protection of aquatic life is 26 ng/L for total mercury and 4 ng/L for methyl mercury. In 2001, British Columbia developed a 30-day average guideline concentration for total mercury to protect freshwater aquatic life (minimum 5 samples). This guideline concentration ranges between 2 ng/L and 20 ng/L and is a site-specific guideline that is derived from the percent of methyl mercury in the water as a proportion of total mercury. For example, when the methyl mercury concentration is 0.5% or less of the total concentration, the total mercury guideline concentration is 20 ng/L. The guideline concentration is progressively reduced as the proportion of methyl mercury exceeds 0.5% of the total concentration. In Williston Reservoir, baseline total mercury was about 1 ng/L in 2001 (Baker et al., 2002), with methyl mercury concentrations of 0.1 – 0.25 ng/L or at least 10% of the total. Thus the calculated guideline concentration would be between 2 ng/L and 4 ng/L, which are very low values and well below the CCME guideline of 26 ng/L. The typical percent of methyl mercury as a proportion of the total is from 1% to 15% (Gill and Bruland, 1990; Watras et al. 1998; Southworth et al. 2004). Based on the site-specific ratio using the BC water quality guidelines, and using Williston Reservoir data, the maximum 30-day average total Hg concentration is calculated as 2 ng/L. This is likely lower than ambient lake and tributary stream data and is obviously not appropriate. But this does illustrate the confusion with the application of guidelines for mercury to protect aquatic life.

2.1.2. Tributary Inputs

Golder (2009a) estimated that the Moberly and Halfway rivers, the two largest rivers discharging to the Peace River between Peace Canyon dam and potential Site C, account for approximately 8% of the total annual discharge. Accounting for stream discharge from the smaller watersheds (Lynx, Ferrell, Cache, Boudreau), perhaps 10% of the mean annual discharge of the Peace River consists of tributary inputs above Site C. Although this is a relatively small percentage, the relative contributions of inorganic and methyl mercury loading on an annual basis cannot be ignored. Mercury concentrations are frequently higher in tributary streams that drain wetland, peatland or logged / disturbed lands. Thus, from a loadings perspective, tributary inputs of inorganic and methyl mercury can be significant. Furthermore, there are specific periods where tributary inputs may constitute a significant amount of the flow. This is especially true during freshet when larger stream inputs from Moberly and Halfway rivers can exceed discharge from Peace Canyon dam during periods of low discharge (Golder, 2009a) from Williston and Dinosaur reservoirs.

2.2. Sediment Characterization and Chemistry

Sampling of sediments of the Peace River carried out by Golder (Appendix I) in July and August 2007 (Appendix I) was limited to five stations (i.e., Peace 1 through 5), with three (Peace 1 through 3) within the proposed reservoir area (Golder, 2009a). Samples were acquired by wading into the stream and collected by shovel. Thus it is uncertain whether the samples were collected from areas that are seasonally dried or permanently wet. This can influence the amount of fine sediment and organic carbon in the sediment sampled. Grain size of the samples collected was very large with large proportions of gravel (30 – 30%) and sand (48 – 58%). Total organic carbon (TOC) concentrations were low (<1%). These samples are likely representative of erosional sediments and do not account for fine sediments with higher TOC in depositional areas.

Mercury concentrations in sediment from all stations were below detection limits (<0.05 mg/kg or ppm), except at Peace 1 (0.08 mg/kg). Non-detectable concentrations are due to large grain size of the sediments and the low TOC concentration, which contains the greatest pool of available mercury that is associated with carbon.

Sediment sampling should take place over a larger area in deeper water in depositional areas. We are aware that such areas may not be common or easily accessible. However, mercury methylation preferentially occurs in habitats where there is fine grain sediment in stable areas with sediment TOC concentrations of 3 mg/L or more.

2.3. Soil Characterization and Chemistry

The distribution and behaviour of mercury in soils is a strong determinant and driver of methylation potential of new reservoirs, both in terms of the magnitude and duration of elevated methyl mercury concentrations. Andersson (1979) reviewed the extensive scientific literature available on mercury in soils. Many additional publications (see reviews by Adriano, 1986; Schuster, 1991; Lodenius, 1994) have appeared since this seminal review, but our basic understanding of mercury in soils has not changed very much. Mercury concentrations in soils from background, non-mineralized areas range from 0.01 to 0.2 µg/g (e.g., Rasmussen, 1994; Lodenius, 1994; McKeague and Kloosterman, 1974), whereas values for soils from mercury-mineralized areas, such as near the Pinchi fault in BC (Plouffe, 1995), range up to several µg/g. Methyl mercury values typically represent <1% of total mercury concentrations and are higher in soil horizons with high organic content. Where soils have developed on uniform parent material vegetation, cover type and cover age are reported to be very important variables affecting concentration of mercury in soils (Grigal et al., 1994).

The total mercury content of soil is most frequently correlated with the organic matter content and less frequently with clay and iron content. Atmospherically-deposited mercury is effectively fixed in the uppermost layer (humus) of forest soils developed on glacial till and granitic bedrock in Sweden (Lindqvist et al., 1991; Aastrup et al., 1991). This fixation in humus is often manifested in sharp decreases (one order of magnitude

within a few centimeters) in mercury concentration as a function of depth in the soil profile. Soils that have developed under deciduous forest canopies or over carbonate bedrock (e.g., limestone, dolomite) generally do not exhibit such distinct vertical gradients in mercury concentrations because these soils experience rapid degradation of particulate organic matter and downward transport of mercury carried by dissolved organic carbon and activity by insects and worms. This apparent dichotomy in the behaviour of mercury in which organic matter can serve as both an immobilizing and a mobilizing agent is important to recognize. Thus, for example, where many other metals will tend to be mobilized under acidic soil conditions, such as may exist under a coniferous forest canopy, mercury will tend to be immobilized because degradation of organic matter is inhibited and condensation of humic acids is favoured under acidic soil conditions.

Soil sampling along the Peace River was limited to three locations from discrete areas along the mainstem of the proposed reservoir. Golder (2009a) stated that soil sampling was situated at steep sided slopes as well as low lying floodplains, modified by erosion and slumping. Soils sampled were situated in fluvial deposits adjacent to the Peace River and may not represent soils that will be flooded upon reservoir creation. Three sample pits were dug with roughly equal proportions of A-horizon organic soils mixed with B-horizon inorganic mineral soils composited into two samples, which we presume are homogenization replicates. We are not certain of this because, for example, replicates 1 and 2 from Site 20 are very different (Golder, 2009a). Nevertheless, total mercury concentrations in soils were mostly below detection limits (<0.05 mg/kg) except for Site 20 and 21 (0.15 and 0.075 mg/kg respectively). These concentrations are very low and typical of uncontaminated soils in remote areas. However, because the organic and mineral layers have been mixed, this may explain why mercury was low.

Sampling of soils for mercury should be stratified according to habitat type and vertically to separate mineral from organic soils. Mercury is preferentially bound up by carbon in the organic layer and it is critical to analyse this layer separate from the mineral layer that typically has much lower mercury concentrations. TOC in replicate 1 of Site 20 was very high (34%) and exceeded all other soil samples, which were less than 2% by weight. We appreciate that the soil sampling strategy was not designed to address the issue of mercury or to sample representative habitats that might be flooded. As such, the limited data presented in the report are of very little use.

2.4.   Vegetation Characterization and Chemistry

The primary exposure pathway of contaminants to terrestrial plants is via the adsorption to root structures, followed by uptake and translocation from roots to shoots and leaves. While this pathway may be important for most metals, the same is not true for mercury. Instead, uptake of mercury to plants is predominantly via plant shoots and leaves (above ground parts) from atmospheric sources as opposed to adsorption via roots (Chaney, 1990). Inorganic mercury becomes gradually accumulated over time in organic soils and

is released and transformed to methyl mercury during flooding to create reservoirs. Understanding the types of plant communities present, both in the watershed and the reservoir footprint, can provide insights into methylation potential within the future reservoir (e.g., availability of plant-based carbon as a nutrient source).

Keystone Wildlife Research (2007) has used Terrestrial Ecosystem Mapping (TEM) as a tool to document and quantify identifiable vegetation and habitat types along the Peace River downstream of Peace Canyon and outwards from the river to include the projected flood zone. Their report documents and describes vegetation types in great detail. However, there does not appear to be quantitative breakdown of dominant habitat or vegetation types on an aerial basis (ha), so we cannot determine the relative quantities or ranking of dominant types. Nevertheless, use of these results is not within the scope of work for this project. However, based on our review of the information contained within the report, there appears to be sufficient information to support development of a detailed sampling and analysis plan to characterize the metals / mercury / TOC baseline in vegetation, based on TEM outputs.

Golder (2009a) collected and composited vegetation (spruce, birch, rose) from six locations between Peace 1 and the potential Site C dam. Vegetation types were combined (in unknown proportions) from each site and metals concentrations presented. However, there is no indication in the report whether the data are reported in wet or dry weight concentrations. Based on our understanding of typical metals concentrations in plants, the data seem to be dry weight concentrations when they should be presented as wet weight concentrations, which is typical for tissue. Nevertheless, mercury concentrations in vegetation are very low, ranging from <0.005 – 0.019 mg/kg. If these are in fact dry weight concentrations, wet weight concentrations will be even lower, less than half of the concentrations above.

Rather than compositing, vegetation tissue samples should be analysed separately by species to properly characterize tissue mercury and / or metals concentrations.

2.5. Fish Tissue

Mainstream Aquatics (2009) collected tissue samples from 25 bull trout (*Salvelinus confluentus*) and 61 mountain whitefish (*Prosopium williamsoni*) for mercury analysis from just downstream of Peace Canyon Dam (30 fish) and between Halfway River and Cache Creek, upstream of Site C (31 fish) in August and September 2008. The range in fish size was sufficient to derive good mercury versus size and age relationships for both species.

There are a few small errors in the report that do not affect the results. For example, in Section 2.3 Laboratory Analyses, it is stated that 1 gm of tissue was digested for mercury analysis. As only 80 mg of tissue was collected in total, this is clearly not possible. The full laboratory report should be included as an Appendix because tissue

sample weight and moisture content affects detection limits and precision, especially in small samples. Furthermore, in checking with the laboratory used (Alberta Research Council Laboratories), tissue analysis of biopsy samples is rarely done. In future, if this laboratory is used, we suggest that duplicate samples get sent to another laboratory or that a subsample of mountain whitefish be sacrificed so that whole muscle samples can be analysed blind against biopsy samples taken from the same fish.

Regression equations were calculated for $\log_{10}$ length on $\log_{10}$ mercury concentration, which is appropriate. However, arithmetic mean mercury concentrations of different size fish were compared between areas. Because larger fish typically have higher mercury concentrations, it is inappropriate to compare mercury concentrations of different size fish. Fortunately, the size difference between upstream whitefish (329 mm) and downstream whitefish (343 mm) was small. A standardized comparison of 350 mm whitefish should be used to compare 'size-standardized' mercury concentrations. Assuming a standardized size of 350 mm, the adjusted mercury concentration is 0.033 ppm wet weight and 0.040 ppm (instead of 0.031 ppm and 0.039 ppm) for upstream and downstream fish, respectively.

Bull trout mercury concentration was 0.07 ppm for the mean size of 473 mm. Assuming a standardized size of 550 mm (e.g., the same as used in Williston Reservoir by Baker et al., 2002), mercury concentration would be 0.09 ppm. This is much lower than found in Williston Reservoir fish (0.56 ppm; although the data are 9 years old and only for Finlay Reach).

Regardless of the minor procedural differences, mercury concentrations of mountain whitefish and bull trout from the Peace River below Peace Canyon Dam are very low.

To better establish baseline conditions prior to flooding, a wider variety of fish species from various levels of the food chain should be sampled. This should include forage fish species (e.g., minnow species), herbivorous benthivores (e.g., sucker), carnivorous benthivores (e.g., whitefish), and piscivores (bull trout and/or lake trout). We are also aware that fish might be feeding preferentially from the tailrace area of Peace Canyon G.S. and that some fishermen are targeting this population. This population should be examined as well.

2.6.   Stable Isotopes

To assist in understanding long-term patterns or changes in mercury concentrations within the proposed reservoir, we are advising that sampling of tissue from invertebrates and fish be conducted for carbon and nitrogen stable isotopes. Food chain structure has been shown to influence contaminant concentrations in lake trout, particularly for mercury and persistent organochlorine compounds (Cabana and Rasmussen, 1994; Cabana et al., 1994). Because methyl mercury becomes increasingly concentrated with increasing steps up the food chain or with each trophic level, trophic position is an

extremely important factor in determining mercury concentrations found in top predators (Rasmussen and Vander Zanden, 2004). This is especially true if trophic structure of the aquatic food web changes after reservoir creation. For example, whitefish may incorporate more fish in their diet when feeding in the tailrace area of upstream generating stations that pass dead or stunned fish downstream.

Advances in stable isotope analysis (SIA) over the past two decades have resulted in a powerful time-integrated tool for determining trophic position that is literally based on the premise that "you are what you eat". Identifying these patterns provides valuable insights into the trophic structure of the system of interest.

The stable isotopes of nitrogen and carbon have been used to complement one another in the characterization of food webs over a broad range of systems. Nitrogen isotopes have been used extensively as a fairly robust means of distinguishing between and quantifying the trophic positions of consumers in aquatic systems (e.g., Peterson and Fry, 1987; Bilby et al., 1996; Vander Zanden et al., 1999; Harvey and Kitchell, 2000; Leggett et al., 2000; Vander Zanden and Rasmussen, 2001; Vander Zanden et al., 2003; Herwig et al., 2004). Carbon isotopes have been used to trace the flow of energy through food webs and are particularly valuable in identifying dietary preferences of consumers (e.g., Rounick and Winterbourn, 1986; Peterson and Fry, 1987; France, 1995a and 1995b; Hecky and Hesslein, 1995; Herwig et al., 2004; da Silva et al., 2005). Together, stable nitrogen and carbon isotopes provide strong insights into trophic structure and feeding preferences, which are invaluable in interpreting observed patterns in contaminant uptake and biomagnification (Rasmussen et al., 1990; Cabana and Rasmussen, 1994; Cabana et al., 1994; Atwell et al., 1998; Kidd et al., 1999).

Collection of tissue samples for stable isotope analysis is relatively simple and analysis of the tissue is quite inexpensive (~$20/sample). Tissue samples at different levels of the food web are required including benthic invertebrates, zooplankton, forage fish, benthivores (e.g., sucker), planktivores (e.g., whitefish) and piscivores (e.g., bull trout, lake trout) in order to characterize isotope ratios at different trophic levels. Establishing a baseline of stable isotope ratios, related to mercury concentrations of zooplankton, benthos and fish provides a rigorous tool for understanding of food web structure and dynamics and its relationship to mercury concentrations. This information will assist in understanding changes in mercury (and/or trophic structure) over time within Site C.

Acquiring tissue samples from invertebrates and fish from Dinosaur Reservoir for mercury and stable analysis will also provide valuable insight into the possible future food web structure and mercury concentrations in fish, given the similarity of the two environments. A sampling program for tissue collection from Dinosaur can be combined with field efforts from the Peace River in a coordinated program to establish current (Peace River) and possible future conditions based on results from Dinosaur.

Consideration can also be given to determining trophic level structure and mercury concentrations in fish in Williston to provide a longer time-horizon perspective on ecological changes that have occurred within the reservoir and implications on mercury in the food web. Acquisition of this information may lend greater credibility and improve our confidence in statements made about mercury in fish.

3. OVERVIEW OF MERCURY DYNAMICS IN RESERVOIRS, QUANTITATIVE MERCURY MODELING AND MERCURY STRATEGY DEVELOPMENT FOR SITE C

This section describes a conceptual strategy for addressing the issue of mercury and methyl mercury as it relates to the potential Site C Reservoir. Following are the main topics discussed:

- Update and review of the literature on reservoir-mercury dynamics during reservoir creation, magnitude and duration of elevated methyl mercury concentrations in various environmental media (e.g., water, sediment, plankton, fish) and recent developments in methyl mercury dynamics.

- A review of existing quantitative mercury models that ultimately predict peak fish mercury concentrations in new reservoirs. Two simple linear models and two complex multi-dimensional models are reviewed with the objective of determining whether or not use of a model is warranted at this time, and if so, which model is recommended, are the existing data on hand sufficient to run the model and what data gaps, if any, exist to run any of the models.

- Conceptual strategy to address perceptual and technical aspects of communication of mercury in the environment and field program execution.

3.1. Mercury in Reservoirs

Mercury is a naturally occurring element that is found in low concentrations in all environmental media including air, water, soil, sediment, plants and at all levels of aquatic and terrestrial food webs. The flooding of terrestrial soils and vegetation to create reservoirs during hydroelectric development provides a new food source of organic nutrients and inorganic mercury to bacteria in the flooded environment. Decomposition of this 'new' organic material by bacteria breaks down the chemical bond between carbon and inorganic mercury so that bacteria absorb and transform some of the inorganic mercury in a new, organic form called methyl mercury. Once incorporated by bacteria, it is now in the base of the food chain and is available to be consumed and accumulated at progressively higher concentrations by higher trophic level animals in the food web.

The process by which sulphate-reducing bacteria decompose carbon and liberate mercury in new reservoirs has been well studied (e.g., Abernathy and Cumbie, 1977; Wright and Hamilton, 1982; Bodaly et al., 1984; Brouard et al., 1989; Hecky et al., 1987; Hecky et al., 1991, and many others). Furthermore, the chemistry of mercury in aquatic systems and the process by which methyl mercury is accumulated and concentrated at higher levels of the food chain, especially by fish, has also been studied extensively (see reviews by Beijer and Jernelov, 1979; Huckabee et al., 1979; Hecky et al., 1991; Bodaly et al., 1997). Despite the vast body of research that has been conducted however, the exact mechanisms that govern the rate and duration of methyl mercury formation are still not well understood, although good progress has recently been made in Canada. Importantly, most researchers agree that the duration that mercury concentrations in biota, especially predatory fish, remain elevated above background is typically between 20 and 30 years, depending on environmental conditions (Bodaly et al., 1996; 1997; Schetagene and Verdon, 1999). The magnitude and duration of increase in run-of-the-river reservoirs is less than for lacustrine systems.

Methyl mercury is absorbed more rapidly than it can be excreted, and thus accumulates in the body. Over time, methyl mercury becomes more concentrated, especially in larger, longer-lived animals that live at the top of the food chain. Because most fish are carnivorous and feed over multiple levels of the food web, they consume and accumulate more methyl mercury than any other animal. Consequently, the vast majority of exposure by humans to mercury is through fish consumption. In BC lakes, piscivorous (i.e., fish eating) fish, such as lake trout (*Salvelinus namaycush*) and bull trout (*Salvelinus confluentus*), have higher mercury concentrations than kokanee (*Oncorhynchus nerka*), lake whitefish (*Coregonus clupeaformis*) and rainbow trout (*O. mykiss*) that consume plankton or insects. In addition, old, large fish tend to have higher mercury concentrations than small, young fish (Bodaly et al., 1984; Strange et al., 1991; Somers and Jackson, 1993). Thus, monitoring programs for fish mercury must consider differences in species composition and must sample over a wide size range of fish.

Over the last 10 years or so a great deal of information about mercury in reservoirs has been learned, primarily based on the results of two experimental flooding experiments at the Experimental Lakes Area (ELA) in northwestern Ontario. These studies have provided insight on our understanding of mercury dynamics in reservoirs that might shed some light on the potential Site C development. These are the ELARP (Experimental Lakes Area Reservoir Project) and FLUDEX (Flooded Upland Dynamics Experiment) research projects.

The ELARP project involved experimental flooding of a wetland complex (peatland surrounding an open water pond) to examine biogeochemical cycling of methyl mercury (St. Louis et al., 2004). Methyl mercury concentrations in water increased 40-fold during the first year of flooding and gradually declined over nine years of monitoring but still remained above background. The authors discovered that the magnitude and timing of mercury methylation in the flooded peatland of the reservoir was very high early on, but

diminished after three years because of de-methylation by bacteria over the flooded peatland. By contrast, methylation in the middle of the reservoir was low early on, but switched three years after flooding. Methyl mercury in zooplankton and forage fish increased and remained high for the full 9 years of the study. Methylation appeared to have been sustained by the relatively small ongoing net methylation in the open water pond and not the flooded peatland nearshore that was the initial driver. St. Louis et al. (2004) speculated that peat may have been carried away from the shoreline and deposited in deeper water and provided a source of carbon and mercury for methylating bacteria. This result has implications for larger reservoirs and could have important long-term implications for methyl mercury concentrations in predatory fish.

The FLUDEX experiment was designed to test the hypothesis that methyl mercury production was related to the amount and quality of flooded organic matter in an upland setting, with much lower carbon concentrations than the peatland scenario of ELARP (Hall et al., 2005). Three upland forest sites were flooded that varied in the amount of carbon stored in soils (30 kg/ha to 45 kg/ha). In all cases methyl mercury concentrations in water and plankton rose quickly and were sustained at high levels for two years after flooding before diminishing in concentration, but not back to pre-flood levels. Rates of methyl mercury production were found to be generally related to the amount of carbon flooded to create the reservoirs and that the large increase in methyl mercury in biotic components was related to methyl mercury production in flooded soil (Hall et al., 2005). Important factors contributing to short-term increases in methyl mercury production were the amount of 'labile' carbon (i.e., easily broken down, relatively 'new' carbon from plants and roots), the magnitude of carbon stored in the litter and fungal/humic layer (15,400 kg/ha) versus carbon in shrubs and moss (1,350 kg/ha), and mineral layer carbon (2,900 kg/ha). Standing trees were a large source of carbon (27,560 kg/ha), but this form of carbon is not easily broken down or available for methylation. In all FLUDEX upland reservoirs flooding resulted in a large increase in methyl mercury mass stored in soils that increased over three years at levels 9 – 25 times greater than concentrations prior to flooding, confirming that flooded soils were the main site of methyl mercury production, a similar result to the ELARP experiment.

While these general patterns are fairly typical, Bodaly et al. (2004), in summarizing key findings of the Flooded Uplands Dynamics Experiment (FLUDEX), discussed results that did not occur exactly as expected (e.g., poor linkage between methyl mercury production and organic carbon store, rapid decline in decomposition rates, uncoupling of methyl mercury production and bioaccumulation). Thus, while our understanding has improved over the past few decades, more research is needed to better understand this complex issue. For the purposes of this assessment, these uncertainties can be mitigated by incorporating a monitoring component to verify any fish tissue concentration predictions.

In the food web, periphyton, zooplankton and fish communities had comparatively low methyl mercury pools, accounting for only 1 – 10% of methyl mercury net biomass. The relative biomass of methyl mercury in fish increased over the course of time reflecting

the phenomenon of bioaccumulation. Hall et al. (2005) concluded that the majority of methyl mercury was produced in soils and was not transferred to the overlying water column. Flooding of wetlands may also not represent the worst-case scenario of methyl mercury production because most of the mercury remains there and was not transferred to the food web. Reservoirs created over upland forest containing relatively low organic carbon stores may result in methyl mercury contamination of reservoir fisheries equivalent to that of reservoirs created over wetland complexes. Furthermore, methyl mercury production and the export of mercury from the reservoirs decreased over the first three years of flooding. However, regardless of the short duration of high methyl mercury production, modeling and empirical data have shown that 2 – 5 years of enhanced production may be sufficient to sustain elevated methyl mercury concentrations in fish for up to 30 years after impoundment in some eastern Canadian reservoirs. This may be partly due to sustained low-level enhancement of methyl mercury production in reservoirs that are not seen in natural lakes. Montgomery et al. (2000) showed that the proportion of methyl mercury in water relative to inorganic mercury was nearly four times higher in reservoirs than in lakes even up to 18 years after reservoir creation.

3.2.   Reservoirs in British Columbia

Most of British Columbia's large hydroelectric stations, including Williston (1968), and Dinosaur Reservoir (1979), were constructed before the relationship between reservoir creation and increases in fish mercury was understood and there are few historic data available. Therefore, it has been difficult to determine to what extent hydroelectric development has been responsible for observed mercury levels in fish and the long-term or historic trend in fish mercury concentrations in BC reservoirs. This will remain a challenge when predicting possible changes in fish mercury concentrations associated with development of Site C and especially because there are no data with which to ground truth mathematical models.

Furthermore, the physical characteristics of BC reservoirs are very different from the eastern Canadian reservoirs for which the mercury models have been developed. For example, most BC reservoirs were created in mountainous regions and in river valleys with steep sides. These environments have relatively small amounts of organic matter in the soils and relatively small littoral areas, characteristics that do not favor the production of methyl mercury. Many reservoirs are also "run-of-the-river" reservoirs with short retention times. During creation of Williston Reservoir, the valley floors of the Finlay, Parsnip and Peace rivers were inundated, flooding large standing forests, low-lying bogs and fens. These areas may have contained large amounts of organic material that contributed to increased methyl mercury concentrations in the new reservoir. However, given that inundation occurred in 1968, more than 40 years ago, it is likely that the 'reservoir phenomenon' has probably passed as most authors agree that elevated mercury concentrations in top level predators does not remain elevated above background for more than 30 years. For example, Bodaly et al. (2007) looked at post-

impoundment time course of elevated mercury for three species of fish for up to 35 years after impoundment in 14 lakes and lake basins. Mercury concentrations in benthivorous lake whitefish (*Coregonus clupeaformis*) peaked within 6 years of impoundment and took between 10 and 20 years to return to background concentrations in most reservoirs. Piscivorous northern pike (*Esox lucius*) and walleye (*Sander vitreus*) were highest 2 to 8 years post-inundation and required 10 to 23 years to return to background concentrations.

Given the large standing crop of forest and organic material that still exists within Williston Reservoir, it is possible that this submerged carbon source may continue to be a source of carbon for methlyating bacteria. However, methyl mercury concentrations in water, zooplankton, benthic invertebrates and lake whitefish in 2001 were relatively low and typical of natural lakes (Baker et al., 2002), which would suggest that mercury levels in Williston reservoir have returned to baseline, notwithstanding elevated concentrations in bull trout. Note there is still a 'fish consumption advisory' for bull trout from Williston Reservoir where consumers are advised to limit their consumption of this species.

Twenty-three km downstream of the WAC Bennett dam that formed Williston Reservoir the Peace Canyon Generating Station formed Dinosaur Reservoir 30 years ago in 1979. This run of the river reservoir has limited storage capacity as it passes the same amount of water discharged to it from Williston. The reservoir is contained largely within a bedrock canyon with a water retention time or flow through rate of about 3 days. At least 10 fish species are present including rainbow trout, lake trout, mountain and lake whitefish, peamouth chub, kokanee, longnose sucker, white sucker, redside shiner and northern pikeminnow (Murphy and Blackman, 2004). The reservoir is isothermal, with low water temperatures in winter (1 – 4°C) and summer (<14°C).

Few fish mercury data exist for Dinosaur Reservoir. The only data we are aware of are from 1988, nearly 20 years after reservoir creation. Mercury concentrations from bull trout (0.07 – 0.15 ppm), kokanee (0.03 ppm), lake whitefish (0.03 – 0.15 ppm) and mountain whitefish (0.03 – 0.14 ppm) were all relatively low (Baker, 1999) and typical of pristine lakes. These data indicate that mercury concentrations in fish from Dinosaur have returned to background. However, because of the absence of earlier data the magnitude of increase in fish mercury concentrations after reservoir creation is unknown.

The most important factors contributing to elevated Hg concentrations in biota in reservoirs are the extent of flooding, the amount of available carbon (wetlands, marshes and peat bogs are the greatest contributors) and soil Hg concentrations in flooded areas. Based on examination of the TEM it would appear that such habitat and soil types are limited and overall, constitute a very small proportion of the terrestrial habitat types forecast to be flooded. Given the relatively small flooded area, limited storage capacity and retention time, cold water temperatures, near neutral pH and lack of wetland habitat flooded increases in methyl mercury over the long term are likely to be small.

3.3. Strategies to lower Methyl Mercury Concentrations in New Reservoirs

Mailman et al. (2006) reviewed a number of strategies to reduce or manage the undesirable effects of river impoundment on mercury concentrations in fish. Those include:

- *Site selection and project configuration* - Selecting sites and project configurations to reduce the amount of littoral and wetland areas to be flooded could effectively reduce mercury methylation in these "hotspots".

- *Controlled burning prior to flooding* - Controlled burning would likely only be applicable to upland areas but would reduce both inorganic mercury and organic carbon and thus reduce stimulation of methylation when burned areas are flooded. Mailman and Bodaly (2005) showed significant reductions in organic carbon and mercury (inorganic and methyl mercury) in burned plants and soils. However, while reducing water methyl mercury concentrations, concentrations in biota were not correlated to methyl mercury in water, possibly due to lower bioavailability from higher DOC.

- *Removal of vegetation* - Removal of vegetation would also effectively reduce the amount of organic carbon available to stimulate methylation after flooding. We understand that this is being proposed by BCH.

- *Capping of bottom sediments* - Capping of bottom sediments would mean capping the riparian wetland soils as part of site preparation prior to flooding. This would effectively isolate the organic-rich materials from ponded water and thus reduce or halt stimulation of methylation with these materials.

- *Dredging of bottom sediments* - Dredging of bottom sediments would mean physical removal of all wetland soils and organic-rich sediments in ponds and marshes prior to flooding. This strategy has the same potential benefits as capping but lacks control of the substrate left behind after dredging that may also be stimulatory to methylation.

- *Removal of Predatory Fish* – This technique has been suggested as a means of reducing the bioavailable pool of methyl mercury in biota, however this is not recommended here because of the already low mercury concentrations in fish (Mainstream Aquatics, 2009).

3.4. Modeling Approaches and Requirements for Predicting Mercury Concentrations in Reservoirs

This section reviews modeling approaches for predictions of mercury in fish in newly-flooded hydroelectric reservoirs, the applicability of such models to BC reservoirs and in particular Site C and the input parameters needed to run the various models. Predictions of mercury in fish that are derived from existing equations and/or dynamic models are highly desirable because they are objective and quantitative.

Four models have been developed based on data from reservoirs in Central and Eastern Canada. Two of the models are based on relatively simple linear regression equations

with relatively simple input parameters that are based on the physical characteristics of the proposed reservoir. (e.g., estimates of flooded area and water flow). The other two models are dynamic, complex and require a large number of input parameters, many of which require field sampling and empirical data. Running these complex models requires a large investment in time from experts intimately familiar with them. All these predictive models would benefit from calibration with data concerning mercury in fish from northern BC reservoirs, however few such data appear to exist.

3.4.1. Model Review

Four models have been developed to predict fish mercury concentrations in central and eastern Canadian hydroelectric reservoirs; two simple regression based models and two multi-dimensional complex models. **Table 1** summarizes the input parameters required for each of the models that we have evaluated. Based on our understanding of existing data we have indicated whether empirical data exist and are sufficient as input parameters, whether data can be inferred or estimated from the literature, or if field data collections are necessary. Our assessment of the individual models and our recommended approach is as follows.

3.4.1.1. *Johnston et al. Multiple Linear Regression models*

Johnston et al. (1991) developed a series of multiple linear regression equations to predict peak body burdens of mercury in boreal hydroelectric reservoirs. The equations were based on data from northern Manitoba reservoirs and were developed for lake whitefish (a benthivorous species), walleye and northern pike (both piscivorous species). Species found in the Site C reservoir, such as rainbow trout and bull trout are not the subject of these equations. Lake whitefish is the only species common to eastern and western reservoirs. These equations were tested on data for Manitoba, Quebec and Labrador reservoirs and the fit of the equations was not as good for reservoirs outside of Manitoba. The equations require only the physical parameters of flooding area, total reservoir area, and volume of proposed reservoirs (**Table 1**) to calculate peak body burdens and concentrations. Time series data are not estimated by this model. Baseline body burdens for a specific area to be flooded can be substituted in the equations for the data which was based on northern Manitoba reservoirs. The equations developed by Johnston et al. include options for considering upstream flooding, but because the Site C reservoir will be developed alone and because upstream reservoirs are old and likely past their period of elevated methyl mercury production (Tetra Tech, 2002; Baker et al., 2002), use of these forms of the equations would not apply to Site C.

The model equations are relatively simple and could be applied to Site C in a few hours by an expert familiar with them, assuming that the model inputs are known. However, they cannot be considered to be precise and may be accurate only to within 0.2 µg/g total mercury in fish muscle only. They lack the credibility of dynamic models that are based on state of the art understanding of mercury dynamics and were not developed

for species found in BC, with the exception of lake whitefish. However, walleye could be used as a surrogate to estimate mercury concentrations in bull trout. These equations do not take flows or water residence times into account and the effect of flushing, which will tend to reduce mercury bioaccumulation in reservoirs, which may be significant for the potential Site C reservoir.

As with all of these models, it would be desirable to calibrate the equations to data from reservoirs in the region of Site C. However, there are few data available for northern BC reservoirs (Baker, 1998; 1999). Therefore, the equations based on data from Quebec and Labrador reservoirs could be applied to the potential Site C reservoir, but the results would need to be treated with caution.

3.4.1.2.   Harris and Hutchinson Linear Regression models

Harris and Hutchinson (2008) developed linear regression models for the prediction of mercury in fish in the proposed Lower Churchill reservoirs in Labrador. The equations predict the peak increase in mercury in northern pike and lake whitefish as a factor of pre-impoundment concentrations. Inputs needed to make the calculations include flooded area, mean annual flow, total reservoir area, and baseline values for mercury in fish in the area to be flooded (**Table 1**). Upstream flooding can be considered using these equations by treating a series of newly flooded reservoirs as though there was one reservoir that was growing in size as the water moved downstream. Because Site C will be developed separately and other upstream reservoirs are past the period of elevated methyl mercury production this treatment would not be required.

These model equations are relatively simple and could be applied to Site C in a few hours by an expert familiar with them. However, as with the Johnston et al. model equations, they are not precise and lack the credibility and predictive capability of dynamic models that are based on state of the art understanding of mercury dynamics. However, this model is a significant improvement upon the equations of Johnston et al. in that they take water residence times (in the form of flows) into account as a factor that probably reduces mercury bioaccumulation in new reservoirs, which is relevant at Site C. As with the Johnston et al. equations, these calculations predict only peak mercury levels in fish, not the time course of elevated levels.

As with the Johnson et al. model, it is not possible to calibrate the equations to data from reservoirs in the region of Site C because of the lack of historic data. Similarly, the equations based on data from Quebec and Labrador reservoirs can be applied to the potential Site C reservoir, but the results would need to be treated with caution.

3.4.1.3. Manitoba Hydro Mercury Model for Reservoirs

The MHMMR model developed by Tetra Tech for Manitoba Hydro (see Harris and Hutchinson [2009] for a user's guide) has been applied to the Notigi reservoir in northern Manitoba (Harris et al., 2009) and was adapted to Williston Reservoir in northern BC (Tetra Tech Inc., 2002). MHMMR is a dynamic model that is mechanistic and state of the art, in that it includes the latest understanding from scientific studies on the dynamics of mercury in aquatic systems. MHMMR mimics the production, destruction and bioaccumulation of methyl mercury in reservoirs in a realistic way using mass balance calculations of elemental, mercuric ion and methyl mercury over time. Rates of the processes of mercury methylation and demethylation are calculated by the model, as are transfers up the food chain. The environment is treated as a number of compartments, including the water column, sediments and food web with seven trophic levels. Fish uptake and concentrations in fish are calculated based on fish bioenergetic equations calibrated with actual or predicted rates of fish growth. Concentrations of mercury in fish are predicted over the life of the reservoir, not just peak values as for the preceding two models.

Many input parameters are needed to run the MHMMR (**Table 1**). The model treats sediment areas separately, including flooded and unflooded areas. Within the subset of flooded areas, the model requires estimates of the areas of flooded uplands and wetlands separately, including estimates of organic (labile vs. refractory) and inorganic particles. Other inputs required include water temperature, hydraulic retention time, thermal stratification, oxygen concentration, pH, dissolved organic carbon concentration, phosphorous and sulphate concentrations, atmospheric deposition of mercury, concentrations of mercury in flooded and unflooded sediments, and the concentrations of particles in both the epilimnion and hypolimnion of the reservoir. Also input by the user are particle settling velocities, phytoplankton and zooplankton densities, surface light and photosynthetic depths and ice cover. Actual or predicted fish growth rates form the basis of the module that predicts mercury in fish from water temperatures and fish bioenergetics. The model can accommodate up to four fish species and users can chose from ten species available. As noted above, lake whitefish is the only BC species accommodated by the model. Fish diets are specified by the user, including size limits of fish eaten by piscivores. Fishing losses can also be accommodated by the model.

This model is complex, difficult to calibrate and would require weeks of time by the developer to run.

3.4.1.4. Hydro-Quebec/University of Sherbrooke reservoir mercury model

Hydro-Québéc (M. Roger Schetagne) and the University of Sherbrooke (Professor Normand Therrien) have developed two model modules that can be used to predict mercury in fish in hydroelectric reservoirs (Hydro-Québéc 2007; Hydro-Québéc 2008).

The first module (HQEAU) predicts water quality parameters, including mercury in water, and the second module (HQHG) uses the output of the first to predict mercury in fish. Both of these modules are dynamic models that calculate actual fluxes and concentrations of mercury and methyl mercury through various environmental compartments. They are also state of the art and incorporate the latest understanding of mercury cycling in freshwaters. HQHG includes six species of fish, including lake whitefish, and like the other models do not include fish common in BC, such as rainbow trout and bull trout.

Input parameters required include for these model modules include: physical characteristics (e.g., flooded volume, residence time, thermal regime) of the proposed reservoir, thermal characteristics, drawdown, the biomass and type of flooded soils and vegetation to be flooded, precipitation, deforestation prior to flooding and the feeding patterns of fish (**Table 1**). The model can usefully be used to simulate the effects of vegetation clearing prior to flooding by running different simulations with different clearing amounts.

Like the MHMMR, the Hydro-Québéc models are complex, require extensive input parameters and would require weeks of time by the developer in order to adapt and apply this model to a new proposed reservoir development. Although the HQ models appear more user friendly than the MHMMR model, at present they have been written in French only.

3.4.2. Conclusions and Recommendations

Mercury contamination is a significant and relatively high profile issue associated with new hydroelectric reservoirs in Canada. The use of established computer models to predict concentrations of mercury in fish would lend credibility to estimates because modeled predictions are objective and quantitative and at a minimum will 'ballpark' maximum fish mercury concentrations. Two simple models based on linear regression equations were reviewed and can be relatively easily applied. The Harris and Hutchinson (2008) model takes flushing times into account and is therefore more realistic and appropriate for the potential Site C reservoir than the Johnson et al. (1991) model. Two dynamic and complex models are also available. Both the Hydro-Québec and Manitoba Hydro models require extensive data collection for input parameters to calibrate and run these models and require the expertise of the developer. Regardless of which model is chosen, all modeling efforts would be limited by the near absence of data available concerning mercury in fish in previous developments in the area of Site C.

We recommend that a staged approach to modeling be carried out. As a first step, the simple calculational model developed by Harris and Hutchinson (2008) should be used to provide first order approximations of predicted mercury concentrations of candidate benthivorous (e.g., lake whitefish) and carnivorous fish species (e.g., walleye as a

surrogate for bull trout) in the proposed reservoir. This could be done easily and relatively quickly.

Given the likely high level of environmental scrutiny targeted at this proposed development, BCH should consider application of the more advanced modeling techniques. Both advanced models reviewed herein support the consideration of many factors, which ultimately will lead to a better understanding of key drivers affecting mercury dynamics within the proposed reservoir. This also allows for a more quantitative approach to exploring the effectiveness (from a cost-benefit analysis perspective) of various management options for limiting mercury accumulation. Based on our review of baseline water chemistry, physical and biological data (Golder, 2009a; 2009b; Mainstream Aquatics, 2009), and our understanding of the physical/hydraulic data in the possession of BC Hydro (e.g., flood volumes, drawdown, flow rate, residence time etc.), the majority of baseline data already exists to run either model. However, given that the Manitoba Hydro model has already been adapted to Williston Reservoir (TetraTech, 2002) there has already been an investment in this model. Based on information in **Table 1** many of the input parameters already exist or could be inferred or estimated. Critical input parameters that require field collection include the following and can be accomplished in a single field season:

- Total and methyl mercury (total and dissolved phase) in mainstream and tributary streams
- Phytoplankton and zooplankton biomass (mg/m^3)
- Zooplankton mercury concentration
- Fish diet
- Fish growth and bioenergetics of key species (i.e., benthic herbivore, benthic omnivore, planktivore, piscivores)
- Stable isotope analysis of zooplankton, benthos and candidate fish species within representative trophic levels

Details of the scope and magnitude of data collection requirements for each of these parameters are described in Task 4 below.

In summary, we recommend that the Harris and Hutchinson (2008) linear model be executed as a preliminary exercise. The 2010 field season should include, at a minimum, collection of empirical data for the above parameters in the event that a complex, dynamic model is desired or required so that all key input parameters are available.

4. BASELINE MERCURY SAMPLING

There are well established protocols for sampling of mercury and methyl mercury in various environmental media. When sampling for mercury and especially methyl mercury in water where concentrations are always extremely low, the risk of inadvertent contamination of samples is very high. Strict sampling protocols and quality assurance/quality control (QA/QC) procedures must be adhered to. Although the risk of contamination is much lower when sampling soil, sediment or tissue (e.g., fish) because mercury concentrations are orders of magnitude higher than in water, QA/QC protocols must still be followed.

Detailed methodologies and QA/QC procedures for the collection of total and methyl mercury in water, sediment and soil are provided in Appendix 1. General methodologies for the collection of biota tissues (vegetation, plankton and fish) are also described in less detail because the risk of contamination is much lower. These protocols should be followed when collecting environmental media for the analysis of mercury and for total metals.

Based on our review of existing environmental data from the Peace River as collected by Golder (2009a; 2009b) and Mainstream Aquatics (2009) a considerable amount of good information has been collected to adequately describe baseline aquatic conditions. However, there are a few key data gaps in this baseline information to adequately describe baseline conditions of mercury in environmental media (e.g., mercury in water) as well as ancillary parameters required by the complex multi-dimensional mercury models.

Table 1 lists the input parameters required to run a complex model. This document reviews existing data acquired by BC Hydro and its amenability to satisfying input parameters of a complex model respectively. Based on data gaps identified in **Table 1** and requirements to adequately quantify and address mercury in the potential Site C reservoir, we recommend that the following data be collected under the categories of water, sediment, soil, vegetation and aquatic biota tissue.

4.1. Sampling Strategy for Water, Soil and Sediment

Water Sampling Strategy – Based on our review of existing data, some additional water sampling is required to satisfy modeling data gaps and support assessment of the potential for the Site C reservoir. The complex reservoir models require input of particulate-bound and dissolved water concentrations of mercury (inorganic) and methyl mercury. Prior water sampling of the Peace River did not include methyl mercury and did not employ an analytical method with a relevant detection limit for total mercury. To

correct this deficiency selected locations within the project area should be re-sampled using "trace metal clean" methods (e.g., USEPA Method 1669 or equivalent) and low level mercury analytical methods (e.g., USEPA Methods 1631, 1630 or equivalents). Local laboratories now have the capability to conduct these analyses.

At a minimum, these four locations to be sampled included (note: other tributaries have not been included due to very low discharge; any other tributary that may have high mercury concentrations [e.g., due to historic gold mining] should also be included):

The four locations to be sampled included:

- Peace River below Peace River Canyon Dam
- Mouth of Moberly River
- Mouth of Halfway River
- Peace River at Site C.

These locations should be sampled in spring at or near freshet (~May) and again in late summer (August). In addition to unfiltered and filtered samples for mercury and methyl mercury analysis, samples should also be collected for analysis of TSS, DOC, pH and anions. A detailed procedure for water sampling and analysis for low level mercury is provided in **Appendix 1**.

Sediment Sampling Strategy – Previous sampling of sediment within the Site C project area was very limited and inadequate because of unclear origin and large grain size. The data collected by Golder (2009a) were insufficient to accurately define metals and mercury concentrations in sediment within the Peace River.

Reservoir modeling will require data for fine grained (silt + clay fraction) sediments which typically exhibit the highest mercury concentrations and harbor the microorganisms and chemical conditions responsible for mercury methylation. Fine grained sediments in large river systems tend to accumulate in pools, behind large rock outcrops or woody debris and in slower moving side channels and sampling should target these areas. Sampling fine grained sediments in such deposits is facilitated by the use of a readily available bilge pump and field fractionation technique (see Method SE-1 in appendix), or possibly using standard Ponar grab techniques from a boat.

On the order of 10 sediment sampling locations within the Site C project reach should be identified for fine grained sediment sampling. The locations need not be evenly spaced over this reach but should include the depositional habitats mentioned above. In addition to metals and total mercury analysis, each sediment sample should also be analyzed for TOC, moisture and particle size distribution (%sand, %silt, and %clay). Further information on sediment sampling is provided in **Appendix 1**. Also see Veiga and Baker (2004) for further details on sediment sampling methods.

Soil Sampling Strategy – The physical and chemical quality of soils that will be flooded are important determinants of the extent and magnitude of any post-flooding increase in mercury in fish. The potential Site C reservoir spans 83 km along the Peace River length and would flood up to 5,300 hectares of riparian and upland soils and vegetation. TEM has already been conducted and based on our review of the information there appears to be sufficient detail in the terrain and soil classifications from which to plan a more detailed study. Therefore, to document the physical and chemical characteristics of the flooded soils, we recommend a stratified random sampling approach to sampling. This will maximize collection of the most relevant information and minimize the cost of sampling and analysis.

Under a stratified random sampling design sample locations are selected randomly within each, or a subset of each, soil type based on TEM results. The expectation is that all samples from within a soil type will have similar properties and that every example of each type does not need to be sampled to obtain an adequate description of the type. For Site C this sampling approach might mean that 'N' examples (locations) of soil type A would be selected at random for sampling and analysis. Sample size will be pro-rated based on GIS quantification (e.g., based on area) of dominant soil types from the TEM information. Soil types can be defined by predominant forest cover (deciduous vs coniferous), terrain (slope, aspect), underlying geology (parent materials), or anthropogenic land use (agriculture, mining), among other classifications. Stratification of sampling effort will be made to target soil and vegetation types that are the largest known contributors to mercury methylation including marsh, bog and swamp. Exposed mineral soils, gravel, cutbanks and other erosional areas need not be sampled.

Design of the sampling program will therefore require quantifying and ranking major soil types with respect to importance to mercury release and cycling. For example, all "wetland type" soils to be flooded would rank high with respect to potential mercury release, while soil that covers a significant fraction of the flooded area would also rank high even if it has a low potential to contribute to mercury release. Once this ranking is available the number of samples to be collected within each soil type can be determined. We estimate that approximately 100 soil samples be collected to adequately describe the mercury and metals regime of the flooded area. However, it may not necessary to analyse all samples. We further recommend that a subset of samples be analysed and a statistical screening be conducted to determine variances within soil types. The remainder of the samples can be archived, pending the outcome of the preliminary analyses.

In deciding on the number of samples within a soil type a margin of error (e.g., 10%) and confidence interval (e.g., 95%) are chosen to estimate sample coefficient of variation (CV) which is then used to calculate the required number of samples. This exercise often suggests the need for prohibitively large sample sizes so compromises will likely be necessary (see esp., Belanger and Van Rees, 2008). CVs for some commonly measured soil constituent like organic matter (CV=15 to 35%) are reasonably well known

and can be used with sampling to determine sample sizes. Using a CV of 20% yields a sample size (N) of 17 if a 10% margin of error with 95% confidence is desired. Because mercury is strongly associated with organic matter in soils it is likely that Site C soils will have CVs for mercury content that are very similar to those for organic matter content and thus the preferred sample size for a given soil type will be <20.

Soil samples should be analyzed for metals, including total mercury, pH, moisture content, and total and labile organic carbon. Analytical methods for all of these except labile organic carbon are straight forward and within the capability of routine laboratories. Labile organic matter is not a routine analysis, and can be measured by a variety of methods (e.g., McLauchlin and Hobbie, 2004). However, a strict measure of labile carbon is not required as input for all the reservoir mercury models.

Humic (organic) and mineral (inorganic) soil layers should be collected and analyzed separately. Mercury sequestered by vegetation, especially trees, accumulates almost exclusively within the humic layer, above the inorganic layer. These two layers are not always present or distinct but tend to be always present under coniferous forest cover and under all undisturbed forest covers where low soil temperatures prevail even in the summer (boreal, subarctic). An excellent review of soil sampling and analysis methods, including forest soils, is provided by Carter and Gregorich (2008).

4.2. Biota Sampling Strategy

Representative vegetation types, zooplankton, benthos and fish should be collected for metals and mercury content in tissues as well as stable isotopes from a subsample of aquatic biota. Approximate sample sizes and sampling procedures for each biotic component is as follows.

4.2.1. Vegetation

Given the lack of industrial sources of atmospheric mercury in the vicinity of Site C, we do not expect to find elevated concentrations of mercury in plant tissues along the 83 km reach of river. However, given the importance of plant material as a source of labile (i.e., readily available) carbon and its role in mercury methylation, additional sampling should be conducted.

Representative vegetation types of common, abundant species should be collected from dominant habitat types within areas proposed to be inundated. Effort and intensity should be stratified to accurately represent the dominant vegetation types with a focus on those habitats with soils that have abundant carbon stores such as peatlands, bogs, fens, marshes and well developed humic soils beneath deciduous forests. Based on results of the TEM procedure and from Keystone Wildlife Research (2007), the dominant vegetation types appear to be various assemblages of 'creamy peavine' seral association, although it is difficult to tell because there is no aerial quantification of

vegetation types. Dominant species appear to be black and white spruce, trembling aspen, willow, dogwood, and prickly rose. Habitat types that are classified as Tamarack-Sedge, Sedge-Wetland, Willow-Sedge Wetland and Willow-Horsetail-Sedge riparian wetland (Keystone Wildlife Research, 2007) should be targeted as these habitat types appear to have well developed organic and peat soils that will contain the greatest store of mercury.

The spatial extent of sampling need not be extensive. Two sampling areas should be chosen within the Peace River corridor that is more or less representative of vegetation types along the entire reach. Because mercury and metals concentrations in vegetation are typically quite low, it is not necessary to conduct a spatially broad survey. Single composite samples of leaves or needles from the dominant individual species will be collected from each area. These areas can be harmonized with areas from which soil samples are collected (see protocol above), so that there are synoptic data.

4.2.2. Zooplankton

Zooplankton should be collected from a minimum of two locations in the Peace River and two locations in Dinosaur Reservoir should be collected to determine total mercury concentration and carbon and nitrogen stable isotopes.

Total mercury is required to establish a baseline for zooplankton from the Peace River and to contrast this mercury in with plankton from Dinosaur Reservoir. Mercury in zooplankton is a key component for transference up the food chain and is an output parameter of the complex predictive models.

A subsample of the zooplankton should be analysed for stable isotopes to help establish baseline conditions for food chain analysis. While the relative change between trophic levels (as seen by changes in the ratios of nitrogen isotopes) is fairly constant among lakes, the absolute values of the ratios can vary significantly. Characterizing ratio's of nitrogen isotopes in primary consumers (e.g., zooplankton and/or benthic invertebrates) serves to "calibrate" the process to allow estimation of absolute trophic status, which facilitates comparisons among systems. Focusing on both the river and the existing reservoir provides a unique opportunity to understand how ecological changes associated with reservoir changes might impact key fish species. Given that much of the zooplankton of the Peace River may be transported from the reservoir, it is possible that the isotope 'signature' of both groups is similar.

4.2.3. Benthic Invertebrates

Benthic invertebrates are a key food chain component of the aquatic food web and an important food group for many fish species including juveniles of piscivorous fish. Similar to zooplankton, to adequately characterize mercury concentrations and stable isotopes, benthos should be collected from at least three locations in the Peace River and three locations in Dinosaur Reservoir.

There are many means by which benthos can be collected and it is not within the scope of this work to provide prescriptive means by which to do so. In Dinosaur Reservoir sediment grabs (e.g., Ponar) could be used to acquire sediment from which benthic invertebrates can be extracted. In the Peace River, artificial substrate traps and / or kick style samplers could be used to gather representative groups. Artificial substrate traps can be placed in the river and allowed to be colonized by invertebrates for later collection (e.g., after 6 weeks). Alternatively, active collection of aquatic life history stages using kick traps can be attempted in shallow riffle sections, or emergent insects collected using 'malaise' or light traps. Malaise traps are passive nets that can be set up adjacent to the shoreline of the river to collect insects that emerge and become trapped.

4.2.4. Fish

Tissue samples from four fish species representing at least three trophic levels should be collected for analysis of total metals, mercury and stable isotopes from both Dinosaur Reservoir and the Peace River in the vicinity of Site C. Candidates for collection include a forage species such as redside shiner, a benthic herbivore such as suckers (e.g., *Catostomus* sp.), a benthic planktivore such as lake whitefish (*Coregonus clupeaformis*) and a top level predator that is also consumed by humans such as bull trout (*Salvelinus confluentus*) or lake trout (*S. namaycush*). General sampling and collection procedures are as follows:

- Non-destructive tissue collection procedures (Baker et al., 2004) should be followed for the majority of fish. A subset of samples (~10 fish / species) should be destructively sampled for analysis of total metals as well as mercury and for stable isotopes (although stable isotopes could likely be handled by biopsy too).

- Acquisition of tissue samples should follow the standard protocols for collection and analysis of data as described in Baker (1998). That is, fish are to be collected across a wide size range to derive mercury – size relationships and compare mercury concentrations on a size-standardized basis.

- Tissue samples, especially biopsy samples must be submitted to a laboratory that is familiar to dealing with such small tissue quantities. Ensure that proper QA/QC procedures are followed and reported by the laboratory.

- Depending on concern by local First Nations regarding fish eating birds such as eagles or loons, mercury data from feathers and/or blood can be acquired to establish a baseline data set.

- Again, depending on local concerns, tissue samples from fish eating wildlife such as mink can be acquired opportunistically from local trappers. Kidney, liver and muscle tissue should be analysed for total metals and mercury.

Veiga and Baker (2002) and Baker (2002) describe the established protocols for sampling of fish tissues using non-destructive techniques (Baker et al., 2004) and

statistical procedures for presenting mercury data from size-adjusted fish to prevent bias by using different size fish.

4.3. Strategy Implementation

This report provides a detailed strategy and supporting rationale for addressing the issue of mercury accumulation in aquatic biota related to development of the potential Site C Reservoir. While there has been a strong focus on the use of scientific literature and models as a tool to explore the issue quantitatively, the strategy also includes a more holistic approach to improving our understanding of the factors likely to affect mercury dynamics at Site C. It is important that Hydro recognize how contentious, emotional and politically charged this issue can be. However, we believe that careful implementation of this integrated strategy will provide BC Hydro with essential information to successfully manage this issue, provided that they proceed in a staged, careful manner.

This strategy is intended to provide a foundation from which to build a cohesive body of information to support informed management decisions and communications. This will require more than a single season of field sampling to acquire or fill in data gaps to address these gaps and proceed with modeling, should BC Hydro choose to do so.

Prior to moving to the implementation stage, this strategy will need to be reviewed against BC Hydro's management options and objectives and revised as necessary. The strategy can then be translated into a more formal Sampling and Analysis Plan (SAP) that will serve as a detailed guide to all aspects of the data collection and analysis process. For example, careful examination of existing TEM information, and soil and vegetation types on an aerial basis should be undertaken in order to determine the optimal soil and vegetation sampling strategy. Consideration should be given to analyzing a subset of samples while archiving additional samples in the event that more detailed information is required or that soil chemistry is more variable than anticipated. The SAP should also include details on data quality objectives, QA/QC, etc. A strong SAP avoids the pitfalls of a "piecemeal" approach.

Finally, the strategy to address mercury at Site C needs to be flexible to adapt to our changing understanding of the issue and to recognize the perspective and concerns of First Nations, local residents and stakeholders. Open and forthright consultation / communication with stakeholders needs to be integrated into the process to ensure that trust and respect is built between all parties and that the issue is approached from a technical and not an emotional aspect.

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Table 1: Summary of input parameters to run the simple linear and complex multi-dimensional mercury models and data gaps.

Parameters	Johnson et al 1991 - Manitoba	Harris and Hutchinson - 2008 Lower Churchill R	Man Hydro MMR	Hydro Quebec	Site C Empirical Data Available?
Simple Linear Models			**Complex Models**		
PHYSICAL PARAMETERS					
Flooding Area - upland	-	-	M	M	Y
Flooding Area - wetland	-	-	M	M	Y
Pre-flood volume / area	M	M	M	M	Y
Post-flood (reservoir) volume	M	M	M	M	Y
Residence time	-	M	M	M	Y
Mean annual discharge	-	M	M	M	Y
Drawdown elevation	-	-	M	M	Y
Mean and total depth	-	-	M	M	Y
Particle settling velocity	-	-	E	-	E
Ice cover	-	-	E	-	Y
Soil biomass - upland	-	-	M	M	E
Soil biomass - wetland	-	-	M	M	E
Precipitation	-	-	M, E	-	E
Tribuary inputs and water quality	-	-	M	M	Y
CHEMICAL PARAMETERS					
Temperature (vertical, seasonal)	-	-	M	M	Y
Oxygen	-	-	M	M	Y
pH	-	-	M	M	Y
Surface light/photosynthesis depth	-	-	E	-	Y
DOC	-	-	M	M	Y
Precipitation	-	-	E	M	E
TSS (hypo, epilimnion)			M	M	E
Phosphorus	-	-	M	M	Y
Anions (Sulphate)	-	-	M	M	Y
Total and dissolved THg + MeHg - Hypo	-	-	M	M	N
Total and dissolved THg + MeHg - Epilim			M	M	N
Atmpospheric Hg deposition	-	-	E	-	E
Sediment/Soil Labile carbon	-	-	M	-	N
Sediment/Soil Refractory carbon	-	-	M	-	N
Soil pH / TOC	-	-	M	M	Y
BIOLOGICAL					
Phytoplankton density	-	-	M	-	N
Zooplankton density	-	-	M	-	N
Zooplankton [Hg]	-	-	E	E	N
Vegetation type / biomass	-	-	M, E	M,E	Y, E
Fish species composition	-	-	M, E	M, E	Y
Fish diet	-	-	M, E	M, E	E
Growth/bioenergetics of fish	-	-	M, E	M, E	N, E
Fishing loss (harvesting)	-	-	E	-	N, E
Baseline Fish [Hg]	E		M	M	Y
DRAWBACKS	No time series prediction	No time series prediction	LKTR, BLTR not in model	LKTR, BLTR not in model	
	No flushing calc	Max Hg values only	complex, time consuming	complex, time consuming	
			Most of these data not	Most of these data not	
	Max Hg values only		available for PR	available for PR	
				French transl only	

M - Measured parameters Y - Yes ░░░░░░░ = significant data gap
E - Estimated parameters N - No
                          - not required by model

Appendix 1

Standard Operating Procedures (SOPs) for Mercury
Sampling in Environmental Media

A-1 SAMPLING AMBIENT SURFACE WATER FOR DETERMINATION OF TOTAL MERCURY AND METHYL MERCURY USING A DIAPHRAGM PUMP

1.0 Scope and Application

This method is for the collection and field filtration of ambient surface and subsurface water samples for subsequent determination of total mercury (THg), total dissolved mercury (DHg), total methyl mercury (MHg) and total dissolved methyl mercury (DMHg) at ultra-trace concentrations (THg and DHg @ $\geq$0.2 ng/L, MHg and DMHg @ $\geq$ 0.02 ng/L) using EPA Methods 1631 (THg and DHg) and EPA Method 1630 (MHg and DMHg).

- The method is applicable to lakes, streams, estuaries and the ocean.

- The method is not intended for sampling effluents at industrial facilities nor for sampling very small streams and seepages where the flow rate is likely to be less that the nominal flow rate of the diaphragm pump (3 gpm).

- The method is based on general guidance and principles outlined in EPA Method 1669 "Sampling Ambient Water for Determination of Metals at EPA Water Quality Criteria Levels", July 1996.

- The method is a "performance validated" alternative to Method 1669, as allowed and encouraged by EPA Method 1669, that has been demonstrated to preclude contamination of samples and blanks as required by the original method.

2.0 Summary of Method

- Upon arrival at the sampling site, one member of the two-person sampling team is designated as "dirty hands"; the second member is designated as "clean hands". All operations involving contact with the sample bottle and the transfer of the sample from the sample pumping system to the sample bottle are handled by the individual designated as "clean hands". "Dirty hands" is responsible for preparation of the sample pumping system, operation of the pump and for all other activities that do not involve direct contact with the sample or sample container.

- "Dirty hands" deploys the weighted sample line overboard and within a water mass not affected by the presence of the boat or samplers.

- "Dirty hands" activates the pump and times pump running time prior to indicating to "clean hands" that sampling for unfiltered analytes can begin.

- "Clean hands" opens sample bottle and rinses it twice with sample water prior to filling and recapping. If additional unfiltered samples (e.g., for TSS) are to be taken the same procedure is followed for additional bottles.

- "Dirty hands" pinches the sample line on the suction side and installs a capsule filter on the discharge line and then flushes several liters of sample water through the filter at a flow rate held low enough (by pinching the suction line) to avoid excessive back pressure in the filter.

- "Clean hands" opens sample bottle and rinses it twice with sample water prior to filling and recapping. If additional filtered samples (e.g., for other metals, anions) are to be taken the same procedure is followed for additional bottles.

- "Dirty hands" secures the pumping system by returning the weighted sample line and pump to a dedicated plastic bag or clean cooler.

- Water samples are re-bagged and placed on ice in a cooler.

- In general water samples are not field-preserved, other than by chilling and maintaining in the dark, due to the increased risk of contamination. However, when there is uncertainty about the elapsed time for arrival at an analytical laboratory, and methyl mercury is to be requested, samples should be field-preserved with hydrochloric acid as specified in EPA Method 1630.

3.0 Definitions

- Ambient water – Waters in the natural environment (e.g., rivers, lakes, streams and other receiving waters), as opposed to effluent discharges.

- Apparatus – The sample container and other containers, filters, tubing, pipettes and other materials and devices used for sample collection or sample preparation, and that will contact samples or blanks.

- Equipment Blank (EQBLK) – An aliquot of reagent water, or other water of known low mercury content, that is subjected in the field to all aspects of sample collection and analysis, including contact with all sampling devices and apparatus. For this method equipment blanks will include water samples that have been pumped through the pump and sample line only (PMPBLK) if no samples are filtered and samples that have been pumped through the pump, sample line and filter (FILTBLK).

- Field Blank (FLDBLK) – An aliquot of reagent water, or other water of known low mercury content, that is placed in a sample container in the field and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, shipping and all analytical procedures.

- Field Duplicate (DUP) – Two identical aliquots of a sample collected in separate bottles at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field

duplicates provide a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

- Matrix Spike (MS) and Matrix Spike Duplicate (MSD) – Aliquots of an environmental sample to which known quantities of an analyte are added in the laboratory. The MS and MSD are analyzed exactly like a sample. The purpose is to quantify the bias and precision caused by the sample matrix. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for this background concentration. For the analyses of mercury and methyl mercury MS and MSD are prepared in the laboratory from a single sample bottle, i.e., separate samples do not have to be collected for this purpose, but sufficient volume (250 mL) must be available to support three determinations (unspiked, MS and MSD).

- May – This action, activity or procedural step is optional.

- May Not – This action, activity, or procedural step is prohibited.

- MDL – Minimum Detectable Level, or the lowest concentration at which the entire analytical system gives a recognizable signal and acceptable calibration point.

- Must – This action, activity, or procedural step is required.

- Reagent Water – Water demonstrated to be very low (e.g., at or < the MDL) in mercury and methyl mercury and free of potentially interfering substances. Reagent water need not be distilled or deionized water but its purity must be verified by analysis. Bottled drinking water is commonly acceptable for reagent water but should always be analyzed prior to use to verify.

4.0 Contamination and Interferences

- Avoidance of sample and apparatus contamination is of paramount importance for this method. The most important factors in avoiding/reducing sample contamination are 1) an awareness of potential sources of contamination and 2) strict attention to work being performed.

- The continuous pumping apparatus (pump, tubing, hydro weight) should only be removed from its clean container (cooler or plastic bag) just prior to sampling. When not being used the system should be stored in a clean plastic bag or a dedicated cooler.

- Sampling personnel must wear clean, non-powdered gloves during all operations involving handling of the apparatus and sample bottles. Gloves should be changed if there is any suspicion that the gloves have contacted surfaces that could be contaminated.

- The specific items comprising the apparatus have been demonstrated to effectively avoid contamination when deployed and operated as described in this method. Do not substitute items or change procedures without first

demonstrating that the substitution or procedural change maintains sample integrity.

- Adhere strictly to the rules provided subsequently with regard to flushing rates and times to avoid contamination carryover. Whenever possible conduct sampling sequentially from sites of lower to higher known or expected contamination.

- Do not use the apparatus to sample effluents known or suspected to contain elevated mercury concentrations. This method is intended only for ambient samples of lakes, rivers, estuaries and the ocean.

- In general there are few analytical interferences that may be encountered in ambient water sampling. However, be aware when sampling anoxic waters from lake hypolimnion that excessive sulphide concentration in samples may require analytical adjustments (e.g., addition of a larger amount of bromine monochloride) to accommodate the interference and record any field detection of hydrogen sulfide on the analytical request form.

5.0 Safety

- Toxic or otherwise harmful concentrations of mercury and methyl mercury are unlikely to be encountered while sampling ambient surface water. However, sampling crews should be trained in the hazards of mercury and how to minimize risks of exposure.

- Operating in or around waterbodies carries the inherent risk of drowning. USCG-approved personal flotation devices must be worn when operating from a boat, when sampling in more than a few feet of water, or when sampling in swift currents.

- Collecting samples in cold weather, especially around cold waterbodies, carries the risk of hypothermia, and collecting samples in extremely hot and humid weather carries the risk of dehydration and heat stroke. Sampling team members should wear adequate clothing for protection in cold weather and should carry an adequate supply of water or other liquids for protection against dehydration in hot weather.

- Sampling team members must cover exposed skin and/or use sunscreen for protection against sunburn and melanoma.

- Sampling teams must develop and employ an emergency response plan when working on all waterbodies including the use of an onshore monitor that is accountable for the whereabouts of the team. The monitor can request aid if team fails to report in at end of workday and can provide assistance to rescuers or team under any scenario where an emergency situation exists.

6.0 Apparatus and Materials

- Diaphragm Pump – Shurflo Model 2088-433-344, 12 volt DC, 3.3 gpm

- Tubing – Cole Parmer, C-flex, 3/8" ID x 5/8"OD, Cat# 06424-79

- Hydro Weight – Use coated iron (not Pb) downrigger weight (5, 10, or 15 lbs)

- Filter – Capsule type, high capacity, with barb fitting (e.g., Pall AquaPrep 600)

- Battery or Power Pack – 12 volt deep cycle battery or portable power pack (e.g., Xantrex Xpower 300)

- Sample bottles – 250 mL borosilicate glass, IChem Series 300.

- Gloves – PVC, Powder-free, clean-room quality

7.0 Reagents and Standards

- Hydrochloric acid – high purity, pre-tested for mercury content, used to field preserve water samples.

- Reagent water – water in which mercury and potentially inferring substances are not detected at the MDL of the analytical method used for analysis of samples OR are detected at concentration no greater than three times the MDL (e.g., typical MDL for THg by Method 1631 is 0.20 ng/L, thus the allowable THg in reagent water should be $\leq$ 0.6 ng/L). Used to prepare field blanks and equipment blanks and to rinse apparatus.

8.0 Sample Collection, Filtration and Handling

- Select surface water sampling locations in accordance with study objectives.

- Sampling sites should exhibit a high degree of cross-sectional homogeneity. Since mixing is principally governed by turbulence and water velocity, the selection of a site immediately downstream of a riffle area will ensure good vertical mixing. Horizontal mixing occurs in constrictions in the channel.

- Look for and avoid flow eddies that often occur near banks and in-stream obstructions.

- Avoid sample locations very near heavily traveled roads, bridges, and overhead utilities. If these features cannot be avoid then sample upstream and sample during periods when these features are least likely to introduce contamination into the river.

- Sampling activity should be planned to collect samples known or suspected to contain the lowest concentrations of mercury first, finishing with samples known or suspected to contain the highest concentrations.

- Upon arrival at the sampling site, one member of the two-person sampling team is designated as "dirty hands"; the second member is designated as "clean hands". All operations involving contact with the sample bottle and the transfer of the sample from the sample pumping system to the sample bottle are handled by the individual designated as "clean hands". "Dirty hands" is responsible for preparation of the sample pumping system, operation of the pump and for all other activities that do not involve direct contact with the sample or sample container.

- "Dirty hands" deploys the weighted sample line overboard and within a water mass not affected by the presence of the boat or samplers.

- "Dirty hands" activates the pump and times pump running time prior to indicating to "clean hands" that sampling for unfiltered analytes can begin.

- "Clean hands" opens sample bottle and rinses it twice with sample water prior to filling and recapping. If additional unfiltered samples (e.g., for TSS) are to be taken the same procedure is followed for additional bottles.

- "Dirty hands" pinches the sample line on the suction side and installs a capsule filter on the discharge line and then flushes several liters of sample water through the filter at a flow rate held low enough (by pinching the suction line) to avoid excessive back pressure in the filter.

- "Clean hands" opens sample bottle and rinses it twice with sample water prior to filling and recapping. If additional filtered samples (e.g., for other metals, anions) are to be taken the same procedure is followed for additional bottles.

- "Dirty hands" secures the pumping system by returning the weighted sample line and pump to a dedicated plastic bag or clean cooler.

- Water samples are re-bagged and placed on ice in a cooler.

- In general water samples are not field-preserved, other than by chilling and maintaining in the dark, due to the increased risk of contamination. However, when there is uncertainty about the elapsed time for arrival at an analytical laboratory, and methyl mercury is to be requested, samples should be field-preserved with hydrochloric acid as specified in EPA Method 1630. Parker and Bloom (2005) provide detailed and current supporting scientific background for these recommendations regarding preservation and storage of water samples for mercury analysis.

9.0 Quality Assurance/Quality Control

- Strict adherence to the procedures described here under Contamination Control will assure collection of uncompromised water samples.

- However, it is also necessary to collect Field Blank and Equipment Blank samples each day that sampling occurs, or whenever the pump or tubing is changed, to demonstrate that contamination has been controlled.

- At least one Field Duplicate must be collected each sampling day or after every 20 samples.

- Additional Field Duplicates may be collected if conditions suggest the need for more, or more are specified in the Sampling and Analysis Plan.

- As noted elsewhere separate samples for Matrix Spikes (MS) and Matrix Spike Duplicates (MSD) do not have to be collected unless the laboratory requests as these analyses can be run by most laboratories using an actual sample.

10.0   Recleaning/Reuse of Apparatus Between Samples

- C-flex tubing – When employed as described in this method this product has been demonstrated repeatedly to be acceptably clean from the manufacturer's packaging without laboratory pre-cleaning and may be used within the same waterbody without risk of cross-contamination to collect samples from multiple locations. As a precaution sampling should always proceed from the cleanest locations to the most contaminated.

- Diaphragm Pump – Reagent water should be flushed through the pump at the end of each sampling day and the pump drained of any water that is not expelled by operating the pump. No other cleaning is needed. Store the pump in a clean polyethylene bag,

- Filter – The high capacity capsule filter may be used to filter more than one sample from the same waterbody provided the filter has not clogged and is first flushed with several liters of water from each location prior to collecting the sample for analysis. If filters are reused in this manner the equipment blank (EQBLK) must be prepared using a filter that has been used at least once and preferably at several locations to collect samples prior to preparation of the blank.

- The use of any chemicals, especially acids, to clean pump, tubing, or filters in the field is generally discouraged because such treatment may change the properties of the materials of which these items are constructed and inefficient flushing of such chemicals may cause sample contamination. If any suspicion exists that any of these items may have been contaminated with mercury, or with substances that might interfere with unbiased sampling and analysis for mercury, the item(s) should be discarded or transferred to a qualified laboratory for cleaning and testing. For example, if hydrocarbon-contaminated water is encountered and contacts the apparatus at any time the sampling components, with the possible exception of the pump, should be discarded. Similarly, if an industrial outfall to be sampled using this method is known or suspected to contain elevated mercury levels do not attempt to clean the apparatus after use. Discard all but the pump and do not use the pump again until it is confirmed to be clean with an equipment blank.

11.0   References

EPA. 1996. *Method 1669-Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*. July 1996. U.S. Environmental Protection Agency, Office of Water, Engineering and Analysis Davison (4303), 401 M Street SW, Washington, DC 204460

Parker, J.L. and N.S. Bloom. 2005. Preservation and storage techniques for low-level aqueous mercury speciation. *Science of the Total Environment*, **337**:253-263.

Photograph 1: Use of clean cooler to protect sample inlet line and hydro weight from contamination when sampling from a boat. Round yellow object on end of C-flex tubing is plastic screen to prevent end of inlet line from touching sediment or sucking in debris.

Photograph 2: Use of the continuous pumping system to collect water samples from a shallow stream. The inlet end of the tubing (out of picture) is screened and weighted. Capsule filter is shown installed on the discharge line from the pump.

A2   SAMPLING SIZE-CLASSIFIED SEDIMENTS USING BECKSON PUMP (GUZZLER METHOD)

The following methodology is one of several approaches to collecting fine sediments for mercury and metals analysis from the bottom of rivers, streams or lakes. Other methods for collection of sediment include grab samples such as a Ponar or Ekman.

1.0 Scope and Application

- This method is for the collection river bed sediment samples for subsequent determination of mercury, methyl mercury, and metals.

- The method is applicable to small rivers and streams that can be waded or that have maximum water depths less than about eight feet. This method is generally used in high gradient streams where sediment rarely is deposited more than a few mm in thickness, where scoops would be ineffective for collection. Although it is primarily intended for streams less than 4' deep, with equipment modification it can be used to at least 8', depending on strength of the current in the sample area.

- The method is based on general guidance and principles outlined in EPA's "Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual" (USEPA 2001).

2.0 Summary of Method

- A one square meter frame is placed on the sediment bed to define the sampling area.

- A hand-operated bilge pump is used to "vacuum" and transfer fine-grained bed sediments into a bucket.

- The contents of the bucket are mixed well and allowed to sit undisturbed long enough to permit sand-sized and large material to settle out.

- The supernatant water in the bucket is decanted into a second bucket and allowed to sit undisturbed long enough to settle out most of the silt- and clay-sized material that is recovered by decanting and discarding the supernatant.

- The silt-clay fraction is poured into a large mouth jar, mixed thoroughly and dispensed into smaller jars for specific laboratory analyses.

- Quantities (volume-weight) of sediment recovered in each step are estimated and recorded.

3.0 Definitions

3.1 Sediment – Submerged deposits consisting of mineral and organic matter.

- Apparatus – Devices used for sample collection or sample preparation, and that will contact samples.

- Equipment Blank (EQBLK) – An aliquot of reagent water, or other water of known low analyte content, that is subjected in the field to all aspects of sample collection and analysis, including contact with all sampling devices and apparatus. For this method equipment blanks consist of rinsate from pumps and buckets.

- Field Blank (FLDBLK) – An aliquot of reagent water, or other water of known low mercury content, that is placed in a sample container in the field and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, shipping and all analytical procedures.

- Field Duplicate (DUP) – Two identical aliquots of a sample collected in separate bottles at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates provide a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

- Matrix Spike (MS) and Matrix Spike Duplicate (MSD) – Aliquots of an environmental sample to which known quantities of an analyte are added in the laboratory. The MS and MSD are analyzed exactly like a sample. The purpose is to quantify the bias and precision caused by the sample matrix. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for this background concentration.

- May – This action, activity or procedural step is optional.

- May Not _ This action, activity, or procedural step is prohibited.

- MDL – Minimum Detectable Level, or the lowest concentration at which the entire analytical system gives a recognizable signal and acceptable calibration point.

- Must – This action, activity, or procedural step is required.

- Reagent Water – Water demonstrated to be very low (e.g., at or < the MDL) in metals (and other water quality constituents) and free of potentially interfering substances. Reagent water is usually distilled or de-ionized water the purity of which must be verified by analysis.

4.0 Contamination and Interferences

- Avoidance of sample and apparatus contamination is of paramount importance for this method. The most important factors in avoiding/reducing sample

contamination are 1) an awareness of potential sources of contamination and 2) strict attention to work being performed.

- Sampling personnel must wear clean, non-powdered gloves during all operations involving handling of the apparatus and sample bottles. Gloves should be changed if there is any suspicion that the gloves have contacted surfaces that could be contaminated.

- The specific items comprising the apparatus have been demonstrated to effectively avoid contamination when deployed and operated as described in this method. Do not substitute items or change procedures without first demonstrating that the substitution or procedural change maintains sample integrity.

- In general there are few analytical interferences that may be encountered in ambient water sampling. However, samplers should record any odors, sheens, colors, or other unusual sample characteristics on the analytical request form to alert laboratory staff of potential analytical issues.

5.0 Safety

- Toxic or otherwise harmful concentrations of metals or other constituents are unlikely to be encountered while sampling ambient sediments in rivers and streams. However, sampling crews should be trained in the general hazards of field sampling (e.g., water-borne pathogens) and how to minimize risks of exposure.

- Operating in or around waterbodies carries the inherent risk of drowning. USCG-approved personal flotation devices must be worn when operating from a boat, when sampling in more than a few feet of water, or when sampling in swift currents.

- Collecting samples in cold weather, especially around cold waterbodies, carries the risk of hypothermia, and collecting samples in extremely hot and humid weather carries the risk of dehydration and heat stroke. Sampling team members should wear adequate clothing for protection in cold weather and should carry an adequate supply of water or other liquids for protection against dehydration in hot weather.

- Sampling team members must cover exposed skin and/or use sunscreen for protection against sunburn and melanoma.

- Sampling teams must develop and employ an emergency response plan when working on all waterbodies including the use of an onshore monitor that is accountable for the whereabouts of the team. The monitor can request aid if team fails to report in at end of workday and can provide assistance to rescuers or team under any scenario where an emergency situation exists.

6.0 Apparatus and Materials

- Piston type bilge pump (similar to Grainger Item: Portable Hand Pump, item # 4P018 $27.10)

- HDPE 5 gal buckets (translucent variety available at Lowe's, with easily removed friction lid is ideal). At least three should be available for each site to be sampled.

- Wrist watch or other timing device w/ second hand/display

- Paddle or lg. spoon, either stainless steel or plastic, as required by the analytical procedure

- Portable analytical balance, 2 kg capacity, 1.0 g resolution

- Analysis-appropriate sample containers.

- Waders and/or PPG as appropriate

- Gloves – PVC, Powder-free, clean-room quality

- Dry ice (if methyl mercury analysis to be requested)

7.0 Reagents and Standards

- Reagent water – water in which metals and nutrients and potentially inferring substances are not detected at the MDL of the analytical method used for analysis of samples OR are detected at concentration no greater than three times the MDL. Used to prepare field blanks and equipment blanks and to rinse apparatus.

- Formula 409 – Commercial liquid cleaner suitable for decontaminating bilge pump and buckets. An effective degreaser as well as providing good removal of surface metal contamination.

8.0 Sample Collection and Handling

- Select sediment sampling sites in accordance with study objectives. Generally at least three sub-locations will need to be selected for sampling at each river location. Samples from these sub-locations may be composited for analysis or submitted separately for analysis to obtain information on within-site variability.

- Avoid sample locations very near heavily traveled roads, bridges, and overhead utilities.

- At sample site, install square meter frame over river bottom to be sampled. If bottom substrate is visible through the overlying water photograph the sampling location with the edges of the frame nearly filling the camera view finder.

- Use a pre-decontaminated pump to pump sediment and water from overlying substrate within the meter frame into one of the pre-cleaned 5 gal.

buckets. Short pump strokes reduce the amount of water and maximize the sediment recovered. Move intake end of pump around as sediment is collected to maximize volume of sediment obtained. In so far as possible limit the depth of penetration of the pump tip to the upper 1 to 2 inches of sand, gravel and cobble. Continue pumping until approximately 4 gallons of water/sediment is in the 5 gal. bucket, or the square meter of bottom is swept relatively clean of fine-grained material.

- After 4 gallons have been pumped, use a clean paddle or spoon to completely suspend the sediment. Stir for about 15 seconds.

- Allow sediment to settle for 30 seconds. All sand in the sample will settle to the bottom of the bucket in this interval.

- Pour the remaining suspension into a separate pre-cleaned 5 gal. bucket. Stow the bucket someplace where it will be moved as little as possible for 30 minutes.

- Measure the volume of sand remaining in the first bucket and discard. If a more quantitative estimate of the dry weight of the coarse fraction is desired collect an representative aliquot of the sand for determination of percent water.

- At the end of the 30 minute settling period, *carefully* pour off and discard the as much of the overlying water as possible. Avoid re-suspending or losing any of the sediment that has settled at the bottom of the bucket.

- Pour the remaining settled sediment into a pre-weighed wide mouth glass sample jar and weigh the jar to determine wet weight of the fine fraction

- Determine from the analytical lab(s) the minimum acceptable sample volume or mass. If, in the field team's judgment, the amount of sediment procured from the first sample is insufficient, repeat the above procedure in an adjacent section of the stream, then composite each additional grab until sufficient volume is achieved.

- As a point of reference, typical dry mass obtained per 5 gallon volume initially pumped is from 30-80 grams, dry weight. This will be almost entirely composed of silt and clay, because sand is excluded during steps 2-4. This may reduce the amount of sediment required for analysis, since sand generally does not sequester contaminants effectively.

- In general sediment samples for metals and nutrient analysis are usually field-preserved only by chilling and maintenance in the dark. Sediment samples for methyl mercury analysis must be frozen and shipped on dry ice. See any specific instructions provided by the analytical laboratory.

9.0 Quality Assurance/Quality Control

- Strict adherence to the procedures described here under Contamination Control will assure collection of uncompromised sediment samples.

- However, it is also necessary to collect Field Blank and Equipment Blank samples each day that sampling occurs, or whenever the pump or tubing is changed, to demonstrate that contamination has been controlled.

- At least one Field Duplicate must be collected each sampling day or after every 20 samples.

- Additional Field Duplicates may be collected if conditions suggest the need for more, or more are specified in the Sampling and Analysis Plan.

- Separate samples for Matrix Spikes (MS) and Matrix Spike Duplicates (MSD) must be collected unless the laboratory specifies that these analyses can be run using an actual sample.

10.0   Recleaning/Reuse of Apparatus Between Samples

- Buckets – Buckets should be scrubbed with Formula 409 and then flushed with river water prior to reuse.

- Bilge Pump – River water should be flushed through the pump at the end of each sampling use followed by diluted Formula 409 cleaner and more river water. Flush the pump at the end of each day with reagent water and drain of any water that is not expelled by operating the pump. No other cleaning is needed unless oily sediments are encountered. Store the pump in a clean polyethylene bag.

11.0   References

USEPA. 2001. Methods for Collection, Storage and Manipulation of Sediments for Chemical and toxicological Analyses: Technical Manual. EPA-823-B-01-002, US Environmental Protection Agency, Office of Water, Washington, DC, 208 p

A3 GENERAL METHODS ON SOIL COLLECTIONS

To collect soil the following general procedures should be followed. Equipment required includes a stainless steel shovel, latex gloves, a tape measure, stainless steel bowls and spoons, plastic mesh sieve, plastic zip-loc bags, sharpie pens, waterproof paper, ice, cooler, notebook.

- use a straight edged stainless steel shovel to cut a 15 cm x 15 cm area of soil to reveal the vertical profile. Take care to avoid mixing of the two soil horizons – the surface organic, humic layer (A horizon), and the lower inorganic (B, C horizons) soil.

- Record the thickness of the humic layer using a tape measure and record depth (cm) in the field book.

- Place the humus soil into a stainless steel bowl and homogenize by hand (using latex gloves) until thoroughly mixed.

- Collect the mineral soil sample from beneath the humic sample and mix in the same fashion.

- Separate large stones and gravel from the soil.

- A clean plastic sieve with 2 mm mesh opening is preferred for removing coarser material. Handle each sample using latex or vinyl disposable gloves and place samples in a plastic Ziploc® bag.

- Clean the mixing bowl, sieve and shovel with a mild soap solution and water between samples to avoid cross-contamination.

- As soon after collection as practicable store the labeled sample bags on ice or in a refrigerator. Place a waterproof paper label inside the bag and label with a sharpie pen on the outside of the bag.

- Seal the cooler and transport to the laboratory with the appropriate chain-of-custody forms which should accompany the shipment.

A4   BIOTA SAMPLING

A4.1 Vegetation

To collect vegetation samples the following equipment is needed: latex gloves, large zip-loc bags, sharpie pens and waterproof paper labels.

- Samples of shrubs, and leaves or needles of trees should be collected by gathering the current year's growth (i.e., tips of coniferous trees and leaves).

- Determine the dominant tree type and focus on one or two species and sample these within the flood zone corridor of the area chosen for collection.

- Determine the species type(s) to be collected and focus on these and composite leaves or needles of the same species in separate bags.

- All vegetation samples should be collected by hand using disposable latex gloves.

- Fill a single large Ziploc® bag by wandering over the sampling area while collecting a few leaves or needles (depending on the species being collected) from many plants or trees to gather a composite.

- Refrigerate samples prior to shipping. Appropriately label the outside of the bag with a sharpie pen and place a waterproof paper label inside the bag. storage and transport to the laboratory for analysis.

- Seal the cooler and transport to the laboratory with the appropriate chain-of-custody forms which should accompany the shipment.

A4.2 Zooplankton

To collect zooplankton the following equipment is needed. A boat with appropriate safety gear, zooplankton net and rope, depth sounder, GPS, Whirl-pac bags, sharpie pen, cooler and ice.

To collect plankton suspended in the water column deploy a 250-µm zooplankton net with at least a 6:1 length to mouth diameter ratio from the port or starboard side of the boat away from the rear end of the boat to avoid the propeller and to avoid propeller wake.

- It may be necessary to weight the net ring so that it sinks below the water surface

- Allow the net to drift back from the boat by 10 – 20 m

- Tow the net at a slow speed (1 – 2 knots) while keeping the top of the net at least 1 m below the surface of the water. Boat speed, weight of the net and/or length of rope deployed might have to be adjusted

- Tow the net for 3 – 5 minutes or until a minimum of 5 grams of zooplankton has been collected.

- Transfer the zooplankton from the net into two labelled Whirl-pac bags. One for analysis of mercury and one for analysis of stable isotopes.

- Freeze the sample as soon after collection as possible.

- Ship the samples to the respective laboratories frozen, on ice with the appropriate chain of custody forms.

A4.3 Benthic Invertebrates

To collect benthic invertebrates using a grab sampler such as a Ponar or Ekman it is recommended that an area with slow current velocity is selected that is a depositional area for sediments. Mobilize a boat with appropriate safety equipment and anchor and the following gear: field collection data forms, waterproof paper, pencils, waterproof markers & clipboard; GPS unit, batteries; depth meter; rope; Petite or Standard Ponar grab; 500 micron (0.5 millimeter), plastic bucket and bin, stainless steel sieve; stainless steel tweezers, small (10 mL) plastic vials with lids. The field collection procedure is as follows:

- With the aid of a GPS unit, **navigate the boat** to the sampling station and record the UTM coordinates (in NAD 83). Approach the station from downstream of the wind direction. In windy conditions, anchor the boat upstream of the station and drift back; it is not necessary to anchor the boat in calm conditions providing the boat remains within a 50 meter radius of the position. Do not allow the anchor to drag through the sampling station. Record the exact UTM coordinates on the field data form.

- Measure the **water depth** at the sampling station using a hand-held or electronic depth meter.

- Begin collecting benthos samples by ensuring that the rope is securely attached to the **Ponar**.

- Lower the **Ponar** to within 1 meter of the bottom of the lake and then lower very slowly over the last meter and allow the rope to go slack. Raise the Ponar to the edge of the boat and check the grab for **acceptability**. The grab is acceptable if the sample:
  - does not contain large foreign objects;
  - has adequate penetration depth (i.e., 10-15 centimeters);
  - is not overfilled (sediment surface must not be touching the top of the Ponar);

- did not leak (there is overlying water present in Ponar); and is undisturbed (sediment surface relatively flat).

Once the grab is deemed acceptable, open the Ponar jaws and drop the sample into the 500 micron sieve being held above a plastic bin in the center of the boat that is filled with water.

- Sieve the sample until only the benthic organisms and coarse materials remain. To sieve the sample, gently raise and lower the sieve into the water in the plastic bin and swing side to side. Care must be taken to ensure the benthic organisms are not damaged or crushed. Do not disturb the sample to the point that it is splashing out of the sieve. Do not forcibly push materials through the sieve; gently break apart any small clay balls. Rinse off any pieces of larger plant material or rocks in the sample and discard.

- Using the stainless steel tweezers pick individual chironomid worms, Trichoptera, Plecoptera and Ephemeroptera larvae and place into a small vial or lid in clean or distilled water and rinse sediment particles from the individual animals.

- Repeat the above procedure until a minimum of 3 gm of invertebrate tissue has been collected.

- Split the biomass into two vials: 2 gm for mercury analysis and 1 gm for analysis of stable isotopes.

- Appropriately label and freeze the samples as soon after collection as practicable.

- Ship frozen on ice to the appropriate laboratory for analysis of total mercury and C and N stable isotopes and moisture content.

A4.4 Fish

There is a well-known positive correlation between fish size (length and weight) and mercury concentration in muscle tissue (Scott and Armstrong, 1972; Bodaly, et al., 1984; Somers and Jackson, 1993). To eliminate the bias associated with differences in fish size, mercury concentrations must be measured over a wide size range, from small, young fish to large, old fish. Then, appropriate statistical procedures are used to determine the mean mercury concentration for a specific fish size, usually the mean size most commonly captured by fishermen. This is called the size-adjusted or "standardized" mean mercury concentration. When this is done for multiple lakes or years, comparisons of mean mercury concentration can be made that are unbiased by differences in fish size.

There is an established protocol that describes the sample size and size range of fish needed to derive a good statistical relationship between mercury concentration and fish size (Strange and Bodaly, 1998). Optimally, tissue from 25 – 35 fish are gathered from

each species, ranging from the smallest to the largest fish typically observed. Because bull trout live much longer and reach a larger size they have a large standardized size (550 mm) relative to lake whitefish (350 mm). The standard protocol that describes the sample size per size interval for lake whitefish and bull trout is as follows:

LENGTH INTERVAL (mm)	LAKE WHITEFISH	BULL TROUT
100-199	7	
200-299	7	5
300-399	7	5
400-499	7	5
500-599	7	5
600-699		5
700-799		5
>800		5
Total	**35**	**35**
"Standardized Size"	**350 mm**	**550 mm**

These standardized sizes fall near the middle of the size range of fish collected and have been used as standardized sizes elsewhere in Canada, which facilitates comparisons between different lakes or years for the same species.

Bull trout or other desirable species should be sampled using non-destructive techniques as described in Baker et al. (2004).

- Place all bull trout captured via angling or from gill nets into a live tub either on shore or in the boat. When captured, measure fish for length (mm) to determine the size category into which they fall.

- For those fish that meet the required size category, place into 20 liter bucket and anaesthetize using clove oil mixed with rubbing alcohol at a rate of 1:10 and then further mixed with water at a rate of 4.4ml per 10 liters.

- Leave fish for 1 – 2 minutes in the clove oil mixture, one at a time, until anaesthetized.

- Measure exact fork length (mm) and total weight (gm) using a digital scale (+/- 5 gm).

- Place the fish on its right side and remove several scales from the left side just beneath the distal part of the dorsal fin.

- Extract two 50 mg tissue plugs using a 4 mm diameter Miltex biopsy punch and place on a small plastic board

- Apply 'Nexcare Liquid Bandage' into each tissue sampling hole and allow to dry for approximately one minute. This antiseptic seal stops any bleeding and facilitates healing.

- While fish were recovering, use a clean stainless steel scalpel to cut away the outer skin from the muscle.

- Transfer the tissue plugs into 5 mL plastic vials using stainless steel forceps into labeled vials.

- Place the biopsied fish in a tub full of fresh water until fully recovered prior to release.

- Place all tissue samples in a cooler with ice and freeze as soon as possible.

- Deliver all frozen tissue samples to a laboratory familiar with analyzing for small (~100 mg) tissue quantities. Ensure the proper chain of custody forms are included.

- Analyse all samples for total mercury and moisture and report as parts per million (mg/kg or ppm) wet weight.

Appendix 2

Mercury in the Environment – Public Piece

Mercury in the Environment – A Summary Piece for Public Consumption

Mercury (Hg) is a naturally occurring metallic element that is present in low concentrations in all media including air, water, soil, sediment, plants and in all animal tissues. The vast majority of mercury in the environment is present in a form known as inorganic mercury that can only be detected by a laboratory. Inorganic mercury is most commonly bound to sulphur or carbon in rocks and soil and is not distinguishable as the shiny, slivery metal known as the pure elemental mercury or quicksilver. This is the concentrated, purified form that is found in thermometers and switches, or as dental amalgam, when bound with silver. This elemental form is the pure, processed form of the metal that is typically not found naturally in the environment.

About half of the mercury deposited into the environment originates as a gas, dispelled from the Earth from volcanos, forest fires, and natural degassing from mercury rich rocks. The other half is released by humans from burning of fossil fuels such as oil and coal; losses from industrial processes and from gold mining activities around the world that still use mercury to capture fine gold, releasing mercury gas into the global atmospheric pool. Gaseous mercury present in very low concentrations in the air adheres to the leaves and needles of trees and other plants ('dry deposition'). Mercury is also deposited directly onto soils, or in freshwater lakes and rivers and the oceans in rainfall or snow and with dust. Over time, this inorganic mercury gradually accumulates in the soil and sediment of lakes and rivers at concentrations at least a million times higher than in air. Human industrial activities have caused mercury concentrations to increase in all environmental media and especially, in fish.

The inorganic form of mercury that is bound up in soil and sediment is not easily taken up or absorbed by plants or animals and typically does not pose any health risk. However, about 1% of the mercury in the environment, whether in water, soil or sediment, is present as 'organic' or methyl mercury, which is the most toxic form of mercury. Methyl mercury is formed naturally by certain bacteria species when they decompose or consume carbon in soil or sediment. During this process a small amount of the inorganic mercury consumed by the bacteria is transformed into the organic or methyl form, that is incorporated into bacteria at the base of the food chain and is now available to be consumed and absorbed into the tissue of other animals.

Methyl mercury (MeHg) is acquired almost exclusively via dietary sources, and being an organic compound, is more easily absorbed than it is excreted or eliminated from the body. Thus, methyl mercury accumulates and becomes more concentrated in animal tissues over time and at progressively higher steps up the food chain, ultimately, with highest concentrations in fish. It is noteworthy that methyl mercury concentrations are always low in the kinds of animals that people regularly consume such as cows, sheep,

chickens, deer, and moose. This is because these animals eat plants that always very low mercury concentrations. Only a few percent of the mercury in the tissue of these animals is methyl mercury.

The same is not true for fish. This is because fish eat other fish that may also have eaten smaller fish or other aquatic animals such as plankton. Because of their highly carnivorous diet, fish consume and accumulate more mercury and more methyl mercury than any other animal. The consequence is that about 95% of the mercury present in fish is in the methyl form and explains why fish have methyl mercury concentrations at least 100 times higher than most other animals. This also means that the vast majority of exposure by humans to mercury is from eating fish, which is why there are well known national advisories against frequent consumption of certain fish species, such as swordfish, marlin, fresh tuna and some other species.

In Canadian lakes there is a general hierarchy in mercury concentrations of fish species, depending on their diet and position in the food web. For example, rainbow trout and kokanee typically consume low mercury food such as insects and plankton and these species tend to have low mercury concentrations. Whitefish consume plankton that live near the bottom and have higher mercury concentrations so they have more mercury in their tissue than rainbow trout. Fish that eat other fish such as lake trout, bull trout and northern pike almost always have higher concentrations of mercury than most other fish species. Because mercury accumulates over time, large, old fish tend to have higher mercury concentrations than small, young fish.

Mercury in Reservoirs

The flooding of soils and vegetation to create reservoirs during hydroelectric development provides a new source of nutrients and inorganic mercury for bacteria in the flooded environment. Bacterial decomposition of this new organic material increases the natural rate of methyl mercury creation in the new reservoir which can last for several years. Ultimately, this causes methyl mercury concentrations to increase in water, plankton, aquatic insects and ultimately, in fish. In Canada, the phenomenon of increased methyl mercury concentrations in the environment and especially in fish as a result of reservoir creation has been well documented, especially in Manitoba, Ontario and Quebec.

The magnitude of increase in fish mercury concentrations and the duration of this increase depend very much on the nature of the reservoir. Reservoirs created over large areas with large stores of organic material such as bogs, marshes and peat land with a long residence time of water (~months) will always produce more methyl mercury for a longer time than reservoirs with minimal flooding, short residence time (~days/weeks) and less organic soils. Large reservoirs that flood carbon rich soils cause fish mercury concentrations to increase from 5 – 7 times background within a few years after flooding.

It may take 30 years before mercury concentrations in fish return to pre-flood levels in these reservoirs. In reservoirs with minimal flooding and carbon-poor soils, fish mercury concentrations may only increase 2 – 3 times above background and return to pre-flood concentrations in 15 – 20 years.

Most of British Columbia's large hydroelectric projects, including Williston (1968) and Dinosaur Reservoir (1980), were constructed before the relationship between reservoir creation and increases in fish mercury was well understood and there are few historic data available. Given that most BC reservoirs were created more than 30 years ago, and based on the trends observed elsewhere in Canada and the world, it is very likely that mercury concentrations in fish in nearly all BC reservoirs have returned to background. In fact, fish mercury concentrations in the vast majority of lakes and reservoirs tend to be quite low. This may be related to the fact that most of our lakes are situated in mountainous regions with poor soil development. For example, there are only three lakes in BC where people are advised to limit their consumption of certain species and only one of these is a reservoir (bull trout in Williston). The other two are related to mining contamination. By comparison, the Ontario 2009-2010 Sport Fishing Guide has fishing advisories for 1,860 lakes where consumers are advised to limit consumption of certain species and sizes of fish. Most of these advisories are for mercury.

Mercury and Site C

If studies on the Peace River Site C Project proceed to Stage 3, it will be desirable to apply the learning from other regions of Canada to the proposed project. Site C is forecast to flood more than 80 km of the Peace River downstream of the Peace Canyon dam near Hudson's Hope. Efforts are currently underway to determine the implications of flooding of vegetation and soil on mercury methylation potential in this new reservoir and implications on fish mercury concentrations. Currently, the concentrations of mercury of mountain whitefish and bull trout from the Peace River at the proposed Site C location are very low, with mean concentrations of 0.04 parts per million (ppm) and 0.09 ppm respectively. These concentrations are typical of fish from remote, pristine lakes and a reflective of the naturally low mercury concentrations of fish in BC lakes and rivers.