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# Technical Memorandum

Date: November 6, 2017
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Our File: NE 16-01

RE: Relationship Between Muskrat Falls Reservoir Elevation and Mercury Concentrations, Lower Churchill River October 2016 – September 2017

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# 1 Executive Summary

Using empirical water quality data collected by AMEC between October 2016 and September 2017, this Technical Memo updates an earlier July 31 2017 Memo aimed at determining if water column methylmercury (MeHg) concentrations have increased within the impoundment and downstream. The investigation considers the nature of soils flooded at different river elevations; possible seasonal effects (e.g., related to water temperature); and possible effects of ancillary water quality parameters linked to MeHg cycling and transport, including total and dissolved organic carbon (TOC/DOC) and total suspended solids (TSS). Finally, we evaluate potential for temporal / seasonal changes in MeHg and other parameters in surface waters at Goose Bay (station N8) that may be related to upstream changes in MeHg concentration. This exercise was partially undertaken to address the concern expressed by the Nunatsiavut Government and the Independent Expert Advisory Commission (IEAC) Oversight Committee that there was "inconclusive evidence linking increases in water levels in the headpond and MeHg production, downstream and in Lake Melville".

In early November 2016, the Lower Churchill River (LCR) was impounded by Muskrat Falls Dam for the first time to an elevation of ~16 m to 21.5 m asl for about one month before dropping back to baseline. In early-February 2017 the river was again impounded and water elevation raised back to ~21 m, where it has since been held. At this elevation, approximately 27% of the total aerial extent of the reservoir lies beneath a water cover, relative to what will be inundated at fully supply of 39 m.

At 21 m asl, the total area of the reservoir is 3865 ha, the majority of which (2897 ha or 70%) is original wetted river area. Of the 1168 ha of flooded habitat, the majority of this (971 ha) consists of gravel bars and riparian soils. Only 197 ha, or 5% of the total surface area, consists of terrestrial habitat with an established humic soil horizon. Riparian soil has very low TOC (<4%) and mercury (<0.03 mg/kg) content, which is typical of mineral soils. Sandy riparian soils do not contain significant humic material and are not expected to make a meaningful contribution to Hg methylation.

Empirical water quality data, focusing on total and dissolved MeHg, TSS, and TOC/DOC were analysed using a series of plots and tables, supported by statistical analyses. A full description of the statistical procedures applied to the water quality data set is provided in **Appendix A**.

Two key assumptions were made: 1) measurements at N1, upstream of the impoundment, are assumed to represent 'baseline' conditions against which downstream changes are evaluated; and 2) measurements at stations N5, N6 and N7 – 0.1 km, ~20 km and 40 km downstream of Muskrat Falls dam respectively, are assumed to represent 'fully mixed' conditions downstream of the impoundment at N4, representing what is discharged to Goose Bay at N8.

General observations regarding the pattern of key water quality parameters are as follows:

- Episodic spikes in TSS at some stations during erosional events caused spikes in total MeHg concentrations, but did not alter dissolved MeHg values, which remained relatively constant. In the absence of TSS effects, the proportion of total MeHg that occurs in the dissolved phase averaged 75% at all stations including within the impoundment.
- The concentration of DOC relative to TOC was almost always >95%. Concentrations of TOC/DOC were largely unchanged spatially from up- to downstream, even during very high TSS events, suggesting that the suspended material was inorganic in nature, not organic soil. Seasonal patterns were evident at all stations, with DOC increasing from 3.5 – 5.0 mg/L during cold months, to 6 – 8 mg/L in summer.
- There was a distinct seasonal pattern in dissolved MeHg everywhere, with an approximate doubling in concentration from winter to summer. In cold, winter/spring months, dissolved MeHg averaged ~0.012 ng/L, increasing to ~0.024 ng/L at N1, upstream of the impoundment during summer (June – September).

We investigated patterns in MeHg and ancillary parameters by asking three questions: 1) has water column dissolved MeHg increased in the impoundment (N4) over and above natural seasonal changes at the upstream reference station N1?; 2) has any increase in dissolved MeHg in the impoundment at N4 persisted at downstream stations N5 to N7 in the Lower Churchill River?; and 3) what are the implications if any, downstream of the river into the estuarine environment (in Goose Bay at N8)?

To determine whether dissolved MeHg concentrations increased at stations downstream of N1 (N4 to N8), we first estimated monthly means by station, and then calculated ratios of monthly means at all other stations relative to N1. Mean dissolved MeHg concentrations at N1 and N4 were similar from March-May, but increased at greater rate at N4 within the impoundment from June through September relative to upstream at N1. Mean concentrations at N5, N6, and N7 were intermediate between N1 and N4 from March-August, with very small absolute differences (~0.003 ng/L). There was no difference between N1 and N5 – N7 in September.

Analysis of time trends was based on comparison of trends in monthly means of dissolved MeHg over time at each of N4 to N8, relative to N1. Our ability to evaluate time trends is somewhat limited because of lack of ‘pre-impoundment’ data. We also do not know if there are any natural differences in MeHg within different reaches of the river (e.g., proximity to a wetland) that have existed before impoundment. We used mixed-effects models to test for downstream differences in dissolved MeHg trends that might be related to the impoundment. It is only since February 2017 has N4 been continuously impounded; consequently, and recognizing the limited data prior to February, we evaluated time trends for February 2017 onwards. However, the data at N1 for February contains two extremely high values, including the highest value in the whole dataset, plus two values at or near the MDL. Therefore, we also fit the models with and without February. With February included, there was a statistically significant increase in slope (time trend) for N4 relative to N1 (with an average monthly increase of about 11%), and a marginally significant increase in slope for N5 (average monthly increase of about 6%).

Estimates for N6 – N8 were positive but not statistically significant. Importantly, these results were largely driven by the high February N1 data. When February data were excluded, the increase in slope for N4 relative to N1 was marginally significant (with an average monthly increase of about 5%). There was no evidence of differences for the remaining sites; i.e., all stations had dissolved MeHg trends similar to that for N1. These results are consistent with the observed ratios of means discussed above.

Based on the empirical evidence, three things are clear: 1) all stations demonstrated a clear seasonal increase in both total and dissolved MeHg between June and September; 2) temporary impoundment in November 2016 and re-flooding in mid-February did not produce a clear increased MeHg water column signal until May 2017; and 3) dissolved water column MeHg concentrations from June to September were slightly higher at N4 within the impoundment (0.004 – 0.007 ng/L) than upstream at N1. This has persisted through September, despite the relatively short water residence time (~1 day) within the small, shallow (5 m deep) reservoir. The absence of change within the impoundment prior to June is likely due to cool water temperatures, low rates of local inputs of autochthonous and allochthonous carbon, the small area of organic soils flooded and short residence time within the impoundment.

Looking downstream from N4, the magnitude of change within the LCR relative to N1 is even smaller. Dissolved MeHg concentrations at N5, just downstream of the impoundment and N1 are very similar over time. While there is a suggestion of slightly higher MeHg concentrations downstream at N6 / N7 during May/June, the differences are very small (<0.003 ng/L). Progressive loss of dissolved MeHg is due to demethylation via photodegradation, and partitioning to DOC and TSS, adsorption to seston and absorption / uptake by biota (periphyton, phyto- and zooplankton, fish).

In the absence of a detectable increase in MeHg delivered by the LCR to Goose Bay as a result of the impoundment, it is reasonable to assume that no detectable or meaningful change in downstream biota mercury concentrations should be expected – either within the river, or extending into Goose Bay and beyond.

We speculate on possible reasons why a proportionally larger increase in MeHg has not been observed as predicted by Calder et al. (2015). These may include low abundance of flooded habitat containing humic soils, low inorganic Hg content of forest soil, poor methylating conditions (cold water, circumneutral pH), conservative assumptions regarding MeHg generation in flooded soils and water column flux and MeHg absorption / adsorption to biota and seston in the water column.

# 2 Introduction and Objective

Azimuth Consulting Group Partnership (Azimuth) was asked to update our July 31, 2017 Technical Memo (Azimuth 2017a) that examined methylmercury (MeHg) concentrations in water within the Lower Churchill River (LCR) in relation to changes in water level elevation due to impoundment by the Muskrat Falls dam. The July memo examined spatial and temporal patterns in MeHg within the LCR between October 2016 and May 2017, during a limited period of impoundment (November + mid-February to May).

The July 31 Memo was reviewed by representatives of the Nunatsiavut Government (NG; Letter to Premier Ball dated August 15, 2017) and by the Independent Expert Advisory Commission (IEAC) Oversight Committee (OC) (IEAC OC briefing, September 18, 2017). The key technical concern expressed in the IEAC's briefing note was that there was "inconclusive evidence linking increases in water levels in the headpond and MeHg production downstream and in Lake Melville". Specifically, the IEAC raised four points:

1. Lack of adequate pre-impoundment baseline data, especially during previous spring and summer seasons against which to compare MeHg concentrations in relation to water level increases;
2. A hesitation to casually link transient increases in MeHg concentrations in water post-February, given this was not observed in the November inundation period;
3. Inability to separate higher water levels and higher water temperature on increased variability in MeHg concentrations, observed between the headpond and Goose Bay since February; and
4. A temperature dependence of MeHg production means there is a lag time before water level driven changes in MeHg are observed in the reservoir and downstream, which may perhaps explain a lack of obvious response over the short time frame to the end of May. Summer data may be more conclusive.

Each of these questions will be addressed here, using near-weekly water chemistry results between October 2016 and end of September 2017. During most of this time, the impoundment has been held near an elevation of 21 m above sea level (asl), about 5 m higher than the baseline elevation.

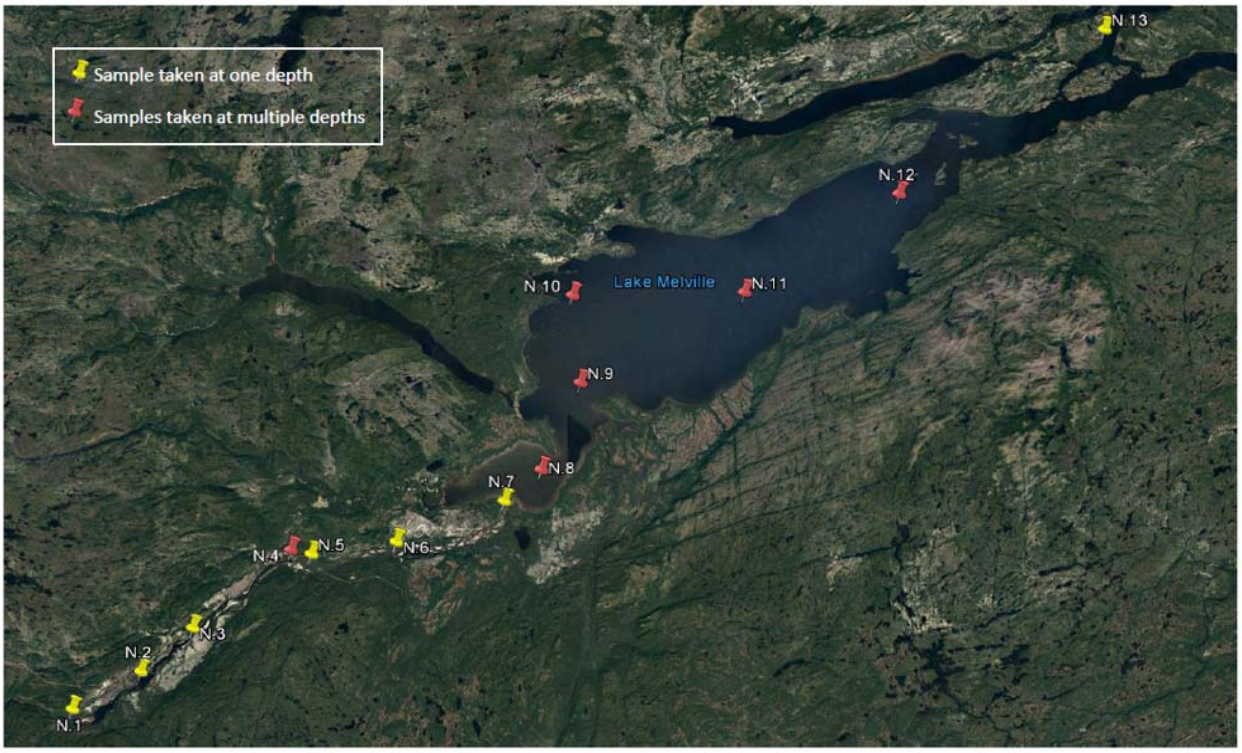
Using empirical water quality data, under the assumptions below, the objective of this memo is to determine if water column MeHg concentration has increased within the impoundment, and whether spatial or temporal patterns downstream can be attributed to changes within the impoundment. Our investigation also takes into account the nature of soils flooded at different river elevations, seasonal effects (e.g., water temperature) and ancillary water quality parameters linked to MeHg cycling and transport, including total and dissolved organic carbon (TOC/DOC) and total suspended solids (TSS). Finally, we examine if there are any temporal / seasonal changes in MeHg and other parameters in surface waters at Goose Bay (N8).

# 3 Background

## 3.1 Location of Monitoring Stations

A map depicting key sampling stations is presented in **Figure 1**. The focus is on stations within the Lower Churchill River (N1 – N7) and in Goose Bay (N8). Station N4 is just upstream of the Dam site and represents the impoundment, while N5 is situated just downstream. Stations N6 and N7 are located about 20 km and 40 km downstream of the Dam, respectively, and are considered representative of what would be discharged from the impoundment to the estuary. N8 is situated in Goose Bay, about 15 km offshore of the river mouth in the 'salt wedge zone' of the estuary, where salinity can reach about half sea water concentrations at the halocline. This memo does not examine water quality parameters at N9 – N13, instead focusing on whether changes can be seen at near-field stations before moving further afield.

**Figure 1**. Map depicting AMEC sampling stations along the Lower Churchill River (N1 – N7), Goose Bay (N8) and Lake Melville (N9 – N13).




## 3.2 Form of Mercury

Discussion of 'mercury' relates to both total and dissolved 'total' mercury (Hg), which includes total and dissolved MeHg concentrations (in parts per trillion or ng/L). "Dissolved" means "filter-passing" where the filter pore size is 0.45 μm. We address those parameters that may strongly influence water column Hg and MeHg concentrations, particularly total suspended solids (TSS) and total and dissolved organic

carbon (TOC/DOC) concentrations (mg/L). The key parameter addressed by this Technical Memo is dissolved MeHg, which is the main contaminant of concern as a by-product of soil decomposition by sulphate-reducing bacteria within new reservoirs (Korthals and Winfrey 1987, St Louis et al. 2007 and many others). Particle-bound MeHg is also subject to fluvial transport and may become bioavailable elsewhere, due to changes in water chemistry that affect its partitioning to particles, or due to consumption by filter-feeding organisms.

## 3.3 Summary of Water Elevation Changes

In early November 2016, the LCR was impounded by Muskrat Falls Dam for the first time. Over the course of about one week, water elevation was raised from the baseline elevation of ~16 m to 21.5 m asl behind the dam and was maintained at this elevation for about one month. In early December, water elevation was dropped back to baseline until early-February 2017. At this time, the river was again impounded and water elevation raised back to 21.5 m asl. Water level was raised to 22.4 m during April and reduced back to 21.5 m in June. From late June through August, water levels were held at 20.4 m. Thus, the headpond area has been inundated for about nine months.

The mean elevation of 21 m is approximately 5 m above baseline, relative to a full supply water elevation of 39 m. At this elevation, approximately 27% of the total aerial extent of the reservoir lies beneath a water cover, relative to what will be inundated at fully supply of 39 m.

## 3.4 Summary of Physical Habitats Affected by Inundation to 21 and 25 m

The area (ha) and extent (as a percent of total reservoir area) of soil with an established humic layer beneath the litter / fermentation layer is the primary driver of mercury methylation in new reservoirs (Johnson et al. 1991, Schetagne et al. 2003, Bodaly et al. 2007, Azimuth 2012). Flooded gravel bars, bedrock and mineral soils do not contain humic material and thus will not contribute in a meaningful way to mercury methylation. These soil types contain very little of the ‘raw ingredients’ required for methylation; a source of available Hg and labile carbon. For example, the total Hg content of soil is correlated with organic matter content and less frequently with mineral soils with high clay and iron content (Anderson 1979, Grigal 2003, Friedli et al. 2007). 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 as sharp decreases (>10x within a few centimeters) in Hg concentration as a function of depth in the soil profile, particularly under acidic soil conditions, such as beneath a coniferous forest canopy.

At progressively higher impoundment elevations above baseline, different amounts (both total and relative) of soil types will be inundated. For perspective, small increases in river elevation will mostly flood gravel bars and riparian habitat with little to no humic soils, while at progressively higher elevations, greater proportions of forest with established soils will be inundated. Thus, a good understanding of the nature of the soils flooded at

different elevations is essential when predicting how water column MeHg concentrations may change.

It is well understood that virtually all of the MeHg fluxed to the overlying surface waters is generated within the top 2 – 5 cm of sediments and flooded soils (Korthals and Winfrey 1997, Eckley et al. 2015). It is also well known that 'wetlands' produce more MeHg and for a longer duration (presumably from deeper depths) than humic soils (St. Louis et al. 1994). Therefore, understanding the spatial distribution and depth / quality of organic soils with an established humic layer and wetlands is important. We examined this at 21 m and 25 m elevation. According to Nalcor/SNC-Lavalin, 21.5 m is the minimum level to reduce river current speeds to acceptable levels at the boom installation location. Increasing the impoundment elevation to 25 m provides favourable conditions for formation of an upstream thermal cover and minimizes the potential for formation of a downstream ice dam that could flood works under construction. We examine the nature of soils inundated at both of these elevations.

**Table 1** presents a GIS-based accounting of the different habitat classifications flooded at 21 m (the current elevation) and 25 m elevation (AMEC 2017). At 21 m, the total area of the reservoir is 3865 ha, the majority of which (2897 ha or 70%) is original wetted river area. At 21 m elevation, the majority of habitat flooded consists of gravel bars and riparian soils (971 ha). Only 197 ha, or 5% of the total surface area consists of freshly inundated terrestrial habitat with an established humic soil horizon.

**Table 1**. Surface area (ha) and percent change in habitat type inudated at 21 and 25 m asl.

| | 21 m asl | | 25 m asl | |
|---|---|---|---|---|
| Habitat Type | Area (ha) | % of Total | Area (ha) | % of Total |
| Black spruce feathermoss | 39.8 | 1.0 | 109.5 | 1.9 |
| Fir - White spruce | 46.3 | 1.2 | 280 | 4.9 |
| Hardwood forest | 1.7 | 0.0 | 30.4 | 0.5 |
| Mixed forest | 31.6 | 0.8 | 137 | 2.4 |
| Spruce - Fir feathermoss | 3.4 | 0.1 | 14.1 | 0.2 |
| Wetland | 72.6 | 1.9 | 112.9 | 2.0 |
| Riparian | 409 | 10.6 | 523 | 9.2 |
| Gravel Bar | 562 | 14.5 | 619 | 10.9 |
| Bedrock | 1.6 | 0.0 | 1.6 | 0.0 |
| Water | 2697 | 69.8 | 3857 | 67.8 |
| Total Area | 3865 | 100 | 5685 | 100 |
| % Vegetated Humic Soils Flooded (including river + unvegetated) | 195.4 | 5.1 | 683.9 | 12.0 |
| % Vegetated Humic Soils Flooded (excluding river + unvegetated) | | 16.7 | | 37.4 |

At 25 m, proportionately more forest / wetland habitat with a humic horizon is inundated than at 21 m, totaling 684 ha, or about 12% of the total surface area of the reservoir. The area of riparian habitat flooded is 523 ha (9% of reservoir area), proportionately much

less than at 21 m elevation. Thus, moving between 21 m and 25 m, there is a 7% increase in surface area of terrestrial habitat flooded, considering only those soils with an established humic horizon.

It is noteworthy that 'riparian habitat' constitutes a relatively large portion (409 ha) of flooded habitat at 21 m, or >2x the area of forested habitat. Empirical field data (AMEC 2017) revealed that riparian soil had very low organic carbon (<4%) and mercury concentration (<0.03 mg/kg), and was largely comprised of sand, with no apparent humic soils (T. Praamsma, AMEC, Personal Communication; October 2017). These conditions are typical of carbon and mercury signatures in mineral soils (Azimuth 2012), suggesting that riparian soils do not contain significant humic material and would not be expected to make a meaningful contribution to Hg methylation.

This is also supported by Harvard's own work. Figure 5 from Schartup et al. (2015) shows the accumulated rate of MeHg flux from organic 'inland' soils and from 'nearshore' soils, collected from riparian habitat. The riparian habitat soils produced a very brief and small signal, suggesting that there is no humic horizon to sustain MeHg production. Implications of this is discussed in **Section 5.0** where we examine the timing of inundation of the impoundment at 21 m and its effect on water column MeHg.

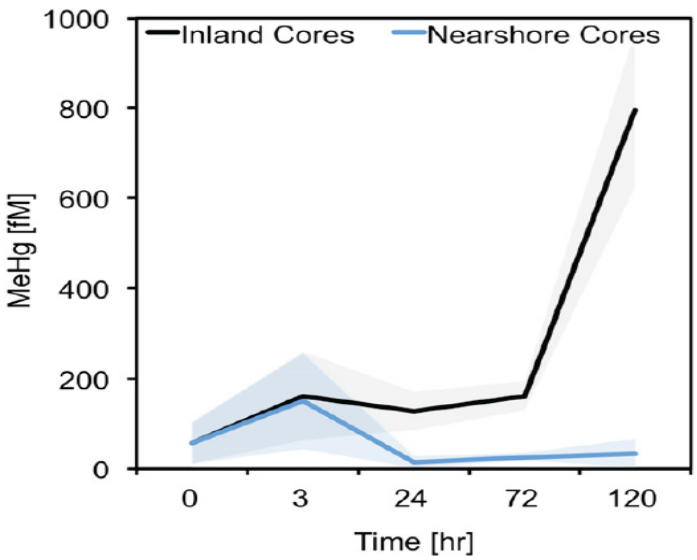



**Fig. 5.** Temporal changes in the MeHg concentration in water overlying experimentally flooded soils in the Lake Melville watershed (*SI Appendix*, Fig. S1). Results are from six cores from the planned reservoir area. Three were collected near the Churchill River and three from the inland regions that will be flooded.

## *3.5 Field Sample Collection*

All water sampling stations were accessed by helicopter and samples hand collected using either a Niskin bottle or a diaphragm pump. Samples were collected 20 cm below the water surface from near mid-river. The only exceptions were at N4 where a boat was sometimes used to collect three vertical samples – just below surface (20 cm), mid-water column and just above the bottom (30 cm). Total water depth at N4 ranged from only 4 – 5 m, so all these data were considered relevant and all were used. At N8 in Goose Bay,

water was also collected below surface and just above the halocline, from a helicopter on floats. Data for stations N2 and N3 were extremely limited and were omitted.

# 4 Evaluation of Data Quality

Prior to analysis of spatial and temporal trends in the data, we first studied the reliability of the water quality data. Specifically, we used a quality assurance / quality control (QA/QC) procedure known as a "Ten + Ten study" to evaluate the precision of water column MeHg data. This is important, because ambient concentrations in water are very close to the Flett Research Method Detection Limit (MDL) of 0.01 ng/L (parts per trillion) for MeHg.

The Ten + Ten study quantitatively assesses both field and laboratory variability of key parameters. On May 25, 2017 AMEC collected 10 consecutive field replicate samples at a single location on a single day – or 10 field replicates. AMEC also collected a 10L volume sample on May 29, with instructions to the laboratory to analyse 10 separate aliquots of this water – or 10 laboratory replicates. This was implemented twice – once in the mainstem of the Lower Churchill River at station N1 and once in the estuary at Goose Bay (N8). Understanding the magnitude of field and laboratory variability is critical in establishing field variability and laboratory precision respectively.

Laboratories also have a variety of internal tests to verify laboratory precision. First, the lab tests Certified Reference Material (CRM) during each run. A CRM consists of a sample with a known concentration of the parameter of interest. These are inserted into the batch for analysis to determine how close the lab result is to the CRM concentration. Typically, the acceptable limits for CRM is +/- 30% either side of the reference value. The lab also runs 'laboratory duplicates' where randomly chosen samples are re-run and compared to the original result, as a 'self-test' of laboratory precision. In addition, values that lie outside of these values are flagged, and in many cases investigated by additional analyses. Results of field and laboratory duplicates are assessed using the relative percent difference (RPD) equation, calculated between original and duplicate measurements. The equation used to calculate a RPD is:

$$RPD = \frac{(A - B)}{[(A + B)/2]} \times 100$$

where: A = analytical result; B = duplicate result. The laboratory data quality objectives (DQOs) to measure analytical precision for most parameters where concentrations are >5 or 10x MDLs range from 20% to 30%. For the purposes of this study, an acceptable RPD for a laboratory duplicate is considered 20% and a field duplicate is 30%, recognizing the greater inherent variability in independently collected samples from a dynamic environment. While all MeHg concentrations measured between October and September are < 5x the MDL, one could argue for larger RPD acceptability criteria – however, given the importance of this parameter, we have not done this.

In addition to mercury, independent field replicate samples and a large aliquot of water was submitted to AGAT Labs for the analysis of TOC and DOC to derive field and laboratory RPD values. TSS and total Hg samples were not assessed because too many of the values were below the AGAT MDLs.

RPDs were evaluated using R statistical software. Raw data appeared approximately normally distributed in almost all cases and therefore were not transformed prior to analysis. Using each set of 10 replicates (field or lab), random pairs of samples were selected and the RPD was calculated. This process was repeated 10,000 times, generating 10,000 RPD estimates. From these we generated an estimate of the mean or 'expected' RPD results, presented in **Table 1**. Key points are as follows:

- The mean RPD values for total MeHg from field and laboratory duplicates on the Lower Churchill Mainstem were 23% and 12% respectively. This is expected, because field duplicates incorporate both field variation as well as laboratory variation. However, for other cases (dissolved MeHg in the Lower Churchill Mainstem, and both total and dissolved in the Estuary), RPDs were either similar for field and laboratory, or were slightly higher for the laboratory.
- For TOC and DOC, mean RPDs were generally lower than for MeHg, and RPDs for lab duplicates were much lower than for field duplicates. The lower RPDs for TOC/DOC, particularly for lab duplicates, are assumed to occur because field concentrations are higher relative to their MDL.

**Table 1**. Results of the 10 + 10 study to measure field and laboratory RPD values.

| | | | Parameter Concentration | | | | |
|---|---|---|---|---|---|---|---|
| **Parameter** | **Sample.Location** | **QA Type** | **median** | **mean** | **sd** | **max** | **mean.RPD** |
| TMeHg | Mainstem | Field | 0.022 | 0.024 | 0.006 | 0.036 | 23 |
| TMeHg | Mainstem | Lab | 0.028 | 0.027 | 0.003 | 0.032 | 12 |
| DMeHg | Mainstem | Field | 0.014 | 0.014 | 0.003 | 0.019 | 22 |
| DMeHg | Mainstem | Lab | 0.016 | 0.016 | 0.003 | 0.019 | 20 |
| TOC | Mainstem | Field | 6.6 | 6.41 | 0.95 | 7.5 | 16 |
| TOC | Mainstem | Lab | 6.05 | 6.2 | 0.47 | 7.4 | 6.7 |
| DOC | Mainstem | Field | 6.25 | 6.02 | 0.96 | 7.3 | 17 |
| DOC | Mainstem | Lab | 5.85 | 5.85 | 0.31 | 6.3 | 5.8 |
| TMeHg | Estuary | Field | 0.02 | 0.021 | 0.004 | 0.027 | 19 |
| TMeHg | Estuary | Lab | 0.024 | 0.025 | 0.005 | 0.033 | 21 |
| DMeHg | Estuary | Field | 0.011 | 0.011 | 0.002 | 0.014 | 14 |
| DMeHg | Estuary | Lab | 0.012 | 0.012 | 0.002 | 0.016 | 19 |
| TOC | Estuary | Field | 4.3 | 4.67 | 0.76 | 6.0 | 16 |
| TOC | Estuary | Lab | 7.4 | 7.3 | 0.53 | 8.3 | 7.4 |
| DOC | Estuary | Field | 4.2 | 4.45 | 1.05 | 6.5 | 23 |
| DOC | Estuary | Lab | 6.55 | 6.75 | 0.47 | 7.7 | 7.0 |

Notes: (a) each row is based on n=10 samples (field) or subsamples (lab); and (b) mean.RPD is the average RPD for 2 randomly selected samples or subsamples

In summary, mean RPD values for laboratory and field replicates for MeHg and TOC/DOC met standard data quality objectives. This was particularly surprising for MeHg values considering that MeHg concentrations were within 1.5 to 2.5x laboratory MDLs.

These results confirm that laboratory data for MeHg – whether for total or dissolved concentrations, including in the river or in surface waters of Goose Bay, can be measured with an acceptably high degree of accuracy, particularly considering the proximity of measured values to the MDL.

# 5 Data Analysis

A full description of the statistical procedures applied to the October 2016 to September 2017 water quality data set is provided in **Appendix A**. Data were analyzed using a series of plots, supported by statistical analyses where warranted. Plots and analyses were implemented using R statistical software and associated packages. A total of 10 figures were generated, and are referenced within this Memo as **Figures A1** to **A10** respectively. **Table A1** depicts monthly mean and median values for total and dissolved MeHg (TMeHg; DMeHg in ng/L) and TSS concentrations (mg/L).

Two key assumptions were made during our interpretation of the water quality data. First, measurements at Station N1 (**Figure 1**), upstream of the impoundment are assumed to represent 'baseline' or reference conditions, including total and dissolved MeHg, against which downstream changes are evaluated. Second, measurements at stations N6 and N7, ~20 km and 40 km downstream of Muskrat Falls dam respectively, are assumed to represent 'fully mixed' conditions downstream of N4 (within impoundment) and N5 (immediately downstream of the dam). Water quality at these stations (N5 – N7) represents what is discharged to Goose Bay with the potential to influence water quality at Station N8 (**Figure 1**). Note that depending on timing of sampling some stations may not represent fully mixed conditions because of possible confounding by TSS (**Photo 1**).

**Photograph 1**. Sediment plume extending from N4 down the Churchill River; note confinement to south bank.

## *5.1 Initial Data Evaluation for Key Parameters*

Total Mercury

- Total mercury data (**Figure A1**) are limited because of naturally low ambient total Hg concentrations and an initial MDL that (AGAT Labs DL of 1.9 ng/L) that was too high. The MDL was lowered to 0.05 ng/L on June 28 when this analysis was switched to Flett Research. No particular patterns are evident during 2017 given the relatively high MDL of 1.9 ng/L. However, it should be pointed out that 1.9 ng/L is still a relatively low concentration and typical of many pristine systems (St. Louis et al. 2004, Driscoll et al. 2007, Bodaly et al. 2004, Krabbenhoft et al. 2007), and no different from values reported by Schartup et al. (2015).
- The only notable observation is that total Hg data in November 2016 (and December 2016 in some cases) are much higher than in any subsequent time period, and across most sites. This pattern is not observed for total dissolved MeHg, nor for TSS. Thus, the 2016 total Hg data appears anomalous and a lab error cannot be ruled out.

Total Suspended Solids

- Total suspended solids concentrations (**Figure A2**) were generally low throughout the system for most of the year except at N4 during March and at N5 from February through June. Elevated TSS was likely associated with slumping of mineral soils of riparian banks (e.g., Photo 1 above) caused by increases in water level elevation and possibly exacerbated by ice scour. In some cases, samples at N4 and downstream, reflected the influence of elevated TSS concentrations (relative to N1), which could influence total MeHg concentrations measured during those events. For example:
- TSS spiked at N4 only on March 7 (1170 mg/L) and 22 (388 mg/L) causing total MeHg to become elevated at 0.140 ng/L and 0.032 ng/L; dissolved MeHg was low and unchanged (0.014 ng/L). Water column TSS was elevated at surface, not at bottom.
- This March spike was observed far downstream at N7 as well (1570 mg/L), causing elevated total MeHg (0.148 ng/L), but not in dissolved MeHg (0.013 ng/L). No changes in water quality were observed at N8 in Goose Bay.
- AT N5, TSS spiked between February 15 (25 mg/L) and 28 (1230 mg/L) causing elevated total MeHg (0.037 and 0.14 ng/L respectively); again, dissolved MeHg remained low (0.013 ng/L) and unchanged.
- TSS was very high at N5 in March (mean 571 mg/L) and remained elevated throughout April to June (10 – 94 mg/L). While total MeHg was somewhat elevated (0.017 – 0.028 ng/L), dissolved MeHg remained consistent at 0.014 ng/L. TSS stabilized near 5 mg/L during summer.

In summary, spikes in TSS resulted in episodic elevations in total MeHg concentrations during discrete events, but did not alter dissolved MeHg values, which remained relatively constant. MeHg has a strong affinity for suspended matter, thus whenever TSS

is elevated, unfiltered (total) results for MeHg may also be affected (**Appendix A, Table 1**).

Total and Dissolved Organic Carbon

- The concentration of DOC relative to TOC was almost always >95%. Thus, while temporal TOC concentrations are depicted over time at each station (**Figure A3**) this plot is also a surrogate for DOC and key points are focused on trends in DOC (**Figure A4**).
- Concentrations of TOC / DOC in water were largely unchanged spatially from up (N1) to downstream (N7), even during very high, episodic TSS events (**Figure A3**). The absence of elevated TOC in the LCR, even during very high TSS events (>500 mg/L) suggests that suspended material in the water column consists of inorganic, mineral soils, not organic soils. There does not appear to be an export of allochthonous organic material to the river from the upstream impoundment.
- Seasonal patterns were evident however, with DOC concentrations increasing from 3.5 – 5 mg/L during cold months (November – April), to range from 6.0 – 8.0 mg/L between May and September. This was consistent at all stations, with no difference between N4 and downstream stations.
- The absence of an increase in DOC concentrations associated with flooding at N4 suggests a very slow decomposition rate that is overwhelmed by the large discharge volume (~ 1700 $m^3/s$). This is also supported by a recent Azimuth memo (2017b) that examined the proportion of 'labile' or easily decomposable carbon in humic soils. We found that about 1% of the organic matter in LCR soils readily converts to DOC when inundated.

The statistical analysis in **Appendix A** found that dissolved MeHg concentration and DOC were highly correlated (**Figure A12**). Many other studies have also observed a positive correlation in nature between DOC and dissolved MeHg (e.g., Mierle and Ingram 1991, St. Louis et al. 1994, Watras et al. 2003). For example, there is an acknowledged relationship between the co-transport of mercury species and humic matter from terrestrial watersheds and MeHg (Johansson and Iverfeldt 1994, Mierle and Ingram 1991). Watras et al. (2003) found that spring MeHg concentrations in Wisconsin lakes were 60-80% of the fall concentrations (95% C.I.), which implies a net gain of 20 – 40% during summer across all lakes. They attributed this to the accumulation of MeHg from autochthonous production and/or allochthonous inputs from the watershed. But it is not a simple story. While organic complexation may increase the substrate pool of available mercury for methylation, DOC can also bind MeHg, ultimately resulting in lower fish bioconcentration factors (McMurtry et al. 1989, Wren et al. 1991, Watras et al. 2003). Thus, water column dissolved MeHg concentrations may depend on how MeHg partitions, whether to DOC or to biota and seston (periphyton, phytoplankton, zooplankton, particulates).

Methylmercury

The fraction of total MeHg (**Figure A5**) that occurs in the dissolved phase (**Figure A6**) averaged 75% over the entire sampling period at all stations. The only exception to this

was at N5 (**Table A1**), and to a lesser extent N4, where very high TSS events caused spikes in total MeHg but not in dissolved MeHg as seen in **Figure A7**. The Spearman rank correlation coefficient between total MeHg and TSS for February and March, omitting data below MDLs, was 0.6 and highly statistically significant ($p<0.001$). There is little point in evaluating the correlation for other months, because TSS values are mostly below MDLs.

Notwithstanding these events, the ratio of dissolved to total MeHg was fairly consistent over time and spatially from N1 to N7 in the river, as well as at N8 (74%) in Goose Bay. Thus, most of the focus of our analysis has been on dissolved MeHg because this is the form that is fluxed from the flooded soils and existing sediment.

Some general patterns in MeHg concentrations within the LCR are as follows:

- At N1, the upstream reference station, total and dissolved MeHg concentrations (~0.026 / 0.030 ng/L; **Figure A6**) from October 2016 to February 2017 were higher than from all other stations and were even slightly higher than summer 2017 concentrations. This is an unusual pattern that was not observed elsewhere in the system; possibility of a lab error in these early data cannot be discounted. After February, the concentrations returned to a more expected pattern, with lowest concentrations in March and April (0.014 / 0.017 ng/L), increasing through the summer to peak in August (0.022 / 0.027 ng/L). This seasonal trend was also observed at all other stations.
- In the impoundment at N4, a pattern of seasonal change was also observed. In winter 2016, dissolved MeHg was ~0.013 ng/L. Dissolved and total MeHg concentrations increasing from 0.015 and 0.018 ng/L respectively in spring, to peak in September at 0.036 and 0.035 ng/L, about 25% higher than at N1.
- At N5, a similar seasonal pattern to N4 was observed. However, as pointed out above, total MeHg concentrations were affected by TSS, elevating monthly mean concentrations at N5 between March and June, such that MeHg concentrations here were similar to, or higher than at N4.
- At N6, 20 km downstream from N4, both total and dissolved MeHg concentrations were significantly lower than at N4/N5 in all months between October and April. From May to September, both total and dissolved MeHg concentrations at N6 were similar to or lower than N4/N5 concentrations.
- At N7, 40 km downstream of the dam at the river mouth, MeHg concentrations were similar to N6. Lower MeHg concentrations downstream of N4 at N5 – N7 may be reflective of natural within-river differences as well as other factors (e.g., demethylation), which are discussed below.
- In surface waters at N8 in Goose Bay, there was a similar seasonal trend as at N1. Dissolved MeHg increased from 0.010 – 0.011 ng/L in May, to 0.015 – 0.018 ng/L from June to September. Concentrations at the halocline (i.e., the transition zone wedge from fresh to salt water) were little changed over time and were very close to the laboratory MDL. There was no apparent increase in MeHg at N8 above seasonal trends that can be attributed to export from the impoundment.

The main observation from initial plots is that dissolved MeHg concentrations in the LCR generally increased from June through September, 2017. All sites, including N1, naturally exhibit elevated dissolved MeHg in summer months, presumably due to increased water temperature and nutritional inputs (TOC/DOC) associated with terrestrial runoff within the LCR mainstem and tributary streams. For example, we found a significant relationship between water column DOC and dissolved MeHg concentrations (**Figure A12**). DOC is a clear 'carrier' of MeHg and local inputs or changes to DOC may have confounding, site-specific effects on ambient MeHg concentrations.

The key questions are: a) has water column dissolved MeHg increased in the impoundment (N4) over and above natural seasonal changes also observed at the upstream 'reference station' N1?; b) has any increase at N4 persisted at downstream stations N5 to N7 in the Lower Churchill River?; and c) what are the implications if any, downstream of the river into the estuarine environment (in Goose Bay at N8)?

## *5.2 Within River Differences in Dissolved MeHg*

Methylmercury concentrations in the LCR are among the lowest observed in pristine systems, with baseline concentrations just above the Flett Laboratory MDL of 0.01 ng/L. Notwithstanding this challenge, it appears that the Flett data are accurate and reliable based on the following three lines of evidence: 1) results of the 10 + 10 study confirmed good precision based on RPD values examining both field and laboratory variability; 2) the ratio between total and dissolved concentrations was very consistent over time, despite being very close (i.e., dissolved constitutes ~75% of the total); and 3) data from N5 to N7 collected on the same day are very similar, as expected in a riverine system where only minor differences would be expected. This gives us confidence that impoundment-related trends in MeHg concentration can be detected.

To determine whether dissolved MeHg concentrations increased at stations downstream of N1 (N4 to N8), we first estimated monthly station means using a Bayesian model (Gelman et al. 1995, Gelman and Hill 2007) and then calculated ratios of monthly means at all other stations relative to N1. The advantage of this Bayesian approach, versus simple point estimates or ANOVA-type estimates, is: (a) it provides posterior distributions for monthly means that can be easily used to generate posterior distributions for ratios versus N1; (b) it accounts for differing numbers of replicates across site/month combinations; and (c) is flexible, easily allowing for different variance structures within or among sites to be specified. An accounting of the statistical approach and decisions are provided in **Appendix A**. Further information regarding our decision making-process regarding various approaches is available upon request.

There was clear evidence of differing sample variation in dissolved MeHg values across months at N1, with much higher variation and higher concentrations for early months (up to and including February 2017) compared to later months (**Figure A6**). The effect of higher reference MeHg concentrations at N1 relative to other stations in the earlier months pushes the ratios to N1 lower at all other downstream stations in the early months. This has some consequences for the analysis as discussed below.

Monthly means[1] for dissolved MeHg concentrations by station are depicted in **Figure A8**, which is reproduced here. There are two key observations related to the data, which confirm earlier patterns observed for the raw data:

- The 95% credibility intervals for N1 means up to and including February 2017 are wide – this is consistent with the high variability in the raw data observed for this month in **Figure A6** (**Appendix A**) and has implications as discussed below.
- All sites except N8 show a general and consistent seasonal pattern of increase in dissolved MeHg concentration from March to September, although the raw data (**Table A1, Figure A6)** suggest a decline starting in mid-September.

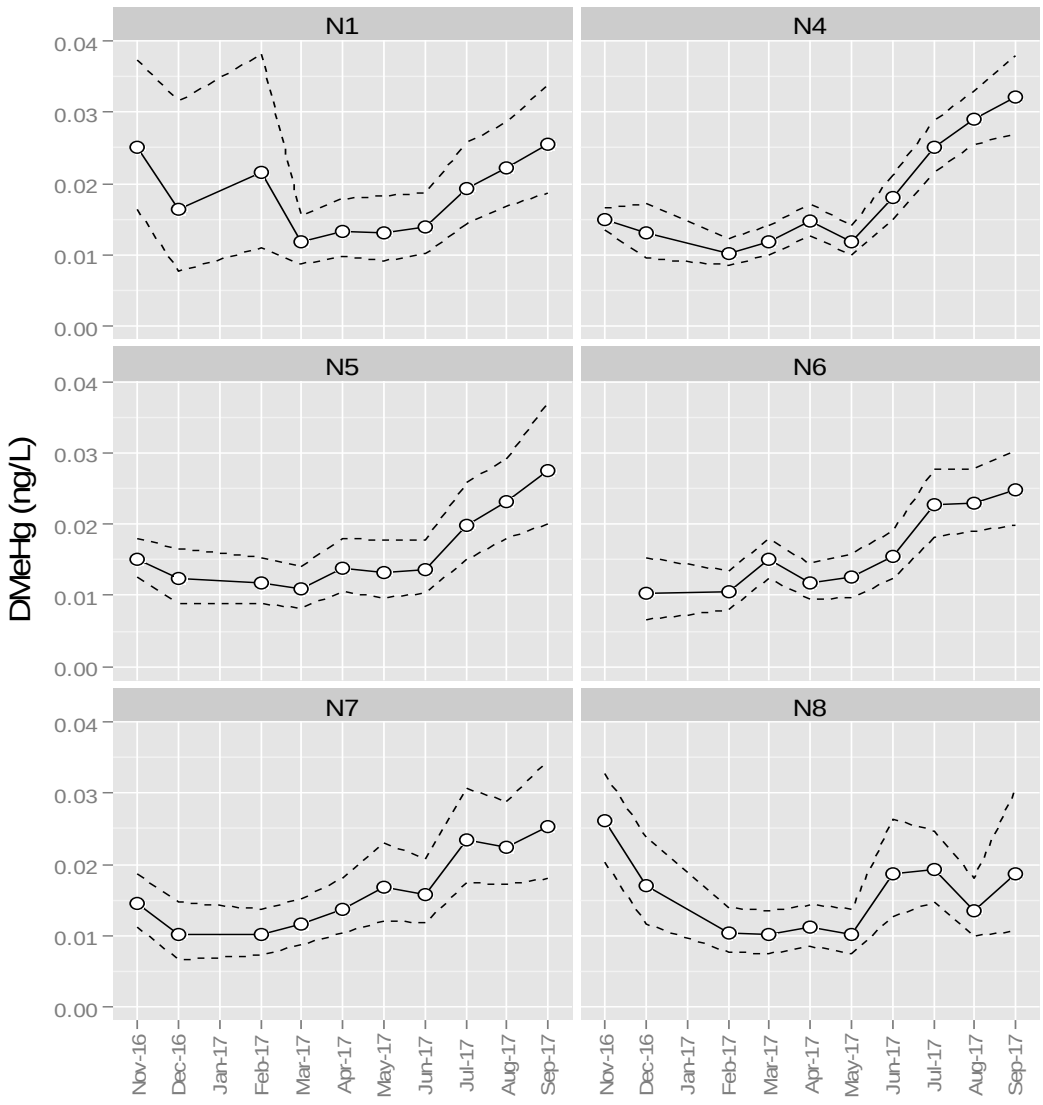



**Figure A8**. Bayesian posterior means and 95% credibility intervals for monthly means by site.

[1] The means of the posteriors are very similar to the averages of raw monthly values, except in a few cases with highly divergent measurements (e.g., Feb-17 at N1); in these cases, the means of the posteriors are very similar to the geometric mean of raw values.

Ratios of the Bayesian posterior distributions for monthly means by site versus those for N1are shown in **Figure A10** (**Appendix A**) In general, the broad overlap of the 95% credibility intervals with a ratio = 1.0 indicates little evidence of differences between site means and those for N1 for any given month. General patterns in dissolved MeHg are as follows:

- Means at N4-N7 are lower than at N1 for November-February.
- Means at N1 and N4 were similar from March-May
- Mean MeHg concentrations were higher at N4 than N1 from June through September, suggesting that dissolved MeHg increased at a greater rate within the impoundment during summer than upstream.
- Means at N5, N6, and N7 were intermediate between N1 and N4 from March-August, with very small absolute differences (~0.003 ng/L). There was no difference between N1 and N5 – N7 in September.
- Although the 95% credibility intervals for the N4:N1 ratios overlap 1.0 for each of the months June to September, there is a clear pattern of higher dissolved MeHg at N4 than at N1 over this period.
- At N8, means do not follow the consistent patterns observed for N4 to N7, being generally similar to N1 means across months, with fluctuations.

Using data from **Table A1**, **Table A2** below depicts the *largest* within month differences in MeHg concentration between N1 and all other stations. In August 2017 this was 0.007 ng/L (a 33% increase over N1; reflected in **Figure A8** above). Note that all of these differences are less that the laboratory DL of 0.01 ng/L and while detectable, they are extremely low.

| Site | Month | Ratio | Difference (ng/L) |
|---|---|---|---|
| N4 | Jun-17 | 1.32 | 0.004 |
| N4 | Jul-17 | 1.33 | 0.006 |
| N4 | Aug-17 | 1.33 | 0.007 |
| N4 | Sep-17 | 1.29 | 0.007 |
| N6 | Jul-17 | 1.20 | 0.003 |
| N7 | Jul-17 | 1.24 | 0.004 |
| N8 | Jun-17 | 1.38 | 0.005 |

## *5.3 Time Trends in Dissolved MeHg in the Impoundment and Downstream, Relative to Upstream*

Statistical means were used to compare trends in dissolved MeHg over time at each of N4 to N8, relative to N1. Our ability to evaluate time trends is limited because of lack of data from the 'pre-impoundment' period. We also do not know if there are any natural intra-riverine differences (e.g., proximity to wetlands or inputs from tributaries) in MeHg between N1 and other stations that existed before impoundment. We also have few seasonal, baseline data at N8. Consequently, we must conservatively assume that in the

absence of impoundment, all stations N1 to N8 would have similar temporal patterns of dissolved MeHg.

We used mixed-effects models to test for differences in dissolved MeHg trends that might be related to impoundment. It is only since February that N4 has been continuously impounded; consequently, and recognizing the limited data prior to February, we evaluated time trends for February 2017 onwards. However, the data at N1 for February contains two extremely high values, including the highest value in the whole dataset, plus two values at or near the MDL. Therefore, we also fit the models with and without February.

Results are provided in **Table A3**. With February included, there was a statistically significant increase in slope (time trend) for N4 relative to N1 (with an average monthly increase of about 11%), and a marginally significant increase in slope for N5 (average monthly increase of about 6%). Estimates for N6 – N8 were positive but not statistically significant. Importantly, these results were largely driven by the high February N1 data. When February data were excluded, the increase in slope for N4 relative to N1 was marginally significant (with an average monthly increase of about 5%). There was no evidence of differences for the remaining sites; i.e., all stations had dissolved MeHg trends similar to that for N1.

These results are consistent with the observed ratios of means discussed in the previous section. It is evident that MeHg concentrations at N4 generally increase relative to N1 across summer months, whereas for stations N5 – N8, there is little evidence of systematic differences with N1 monthly means except for the low ratios associated with February.

**Table A3**. Estimates of differences in time trends of DMeHg relative to site N1.

| | Data for Feb-Sep | | | | Data for Mar-Sep | | | |
|---|---|---|---|---|---|---|---|---|
| Site | Est | SE | P-value | Change | Est | SE | P-value | Change |
| N4 | 0.103 | 0.032 | 0.018 | 1.11 | 0.049 | 0.029 | 0.089 | 1.05 |
| N5 | 0.060 | 0.035 | 0.093 | 1.06 | 0.017 | 0.034 | 0.620 | 1.02 |
| N6 | 0.051 | 0.043 | 0.281 | 1.05 | -0.015 | 0.031 | 0.639 | 0.99 |
| N7 | 0.065 | 0.042 | 0.152 | 1.07 | -0.001 | 0.035 | 0.973 | 1.00 |
| N8 | 0.023 | 0.052 | 0.675 | 1.02 | -0.029 | 0.044 | 0.524 | 0.97 |

Notes: “Change” (= exp[Est]) provides an estimate of the monthly proportional difference relative to site N1 (e.g., 1.05 indicates a 5% monthly increase in DMeHg relative to site N1).

# 6 Discussion and Summary

## *6.1 Site-Specific Terrestrial Features and Methylation Potential*

Inundation of the Lower Churchill River above the Muskrat Falls dam to an elevation of 21 m (about 5-6 m above the pre-flood baseline) has flooded 1168 ha of terrestrial habitat. Of this, 195 ha consists of terrain with an established humic soil horizon. Much larger portions inundated at this elevation consist of gravel bars (562 ha) with no organic material and riparian habitat (409 ha) with minimal or no organic soils containing a humic layer (AMEC 2017).

The humic horizon beneath the litter layer of newly inundated soil is the principal source of raw materials (i.e., inorganic Hg and carbon) for MeHg generation that is fluxed to overlying surface water of new reservoirs (Povarti and Verta 1995, Bodaly et al. 1997, 2004, Hall et al. 2005). Furthermore, it is only the top few cm of this layer that is the major contributor to this flux. For example, the figure below from Eckley et al. (2015) clearly showed high MeHg generation in the top 0 – 2 cm of seasonally inundated soil/sediment of the Cottage Grove Reservoir in Oregon compared to deeper depths. 'Old' reservoir sediments were no longer a significant source, based on % contribution. Recently, a similar phenomenon was observed at the Experimental Lakes Area (ELA) where 'old' reservoir soils still retained high MeHg concentrations in the top few cm of the humic layer (Rolfhus et al. 2015). This phenomenon has also been observed elsewhere (e.g., He et al. 2007, Goulet et al. 2007, Feng et al. 2011).

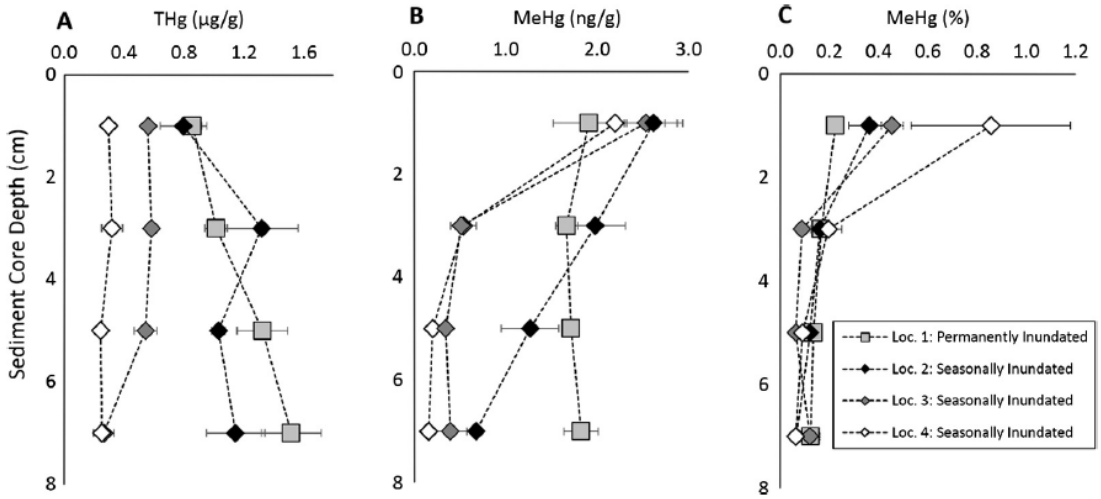



**Figure 2**. Sediment total mercury (THg) and methylmercury (MeHg) from permanently and seasonally flooded sediment, Cottage Grove Reservoir OR (from Eckley et al. 2015).

Understanding flooded sediment redox conditions is also important in determining the depth of MeHg generation that is available to be fluxed upwards. MeHg flux from sediment is strongly regulated by changing redox processes (e.g., Gill et al. 1999) that occur in the upper few centimeters, including on a diurnal cycle. Daylight increases benthic primary production, leading to more oxygenated interfacial water and formation

of iron and manganese oxides that can sequester and attenuate the upward diffusion of MeHg from porewater. There is no reason to doubt that similar redox processes occur in flooded soil in this region, possibly limiting fluxes of MeHg to overlying water.

There is no dispute that flooding of organic, terrestrial soils should cause an increase in MeHg production in new reservoirs, including this one. However, the timing and magnitude of this production is dependent on many physical and chemical factors. The most important of these are areal extent of humic soils and abundance relative to total reservoir size, the proportion of wetland habitat flooded (St. Louis et al. 1994), water residence time / discharge rate, water pH (optimum MeHg generation occurs at pH 5.5 – 6.5) and the abundance of key 'nutrients' in sediment, especially sulphate and an available source of labile carbon and inorganic mercury (Verta et al. 1986, Johnson et al. 1991, Hurley et al. 1995, Bodaly et al. 2007, Azimuth 2012). The role of water temperature is a bit uncertain but the consensus is that more MeHg will be generated in bottom sediments exposed to warmer temperatures (i.e., >10C) than cold temperatures. This is explored further below.

Lower Churchill Reservoir soils and reservoir features appear unremarkable with respect to methylation potential. At 21 m elevation only 5% of the total flooded area consists of forested / wetland habitat with a thin (~8 cm) but established humic horizon, and a typical organic carbon content (20 % - 50%) (AMEC 2017) of which a small fraction is labile (Azimuth 2017b). Total mercury concentration in LCR forested soil (0.05 – 0.20 mg/kg) is similar to or lower than soil Hg concentrations measured elsewhere (0.01 to 0.2 mg/kg) in boreal soils in Canada and Scandinavia (McKeague and Kloosterman 1974, Rasmussen 1994, Lodenius 1994, Azimuth 2012).

Given these site-specific baseline conditions and the small area of flooded terrestrial habitat with established humic soils, the magnitude of MeHg fluxed to overlying surface waters at 21 m elevation is likely relatively low. While the potential contribution of riparian areas to methylation is uncertain, given their low mercury signature and lack of humic soil horizon, we believe that this habitat makes a negligible contribution to Hg methylation potential.

It should be pointed out that Schartup et al. (2015) stated that 'Virtually all the planned flooded region (41 $km^2$) will be inland soils with an intact litter layer, in some cases also covered by vegetation and trees'. Furthermore, Calder et al. (2016) used "satellite data to determine the organic carbon content of the upper 30 cm of soil" in the proposed reservoir. The Calder et al. (2015) assumptions appear to be conservative and do not reconcile with empirical terrestrial conditions established by the AMEC (2017) soil survey. This may have implications with respect to modeled methylation potential as discussed further below.

## *6.2 Site-Specific Aquatic Baseline Conditions*

As mentioned at the outset, the IEAC had four main concerns, each of which are addressed here.

1. Lack of adequate pre-impoundment baseline data, especially during previous spring and summer seasons against which to compare MeHg concentrations in relation to water level increases;
2. A hesitation to casually link transient increases in MeHg concentrations in water post-February, given this was not observed in the November inundation period;
3. Inability to separate higher water levels and higher water temperature on increased variability in MeHg concentrations, observed between the headpond and Goose Bay since February; and
4. A temperature dependence of MeHg production means there is a lag time before water level driven changes in MeHg are observed in the reservoir and downstream, which may perhaps explain a lack of obvious response over the short time frame to the end of May. Summer data may be more conclusive.

Although baseline, pre-flood water column mercury data are limited, empirical Hg data collected since October are similar to Harvard data between 2012 and 2015. Schartup et al. (2015) recorded mean MeHg concentrations of 40 and 68 femtomolar (fM; $10^{-15}$ moles/L) in tributary streams in September 2012 and June 2013, which are equivalent to 0.008 ng/L and 0.014 ng/L respectively. More recently, Calder et al. (2016; Supplementary Table S4) reported average MeHg concentrations of 0.027 ng/L in winter, 0.023 ng/L in spring, 0.005 ng/L in summer and 0.011 ng/L in fall 2013 – 2015. They did not state why their summer/fall values are low and opposite to the observed trend in 2016 – 2017 data of highest MeHg concentrations in summer.

In the current dataset, baseline MeHg concentrations in the LCR ranged from the MDL of 0.01 ng/L to ~ 0.03 ng/L. With the exception of a few episodic TSS related events, at least 75% of the measured total MeHg concentration is in the dissolved phase – so comparisons of spatial and temporal patterns using dissolved MeHg, is reasonable. It is noteworthy that the percentage of total mercury in water that occurs as MeHg typically ranges from 1% to 10% (Hurley et al. 1995, Krabbenhoft et al. 1999, St. Louis et al. 1995, Bodaly et al. 1997, 2004). In the LCR, average MeHg concentration in the LCR was <2% of total mercury concentration.

Thus, several years of occasional MeHg measurements in water by the Harvard scientists and nearly one full year of data at station N1 are fairly consistent to each other. However, there is certainly variability in the pre-impoundment data, both seasonally and between years – to a greater magnitude than has been observed within the impoundment. While the MeHg data set is somewhat constrained and would benefit from a longer baseline database, the range in MeHg concentrations observed between October 2016 and September 2017 is not atypical and is consistently low. As we note, there is no information indicating whether or not there are natural within-river differences in MeHg. So, it must be assumed that N1 concentrations for the one-year period between October 2016 to September 2017 are representative of what we would expect throughout the LCR under natural conditions (i.e., no impoundment). To the extent that this assumption is reasonable, the first concern of the IEAC is addressed.

The next three concerns expressed by the IEAC are related and speak to possible effects of water temperature and a potential ‘time lag’ in MeHg production since flooding in November and again in mid-February. Lack of methylation in cold water has been

implicated as to why no differences in water column MeHg were observed between N1 and N4 – N7 between February and May 2017.

The influence of temperature on the timing and magnitude of MeHg production in newly flooded soils is somewhat uncertain because it has not been well studied. While methylation appears to be higher during warm, summer months, methylation certainly occurs over winter in cold water in northern Canadian reservoirs (Schetagne and Verdon 1999, Schetagne et al. 2003, Bodaly et al. 2007), given the magnitude of increase in fish mercury concentrations observed there.

Based on the empirical evidence, three things are clear: 1) all stations demonstrated a clear seasonal increase in both total and dissolved MeHg between June and September. This may be due to a combination of higher water temperatures and inputs of autochthonous and allochthonous carbon (TOC/DOC) from upstream and local tributary sources; 2) temporary impoundment in November 2016 and re-flooding in mid-February did not produce a clear MeHg water column signal until May (Azimuth 2017a; **Table A1**) and 3) dissolved water column MeHg concentrations were slightly higher at N4 within the impoundment (0.004 – 0.007 ng/L) than upstream at N1, from June to September 2017.

Note that in the Schartup et al. (2015) soil incubation experiment described above in **Section 3.4**, they reported a 14-fold increase in MeHg concentration after only 5 days in the overlying water column flooding of humic soils. While the temperature of incubation was not reported, this rapid response by the bacterial community suggests the 'lag' due to cold water temperature would likely be on the order of weeks, not months. The small, delayed response at N4 is more likely due to the relatively small area of terrestrial habitat flooded with an established humic horizon described in **Section 3.4**.

In summary, 11 months of water chemistry information from the LCR focused on MeHg showed a distinct seasonal component throughout the river between N1 and N7 and extending into Goose Bay. A definite 'signature' of elevated MeHg evolved within the reservoir at N4 beginning in June 2017 (**Table A1, Figure A8**) that has persisted through September, despite the relatively short water residence time (~1 day) within the small, shallow (5 m deep) reservoir. The final section explores the magnitude and significance of MeHg generation in N4 and its persistence downstream.

## *6.3 Summary of Spatial and Temporal Patterns of Water Column MeHg in the Lower Churchill River*

Dissolved water column MeHg concentrations were slightly higher at N4 within the impoundment (0.004 – 0.007 ng/L) than upstream at N1, from June to September 2017 (**Table A1, Figure A6**). This small magnitude of change is about half the laboratory MDL of 0.01 ng/L. Prior to this time, mean monthly concentrations at N4 were either similar to, or lower than at N1. As discussed above, the low magnitude and absence of change within the impoundment prior to June is likely due to a combination of factors including cool water temperatures, lower rates of local inputs of autochthonous and allochthonous carbon, the small area of organic soils flooded and short residence time within the impoundment. Looking downstream from N4, the magnitude of change within the LCR relative to N1 is even smaller, as shown in **Figure A10** (below).

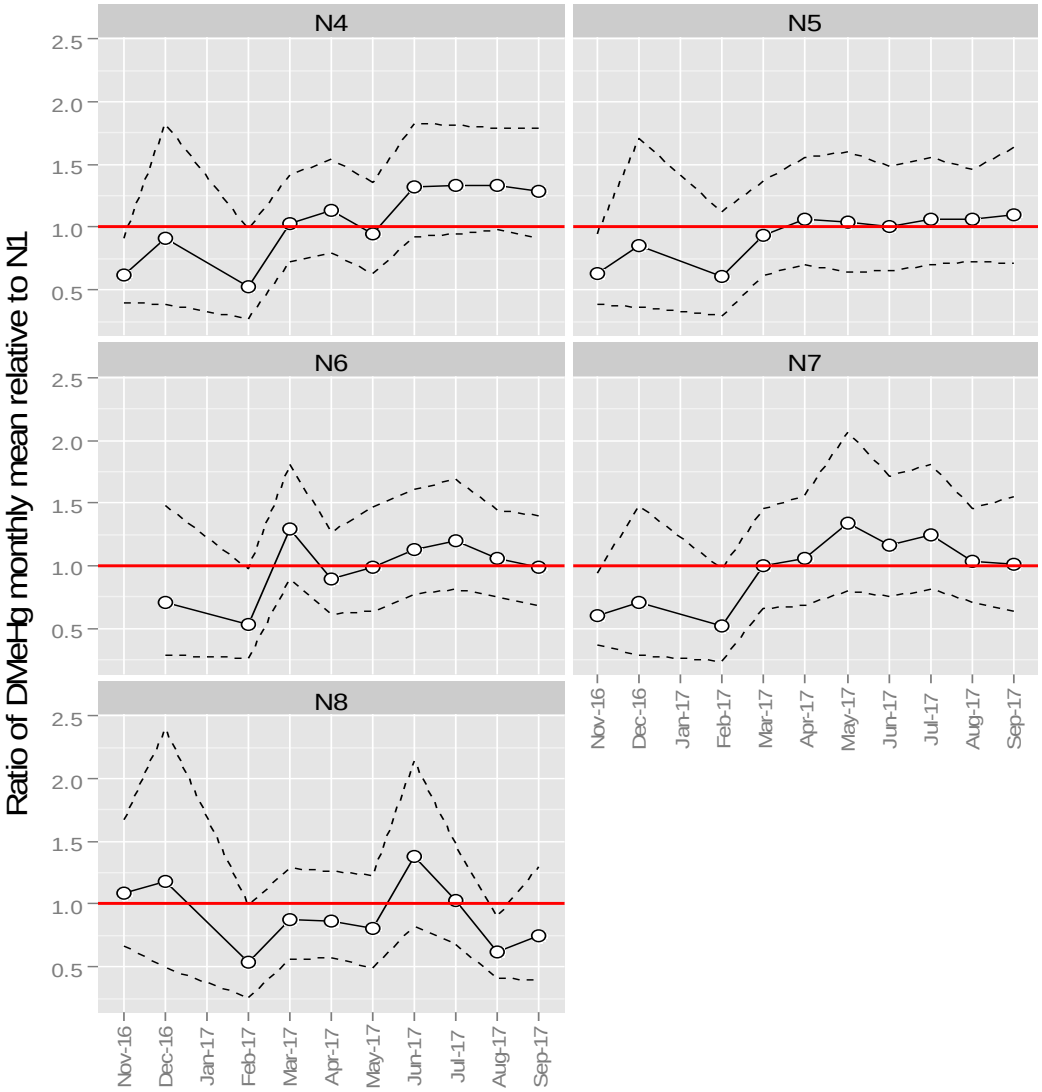



**Figure A10**. Ratios of the Bayesian posterior distributions for monthly means by site versus those for N1.

Notes: Red line at ratio of 1. Points above the line indicate higher monthly mean than N1. Points below the line indicate lower monthly mean than N1

This plot clearly shows that dissolved MeHg concentration at N4 is consistently elevated above N1 from June to September 2017, but that dissolved MeHg concentrations at N5 and N1 are very similar. While there is a suggestion of slightly higher MeHg during May/June at N6 and N7, the differences are very small (<0.003 ng/L) and well within the range of natural variability and possible natural intra-riverine differences. This plot clearly demonstrates that monthly MeHg concentrations downstream of the reservoir between N5 and N7 at the river mouth are marginally higher or no different from upstream.

Both Schartup et al. (2015) and Calder et al. (2016) acknowledge that a progressive loss of MeHg should be expected moving downstream of the reservoir, due to demethylation (and partitioning to other media). Demethylation through photodegradation via interaction with solar radiation (e.g., Sellers et al. 1996) has been shown to be an

important driver of water column loss of MeHg. In addition, absorption and uptake by the biotic component of the river including periphyton, phytoplankton, benthos and fish, as well as adsorption of MeHg by seston and other particulates in the water column such as TSS will 'remove' MeHg. Also, DOC has been shown to be a strong moderating factor of MeHg, including in this study. For example, **Figure A12** shows a clear positive correlation between DOC and dissolved MeHg, partly explaining seasonal changes in MeHg concentrations in the LCR between winter/spring and summer. For example, Miskimmin et al. (1992) demonstrated that increased concentrations of DOC decreased net methylation rate, possibly because of a complexation between DOC and inorganic mercury. Ravichandran (2004) and others report that dissolved organic matter interacts very strongly with inorganic and methylmercury, affecting its speciation, solubility and availability in the aquatic environment.

Notwithstanding the above, **Figure A10** clearly demonstrates that monthly dissolved MeHg concentrations downstream of the impoundment between N5 and N7 are lower than at N4 and that there does not appear to be a consistently detectable increase in MeHg discharged to Goose Bay relative to what is observed at N1. Assuming that downstream concentrations in the LCR are similar to upstream 'reference' values, surface water values at N8 in Goose Bay are independent of MeHg concentrations, even after nearly 9 months of impoundment (**Figure A6**).

It is also reasonable to assume that in the absence of an increase in MeHg delivered by the LCR to Goose Bay as a result of the impoundment, that no change in downstream biota mercury concentrations should be expected – either within the river, or extending into Goose Bay and beyond. Implementation of the planned zooplankton sampling program will monitor this.

Given the very small increase in MeHg within the reservoir and lack of change downstream, this begs the question why hasn't a greater change occurred? Calder et al. (2015) predicted that water column MeHg concentrations in the reservoir and LCR would increase about 10x above baseline concentrations, to peak near 0.20 ng/L at full reservoir elevation. Furthermore, they stated that 'substantial increases in MeHg will occur in the downstream estuary from flooding of the Muskrat Falls reservoir' and that 'mean MeHg concentrations in Lake Melville surface waters will increase 2.6-fold'.

Flooding of the LCR to 21 m elevation has impounded 27% of the reservoir area relative to full elevation. Yet a much smaller proportional increase in MeHg has been observed within the impoundment and little detectable change downstream. Possible reasons why a proportionally larger increase has not been observed may include low abundance of flooded habitat containing established humic soils, low inorganic mercury content of forest soil, poor methylating conditions (cold water, circumneutral pH), conservative assumptions regarding MeHg generation in flooded soils and water column flux and MeHg absorption / adsorption to biota and seston in the water column.

We speculate that raising the impoundment to 25 m may further increase water column MeHg concentrations, but is not likely to produce the magnitude of increase predicted by Calder et al. (2016), based on the empirical evidence collected to date. Ongoing data collected through the remainder of 2017 and 2018 will strengthen and allow for improved resolution of spatial and temporal trends in LCR MeHg concentrations.

# 7 References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**Azimuth Consulting Group Partnership – November 2017**

**Appendix A – Statistical Analysis of Lower Churchill River Water Quality**

This appendix contains plots and statistical analyses of water quality data in support of Azimuth's October 2017 Technical Memorandum. The sections of this appendix include:

- Summary of available data
- Initial data evaluation
- Analysis of differences in DMeHg between the Impoundment (and downstream) and upstream
- Analysis of time trends in DMeHg in the impoundment and downstream, relative to upstream
- Relationship between DMeHg and DOC
- Other modelling approaches
- Conclusions

## 1. Available Data

Water chemistry data were provided to Azimuth by Nalcor Energy (St. John's Newfoundland), in an excel spreadsheet compiled by AMEC Foster Wheeler. Water samples were collected by AMEC on an approximately weekly basis for most of the period between October 2016 and September 2017. Laboratory analyses for all parameters except total and dissolved methylmercury (TMeHg / DMeHg) were by AGAT laboratories. Methylmercury analyses were by Flett Laboratories, Winnipeg MB. From June 2017 onwards, total inorganic mercury (THg) samples were also analysed by Flett.

Data can be summarized as follows:

- Data were available for the period October 2016 to September 2017 (12 months). In most months, including the most recent 8-month period February to September 2017, samples were collected weekly.
- Mercury variables were THg, TMeHg and DMeHg. All mercury data were standardized to units of ng/L.
- THg was based on the Flett lab data when available (after June 2017) because of its lower detection limits. Prior to the analysis of THg by Flett, the original AGAT Laboratories data were used.
- Raw data did not include any values below method detection limits (MDLs) where the sample-specific MDLs were elevated above the range of observed data. Therefore, no data points were removed due to sample-specific elevated MDLs.
- Sites considered in the analysis were N1, and N4 to N8. There were virtually no data for N2 and N3, so these were ignored. N9 to N13 are downstream of the estuary, so these too were ignored.
- Data for N8 were limited to surface samples only, to avoid including samples at or below the halocline.
- Several supporting variables were measured. Analyses focused on dissolved and total organic carbon (DOC / TOC) and total suspended solids (TSS) because these are most likely to affect MeHg.

## 2. Initial Data Evaluation

The general question of interest is whether concentrations of MeHg have increased in the impoundment (N4) and downstream (N5 to N8), beyond any seasonal patterns that might be expected naturally (as represented by N1 upstream). Plots were used initially to explore this question, supported by subsequent statistical analyses.

Plots of the data are provided as follows:

- Time series by site for THg (**Figure A1**)
- Time series by site for TSS (**Figure A2**)
- Time series by site for TOC (**Figure A3**)
- Time series by site for DOC (**Figure A4**)
- Time series by site for TMeHg (**Figure A5**)
- Time series by site for DMeHg (**Figure A6**)

For a subset of the variables – DMeHg, TMeHg and TSS – monthly summary statistics are provided in **Table A1**.

The general patterns observed in the data are as follows:

**Total Mercury** – The data for THg are limited because of naturally low ambient THg concentrations and a detection limit that was too high to detect this prior to June 2017. The only notable observation is that November 2016 data (and December 2016 data in some cases) are much higher than in any subsequent time period. This pattern is not observed for TMeHg or DMeHg, nor for TSS. Thus, the 2016 THg data appear anomalous.

**Total Methylmercury** – There were a few spikes in TMeHg during February/March 2017 in the impoundment (N4) and downstream (most notably at N5). These spikes were clearly associated with high sample values of TSS (**Figure A7**). The Spearman rank correlation coefficient between TMeHg and TSS for those two months, omitting data below MDLs, was 0.6 and highly statistically significant ($p<0.001$). There is little point in evaluating the correlation for other months because TSS values are mostly below MDLs.

**Dissolved Methylmercury** – The main observation from initial plots is that DMeHg has generally increased from June to September 2017 at all sites. The same pattern appears for TMeHg, but to a much lesser degree. The <u>key question</u> is whether water column DMeHg has increased in the impoundment (N4) – over and above seasonal changes that occur naturally (including at the upstream 'reference' station N1) – due to MeHg flux from the newly flooded soils. We also consider whether any observed patterns in the impoundment are also observed at downstream stations N5 to N7 in the Lower Churchill River, or in the estuarine station at Goose Bay N8. We also note that DOC appears to have some relationship with DMeHg, which is further examined below.

## 3. Analysis of Differences in DMeHg Between the Impoundment (and Downstream) and Upstream

Methods

To determine whether DMeHg at downstream sites (N4 to N8) has increased relative to N1, we first estimated monthly means by station, and then calculated ratios of monthly means relative to N1.

A Bayesian model (Gelman et al. 1995, Gelman and Hill 2007) was used to estimate monthly means by site. The advantage of this approach, versus simple point estimates or ANOVA-type estimates, is that the Bayesian approach (a) provides posterior distributions for monthly means that can be easily used to generate posterior distributions for ratios versus N1; (b) easily accounts for differing numbers of replicates across site/month combinations; and (c) is flexible, easily allowing for different variance structures within or among sites to be specified.

There are two key components of a Bayesian model that must be specified: the likelihood function and prior probability distribution (prior). The likelihood function for our model was as follows:

(1) $$\log(y_{ijt}) \sim \mathrm{N}(m_{jt}, \sigma_j^2),$$

which simply states that for a given site $j$ and month $t$, the logarithms of observed DMeHg values ($y_{ijt}$) are assumed to be normally distributed with mean $m_{jt}$ and variance $\sigma_j^2$. Here, the variances for observations are assumed to be site-specific, but could be grouped across sites, etc. The priors for the mean parameters ($m_{jt}$) were specified as extremely diffuse normal distributions, while the priors for sigma parameters ($\sigma_j$) were specified as very broad uniform distributions[1]. These are conventional "noninformative" priors (e.g., Gelman and Hill 2007, Kery 2010) that are intended to have essentially no influence on parameter inferences; that is, they are intended "to let the data speak for themselves" (Gelman et al. 1995, p. 52).

The combination of the likelihood function and prior provides a posterior probability distribution (posterior) for the model parameters. To fit a given Bayesian model, we used the software OpenBUGS called from R (Sturtz et al. 2010, see Gelman and Hill 2007 and Kery 2010 for example applications). The BUGS package uses an MCMC (Markov chain Monte Carlo) algorithm based on the Gibbs sampler to approximate the posterior distribution of a Bayesian model, providing a "sample" of the posterior of arbitrary size. In general terms, when the sampling algorithm converges well, a sample posterior of sufficient size provides a very accurate and complete statistical inference for the parameters, from which we can compute the mean, variance, percentiles, etc. for a given parameter, as well as the covariance among parameters. For a given model, each of three randomly-seeded MCMC sampling chains were simulated for 30000 iterations, which provided excellent convergence. The final 2000 iterations of each chain were kept, providing a sample of 6000 parameter combinations for the joint posterior distribution of all parameters.

Models were fit to monthly data for sites N1 and N4-N8 for all months except October 2016 and January 2017. For October 2016, there was only a single sample collected at most sites (with a DL value for

[1] i.e., m ~ N(0, 10000) and sigma ~ Uniform(0, 100)

DMeHg at site N1), which did not allow for meaningful estimates or comparisons with N1. Similarly, January 2017 was excluded because of limited samples (a single sample at sites N6 and N8 only).

There was clear evidence of differing sample variation in DMeHg values across months at site N1, with much higher variation for early months (up to and including February 2017) compared to later months. To provide more precise (reliable) estimates of monthly means for N1 in later months, we used two sigma parameters ($\sigma_j$) for this site in our final model (one for months up to and including February, and one for months after February)[2]. We also examined models with common variance terms for sites N4-N8, which had similar estimates for $\sigma_j$; however, results were essentially identical to the model with site-specific parameters, for which results are reported below.

A key benefit of our Bayesian approach was that it allowed for rigorous comparisons of monthly means between N1 and the other sites. Specifically, we used the joint sample posterior for monthly means to compute the posterior distributions for differences and ratios in means compared to site N1. For example, the posterior samples for mean DMeHg at a given site can be divided by the posterior samples for N1, providing posterior distributions for the ratio of monthly means.

Results

Monthly means[3] for DMeHg by sites are provided in **Figure A8**. There are two key observations related to the data, which confirm earlier patterns observed for the raw data:

- The 95% credibility intervals for N1 means up to and including February 2017 are wide – this is consistent with the high variability in the raw data observed for this month in **Figure A6**.
- All sites except N8 show a general and consistent pattern of increase in DMeHg concentration from March to September, although the raw data (**Figure A6)** suggest a decline starting in mid-September.

Standardized residuals[4] of DMeHg for the Bayesian model of monthly means are shown in **Figure A9.** There was little evidence of spatial or temporal correlation among residuals. This is not surprising because the monthly means themselves capture the dominant patterns of spatial and temporal correlation among sites (e.g., compare means in **Figure A8** with raw data **Figure A6**).

Ratios of monthly means at N4 to N8 relative to N1 are shown in **Figure A10**. In general, the broad overlap of the 95% credibility intervals with a ratio = 1.0 indicates little evidence of strong differences between site means and those for N1 for any given month. General patterns are as follows:

- Means at sites N4-N7 are generally lower than at N1 for November-February.
- Means at N4 were similar to N1 from March-May, but higher at N4 from June-September.

[2] The DIC (deviance information criterion) for the model with a single sigma (across all months at N1) was 132.1, whereas the DIC for the two-sigma model was 123.1. Thus, the two-sigma model for N1 was clearly superior (see Gelman and Hill 2007 for information on DIC).

[3] The means of the posteriors are very similar to the averages of raw monthly values, except in a few cases with highly divergent measurements (e.g., Feb-17 at N1); in these cases, the means of the posteriors are very similar to the geometric mean of raw values.

[4] For a given month and site, standardized residuals for each (log) sample value were computed by subtracting the posterior mean of the monthly mean parameter and dividing by the posterior mean for the sigma parameter.

- Means at N5, N6, and N7 were similar to or slightly higher (~0.005 ng/L) than those for N1 from March-August. There was no difference in September.
- Means at site N8 do not follow the consistent patterns observed for N4 to N7; they are generally similar to N1 means across months, with fluctuations. In the near absence of differences at N6/7, this is not surprising.
- Although the 95% credibility intervals for the N4:N1 ratios overlap 1.0 for each of the months June to September, there is a clear pattern of higher DMeHg at N4 than at N1 over this period.
- For sites N4-N8, the largest positive differences relative to N1 are shown below in **Table A2**. For these cases, the maximum difference in monthly means in absolute terms was 0.007 ng/L (Aug-17 at N4, a 33% increase over N1).

**Table A2**. Maximum difference in DMeHg concentration difference by month between N1 and downstream stations.

| Site | Month | Ratio | Difference (ng/L) |
|---|---|---|---|
| N4 | Jun-17 | 1.32 | 0.004 |
| N4 | Jul-17 | 1.33 | 0.006 |
| N4 | Aug-17 | 1.33 | 0.007 |
| N4 | Sep-17 | 1.29 | 0.007 |
| N6 | 17-Jul | 1.20 | 0.003 |
| N7 | 17-Jul | 1.24 | 0.004 |
| N8 | 17-Jun | 1.38 | 0.005 |

In conclusion, the data provide some evidence of higher DMeHg at N4 than at N1 in recent months June to September. For N5 to N7, DMeHg is similar to or slightly higher than at N1 over the last 6 months. At N8 DMeHg concentrations show some seasonal trends, but are generally lower than at N1 and do not show any systematic changes related to the impoundment at N4.

### 4. Analysis of Time Trends in DMeHg in the Impoundment and Downstream, Relative to Upstream

Next, we compared trends in DMeHg over time at each of N4 to N8, relative to N1. Our ability to evaluate time trends is limited because of the lack of data from the 'pre-impoundment' period. We do not know if there are any natural differences between N1 and other stations that existed before impoundment. Consequently, we must assume that in the absence of impoundment, all stations N1 to N8 would have similar temporal patterns of DMeHg.

To test for differences in DMeHg trends that might be related to impoundment, we fit mixed-effects models to individual measures (y) with form:

log(y) = Site + Time + Site*Time + Month + Month*Site + error,

where Site is a factor (dummy) variable allowing different intercepts (mean levels) by site; Time is month as a continuous covariate (1, 2, 3, …) allowing estimation of the slope of the time trend in DMeHg; Month is a factor (dummy) variable representing month-specific differences (treated as random effects)

common to both sites; and Month*Site is an interaction representing month-specific differences (treated as random effects) specific to a given site.

The interaction of interest is Site*Time, which provides an estimate of the difference in the time trends (slopes) between sites. This model was fit using five site pairs (N1 versus N4, N5, N6, N7, or N8) to estimate differences in trends relative to N1. It is only since February that N4 has been continuously impounded; consequently, and recognizing the limited data prior to February, we evaluated time trends only for the period February 2017 onwards. However, the data at N1 for February appear anomalous (two extremely high values, including the highest value in the whole dataset, plus two values at or near the MDL). Therefore, we fit the models with and without February. Models were fit in R using the `lmer` function of package "lme4" (Bates et al. 2015), with coefficient tests provided by the "lmerTest" package.

Results are provided in **Table A2**. With February included, there was a significant (P = 0.018) increase in slope (time trend) for N4 relative to N1 (with a monthly proportional increase of 1.109 or ~ 11%), and a marginally significant (P = 0.093) increase in slope for N5 (~ 6% monthly increase). Estimates for N6-N8 were positive but uncertain (P > 0.10). Importantly, these results were largely driven by the high February N1 data. When February data were excluded, the increase in slope for N4 relative to N1 was marginally significant (P = 0.089; 5% monthly increase), while there was no evidence of differences for the remaining sites (i.e., they had trends in DMeHg similar to that for N1).

These results are consistent with the observed ratios of means provided in **Figure A10**. Visually, it is evident that N4 generally increases relative to N1 across months, whereas for sites N5-N7, there is little evidence of systematic differences with N1 monthly means except for the low ratios associated with February.

Residuals for the mixed-effects models are shown in **Figure A11** for the February to September 2017 period. Again, there was little evidence of spatial or temporal correlation among residuals, indicating that model terms (e.g., Time, Site*Time, Month, and Month*Site) adequately accounted for the dominant patterns of spatial and temporal correlation among sites.

### 5. Relationship Between DMeHg and DOC

Initial plots had indicated that DOC may be elevated in cases where DMeHg is elevated. Plots of DMeHg vs DOC for each site are shown in **Figure A12**. The association between elevated DMeHg and elevated DOC is especially clear for sites N1 and N8. For N1, the six samples with DOC above 8 mg/L occurred in November 2016. The two high DMeHg values in February (~ 0.035 and 0.05 ng/L) at N1 had corresponding DOC around 6 mg/L and stand out in the N1 panel. For N8, the high DMeHg and DOC levels occurred mostly in 2016 (e.g., compare raw data over time in **Figures A5 and A6**). Across all sites, the Spearman correlation between DMeHg and DOC was 0.50 (P < 0.001). Across sites N4-N7, the Spearman correlation was 0.45 (P < 0.001). Thus, although the association is visually much less clear for sites N4-N7 (**Figure A12**), there is still a strong pattern toward higher DMeHg with higher DOC.

We fit mixed-effects models to further test the relationship, using either DOC or log(DOC), and either site-specific slopes or a common slope. Results are not shown, but the best model was a common linear relationship across sites between log(DMeHg) and DOC (P < 0.001), explaining approximately 20% of the

variation. Thus, DOC in part explains the relatively high DMeHg values at N1 in Nov-16, confirming what is shown in the plots.

As discussed in the next section, we also explored ways to account for DOC in the earlier analyses.

## 6. Other Modeling Approaches

We applied more sophisticated Bayesian models to the DMeHg data across sites. However, in all cases, the models did not appear to provide estimates of monthly means or differences relative to N1 that were any more informative than those derived using the simple Bayesian model applied above (referred to here as the "base" model).

In a first set of analyses, we used random-walk processes to model site-specific monthly means. These time series models, which are commonly referred to as "state space models" or "dynamic linear models" (Hamilton 1994; Harvey 1989; Neff et al. 2012), are designed to estimate the underlying trend ("signal") in a variable amidst random variation or measurement error ("noise"). In short, the resulting estimates of monthly means were similar to the base-model estimates, but with some variation "smoothed" out, in particular for N1 during early months. However, the reliability of these estimates is questionable: with such short time series, the variance estimates associated with the random-walk processes are highly uncertain for all sites. Such models may be of greater use as more months of sampling are added, but do not appear helpful for the current dataset, for which the precision of monthly DMeHg samples appears quite high for most months and sites, and for which trends are already quite evident (see **Figure A6**).

In a second set of analyses, we developed mixed-effects models (i.e., Bayesian hierarchical models; Gelman and Hill 2007) with common (across-site) and site-specific terms to model variation in monthly means (analogous to random effects). The estimates from these models implied greatly reduced site-specific variation in monthly means across sites N1 and N4-N7. That is, a clear common trend in monthly means was estimated across these sites, with relatively minor site-specific differences from that trend. In essence, site-specific means were pulled strongly toward a common trend, including the early data for N1 (e.g., the November and February means). Typically, such results would be interpreted as follows: there is little statistical support for the site-specific monthly differences observed in the raw data (e.g., hierarchical estimates for sites N5-N7 were very similar to those for N1, with clear but reduced differences between N1 and N4 means in months June-September). However, it could be argued that a key assumption of the hierarchical model – that all sites are representative of a common "population" of sites – is not appropriate. Clearly, we expect *a priori* that impoundment will affect DMeHg levels differently across sites. Consequently, we much prefer the mean estimates provided by the base model (which are analogous to fixed effects). Nevertheless, it's useful to point out that, in general, there is little statistical evidence in the data of strong differences among sites, with the exception of elevated N4 means (June-September) relative to N1, as well as a quite distinct trend for N8 data. It is important to note that the strong reduction in site-specific differences in these Bayesian models is not applicable to the mixed model used above to assess linear trends in monthly means (**Table A2**), because in that model, deterministic trends by site were explicitly specified and modeled as fixed effects.

During analyses of both the random-walk models and the hierarchical models, we examined models with DOC as a covariate. Positive and "significant" relationships between DOC and DMeHg were estimated; however, the overall influence of including DOC on estimates of monthly means was minor. More importantly, DOC measurements were missing for some samples, including August N4 samples

with high DMeHg values. Thus, the potential value of including DOC appeared minimal compared to the loss of DMeHg data that occurred when DOC was included.

In summary, although a variety of more sophisticated time-series models and/or mixed-effects models could be applied, the usefulness of such methods are constrained by the relatively short duration of the current dataset. For now, we strongly prefer our simple (and transparent) approaches to estimating and comparing monthly means for DMeHg values across sites.

## 7. Conclusions

Plots and statistical models indicate that DMeHg was generally elevated over the summer months (June to September) in the impoundment (N4) relative to upstream (N1). Furthermore, although DMeHg has increased (naturally) at N1 since February, the slope of increase over time has been steeper at N4 than at N1. Evidence of these patterns persisting downstream of the impoundment at N5 to N7 is limited, and nonexistent at N8. We would expect that the pattern at N4 could persist downstream to some extent, but is presumably difficult to discern because the differences compared to N1 are small relative to random variation in the data.

## 8. References


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**Table A1**. Monthly Summary Statistics for DMeHg, TMeHg and TSS at N1 and N4-N8, October 2016 to September 2017

Notes: for sample size 'n', numbers in parentheses indicate how many samples were below Method Detection Limits (MDLs). Means were calculated by setting values below MDLs as equal to MDLs, therefore means are biased high where values < MDLs were present. Where half or more of samples are below MDLs, estimates of the median will also be biased high.

**DMeHg**

| | N1 | | | N4 | | | N5 | | | N6 | | | N7 | | | N8 (surface only) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Month** | **n** | **mean** | **med** | **n** | **mean** | **med** | **n** | **mean** | **med** | **n** | **mean** | **med** | **n** | **mean** | **med** | **n** | **mean** | **med** |
| 16-Oct | 2 (1) | 0.010 | 0.010 | 6 (3) | 0.013 | 0.010 | 2 | 0.010 | 0.010 | 2 (1) | 0.010 | 0.010 | 2 (1) | 0.010 | 0.010 | 2 | 0.024 | 0.024 |
| 16-Nov | 9 | 0.026 | 0.029 | 25 (6) | 0.016 | 0.015 | 9 (1) | 0.016 | 0.014 | NA | NA | NA | 5 | 0.015 | 0.016 | 5 | 0.026 | 0.025 |
| 16-Dec | 3 | 0.016 | 0.013 | 3 | 0.013 | 0.013 | 3 (2) | 0.013 | 0.010 | 1 (1) | 0.010 | 0.010 | 2 (1) | 0.010 | 0.010 | 2 | 0.019 | 0.019 |
| 17-Jan | NA | NA | NA | NA | NA | NA | NA | NA | NA | 1 | 0.010 | 0.010 | NA | NA | NA | 2 (2) | 0.010 | 0.010 |
| 17-Feb | 4 (1) | 0.026 | 0.023 | 8 | 0.010 | 0.010 | 4 (1) | 0.012 | 0.012 | 3 (2) | 0.010 | 0.010 | 3 (1) | 0.010 | 0.010 | 6 (2) | 0.010 | 0.010 |
| 17-Mar | 4 | 0.012 | 0.011 | 10 | 0.012 | 0.011 | 4 (1) | 0.011 | 0.011 | 5 | 0.015 | 0.015 | 4 | 0.012 | 0.012 | 6 (1) | 0.011 | 0.010 |
| 17-Apr | 4 | 0.014 | 0.013 | 12 | 0.016 | 0.013 | 4 | 0.015 | 0.014 | 4 | 0.012 | 0.012 | 4 (1) | 0.014 | 0.013 | 8 (3) | 0.011 | 0.010 |
| 17-May | 3 (1) | 0.014 | 0.010 | 9 (1) | 0.012 | 0.010 | 3 | 0.014 | 0.010 | 3 (1) | 0.013 | 0.012 | 3 (1) | 0.018 | 0.020 | 6 (2) | 0.011 | 0.010 |
| 17-Jun | 4 (1) | 0.015 | 0.014 | 9 (2) | 0.019 | 0.020 | 4 | 0.014 | 0.014 | 4 | 0.016 | 0.017 | 4 (1) | 0.017 | 0.016 | 4 | 0.016 | 0.017 |
| 17-Jul | 4 | 0.019 | 0.019 | 12 | 0.025 | 0.026 | 4 | 0.020 | 0.021 | 4 | 0.023 | 0.023 | 4 | 0.023 | 0.023 | 8 (2) | 0.015 | 0.013 |
| 17-Aug | 5 | 0.022 | 0.021 | 15 | 0.029 | 0.029 | 5 | 0.023 | 0.023 | 5 | 0.023 | 0.025 | 5 | 0.023 | 0.024 | 6 (2) | 0.012 | 0.010 |
| 17-Sep | 4 | 0.026 | 0.026 | 9 | 0.032 | 0.031 | 3 | 0.027 | 0.027 | 4 | 0.025 | 0.024 | 3 | 0.025 | 0.026 | 1 | 0.018 | 0.018 |

**TMeHg**

| | N1 | | | N4 | | | N5 | | | N6 | | | N7 | | | N8 (surface only) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Month** | **n** | **mean** | **med** | **n** | **mean** | **med** | **n** | **mean** | **med** | **n** | **mean** | **med** | **n** | **mean** | **med** | **n** | **mean** | **med** |
| 16-Oct | 2 | 0.022 | 0.022 | 6 (1) | 0.015 | 0.015 | 2 (1) | 0.016 | 0.016 | 2 (1) | 0.017 | 0.017 | 2 (1) | 0.024 | 0.024 | 2 | 0.032 | 0.032 |
| 16-Nov | 9 | 0.035 | 0.040 | 25 | 0.021 | 0.022 | 9 | 0.021 | 0.022 | NA | NA | NA | 5 | 0.021 | 0.018 | 5 | 0.030 | 0.032 |
| 16-Dec | 3 | 0.030 | 0.024 | 3 | 0.021 | 0.021 | 3 | 0.015 | 0.015 | 1 | 0.013 | 0.013 | 2 | 0.017 | 0.017 | 2 | 0.023 | 0.023 |
| 17-Jan | NA | NA | NA | NA | NA | NA | NA | NA | NA | 1 | 0.019 | 0.019 | NA | NA | NA | 2 (2) | 0.010 | 0.010 |
| 17-Feb | 4 | 0.028 | 0.026 | 8 | 0.016 | 0.015 | 4 | 0.059 | 0.038 | 3 | 0.015 | 0.015 | 3 | 0.012 | 0.011 | 6 | 0.011 | 0.011 |
| 17-Mar | 4 | 0.017 | 0.016 | 10 | 0.032 | 0.019 | 4 | 0.087 | 0.074 | 5 | 0.025 | 0.030 | 4 | 0.056 | 0.027 | 6 (1) | 0.011 | 0.010 |
| 17-Apr | 4 | 0.017 | 0.017 | 12 | 0.023 | 0.017 | 4 | 0.028 | 0.028 | 4 | 0.016 | 0.017 | 4 | 0.020 | 0.016 | 8 | 0.016 | 0.016 |
| 17-May | 3 | 0.018 | 0.020 | 9 | 0.025 | 0.027 | 3 | 0.017 | 0.017 | 3 | 0.017 | 0.021 | 3 | 0.025 | 0.018 | 6 | 0.015 | 0.011 |
| 17-Jun | 4 | 0.025 | 0.026 | 9 | 0.031 | 0.027 | 4 | 0.026 | 0.025 | 4 | 0.025 | 0.025 | 4 | 0.027 | 0.029 | 4 | 0.026 | 0.027 |
| 17-Jul | 4 | 0.023 | 0.023 | 12 | 0.033 | 0.035 | 4 | 0.028 | 0.028 | 4 | 0.028 | 0.028 | 4 | 0.029 | 0.030 | 8 (1) | 0.020 | 0.022 |
| 17-Aug | 5 | 0.027 | 0.028 | 15 | 0.033 | 0.033 | 5 | 0.028 | 0.028 | 5 | 0.027 | 0.025 | 5 | 0.030 | 0.035 | 6 | 0.019 | 0.019 |
| 17-Sep | 4 | 0.023 | 0.022 | 9 | 0.036 | 0.035 | 3 | 0.027 | 0.025 | 4 | 0.029 | 0.029 | 3 | 0.025 | 0.024 | 1 | 0.028 | 0.028 |

**TSS**

| | N1 | | | N4 | | | N5 | | | N6 | | | N7 | | | N8 (surface only) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Month** | **n** | **mean** | **med** | **n** | **mean** | **med** | **n** | **mean** | **med** | **n** | **mean** | **med** | **n** | **mean** | **med** | **n** | **mean** | **med** |
| 16-Oct | 2 (2) | 5.0 | 5.0 | 6 (6) | 5.0 | 5.0 | 2 | 24.0 | 24.0 | 2 (1) | 288.0 | 288.0 | 2 | 7.5 | 7.5 | 2 (1) | 9.0 | 9.0 |
| 16-Nov | 9 (7) | 6.0 | 5.0 | 25 (20) | 5.3 | 5.0 | 9 (4) | 10.8 | 7.0 | NA | NA | NA | 5 (2) | 5.6 | 5.0 | 5 (5) | 5.0 | 5.0 |
| 16-Dec | 3 (1) | 12.0 | 13.0 | 3 (2) | 6.3 | 5.0 | 3 (2) | 7.7 | 5.0 | 1 | 13.0 | 13.0 | 2 (1) | 9.0 | 9.0 | 2 (1) | 6.5 | 6.5 |
| 17-Jan | NA | NA | NA | NA | NA | NA | NA | NA | NA | 1 | 21.0 | 21.0 | NA | NA | NA | 2 | 9.0 | 9.0 |
| 17-Feb | 4 (3) | 13.5 | 5.0 | 8 (4) | 53.3 | 5.0 | 4 | 432.0 | 224.0 | 3 | 16.3 | 9.0 | 3 (1) | 10.3 | 9.0 | 6 (2) | 10.3 | 7.5 |
| 17-Mar | 4 (3) | 7.3 | 5.0 | 10 (2) | 200.6 | 9.5 | 4 | 571.0 | 647.0 | 5 (2) | 6.4 | 5.0 | 4 | 433.3 | 71.0 | 6 (4) | 5.7 | 5.0 |
| 17-Apr | 4 (4) | 4.0 | 4.0 | 12 (5) | 4.5 | 5.0 | 4 | 37.3 | 39.0 | 4 (1) | 15.0 | 15.5 | 4 | 36.8 | 26.5 | 8 (2) | 7.3 | 6.0 |
| 17-May | 3 (3) | 4.3 | 5.0 | 9 | 17.6 | 14.0 | 3 | 48.3 | 41.0 | 3 | 42.0 | 32.0 | 3 | 86.3 | 127.0 | 6 (3) | 9.7 | 7.5 |
| 17-Jun | 4 (3) | 7.5 | 5.0 | 9 (7) | 5.1 | 5.0 | 4 | 38.8 | 29.0 | 4 | 12.3 | 10.5 | 4 | 10.8 | 10.5 | 4 | 9.0 | 9.5 |
| 17-Jul | 4 (4) | 5.0 | 5.0 | 12 (9) | 5.4 | 5.0 | 4 (2) | 5.8 | 5.5 | 4 (1) | 12.5 | 6.5 | 4 (1) | 7.8 | 5.5 | 8 (7) | 5.0 | 5.0 |
| 17-Aug | 5 (3) | 3.0 | 2.0 | 15 (4) | 3.7 | 3.0 | 5 (1) | 5.0 | 5.0 | 5 (1) | 5.3 | 5.0 | 5 (1) | 7.3 | 6.0 | 6 (2) | 4.5 | 5.0 |
| 17-Sep | 4 (2) | 2.0 | 1.5 | 9 (6) | 1.6 | 2.0 | 3 (2) | 3.5 | 2.0 | 4 | 5.2 | 3.8 | 3 (1) | 3.5 | 3.0 | 1 | 3.0 | 3.0 |

**Table A3**. Estimates of differences in time trends of DMeHg relative to site N1.

Notes: "Change" (= exp[Est]) provides an estimate of the monthly proportional difference relative to site N1 (e.g., 1.05 indicates a 5% monthly increase in DMeHg relative to site N1).

| | Data for Feb-Sep | | | | Data for Mar-Sep | | | |
|---|---|---|---|---|---|---|---|---|
| Site | Est | SE | P-value | Change | Est | SE | P-value | Change |
| N4 | 0.103 | 0.032 | 0.018 | 1.11 | 0.049 | 0.029 | 0.089 | 1.05 |
| N5 | 0.060 | 0.035 | 0.093 | 1.06 | 0.017 | 0.034 | 0.620 | 1.02 |
| N6 | 0.051 | 0.043 | 0.281 | 1.05 | -0.015 | 0.031 | 0.639 | 0.99 |
| N7 | 0.065 | 0.042 | 0.152 | 1.07 | -0.001 | 0.035 | 0.973 | 1.00 |
| N8 | 0.023 | 0.052 | 0.675 | 1.02 | -0.029 | 0.044 | 0.524 | 0.97 |

**Figure A1**. Time series for THg by site

Notes: Red triangles indicate data points below MDLs. Dashed line shows the mean of daily samples.

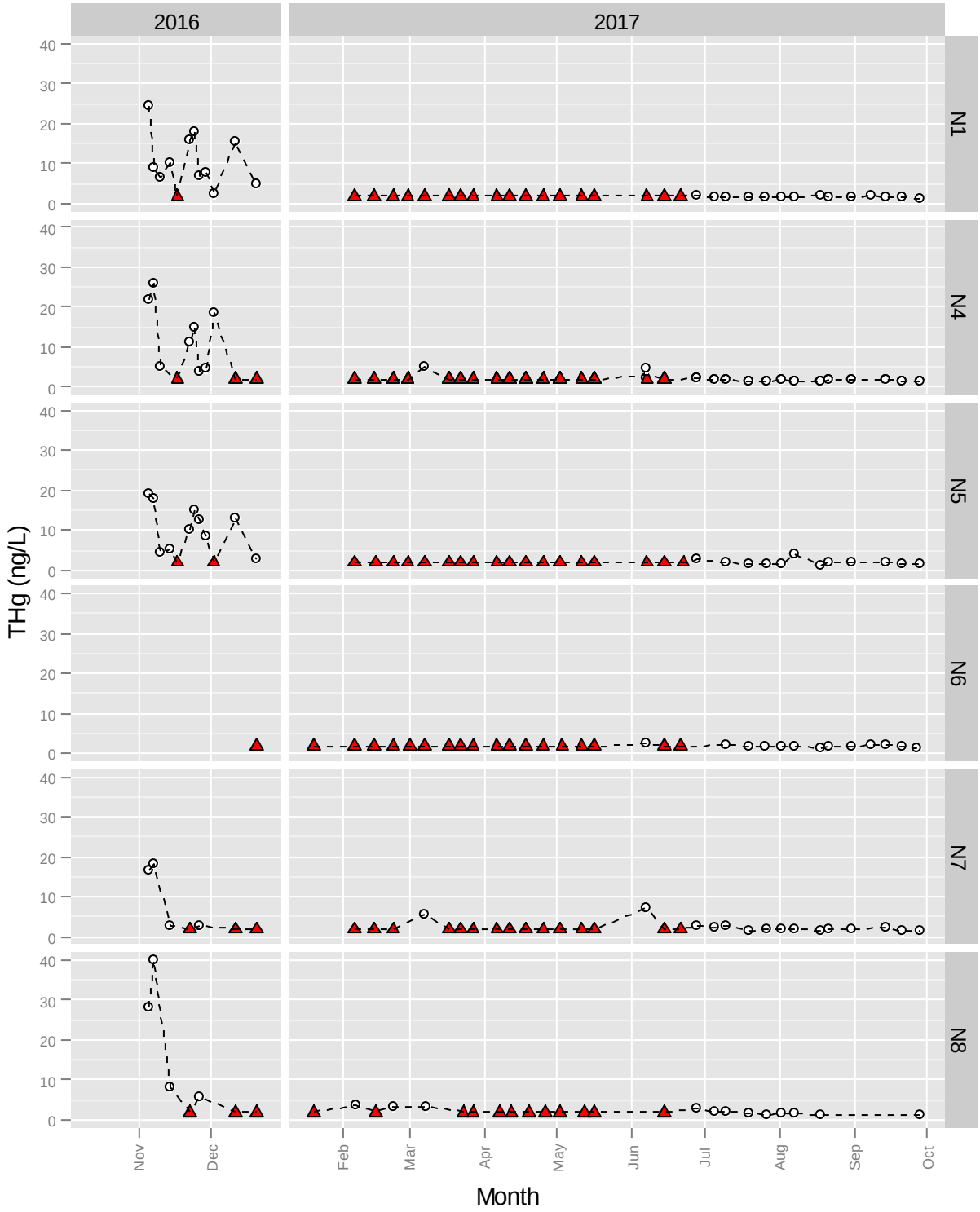


**Figure A2**. Time series for TSS by site

Notes: Red triangles indicate data points below MDLs. Dashed line shows the mean of daily samples.

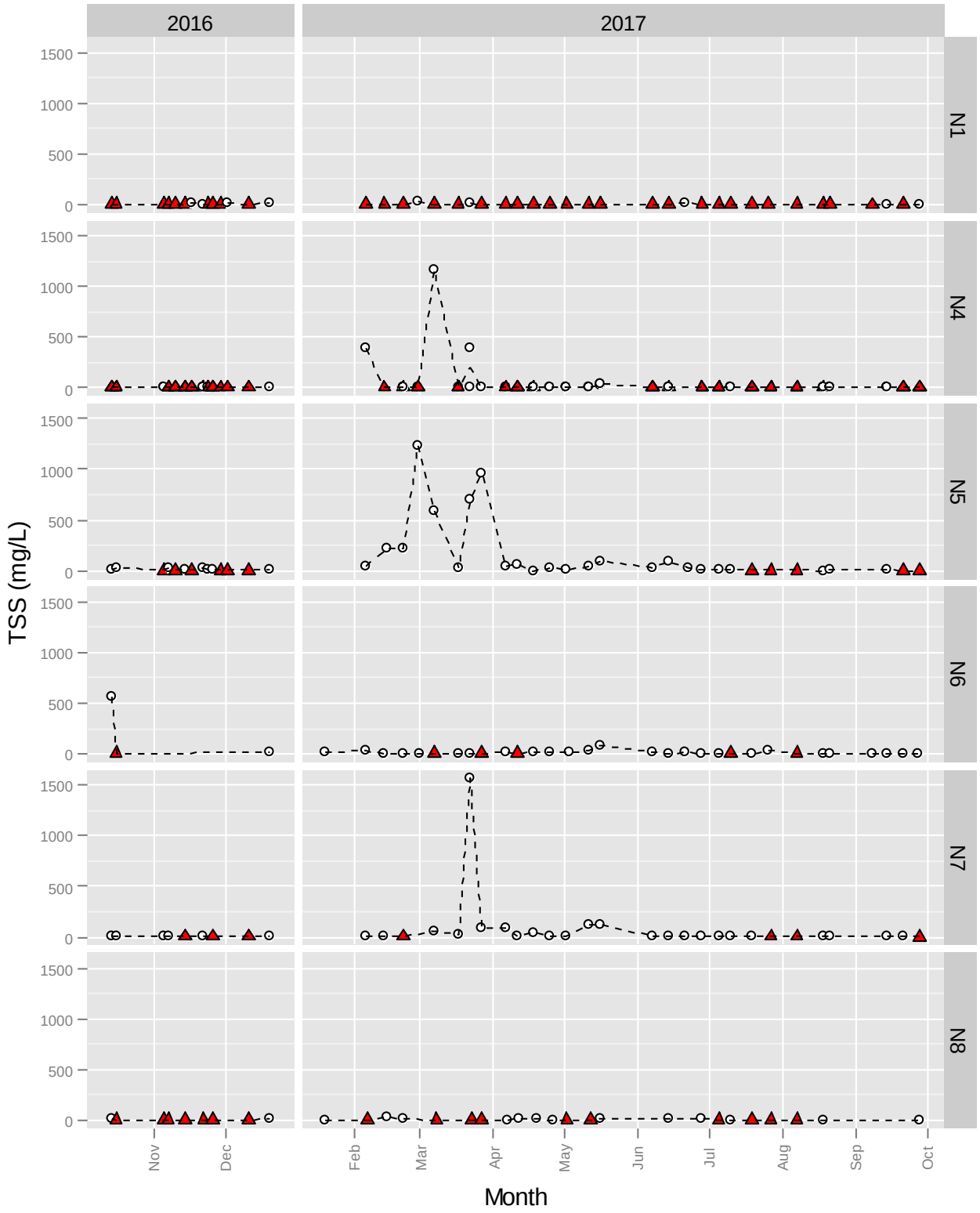


**Figure A3**. Time series for TOC by site

Notes: Red triangles indicate data points below MDLs. Dashed line shows the mean of daily samples.

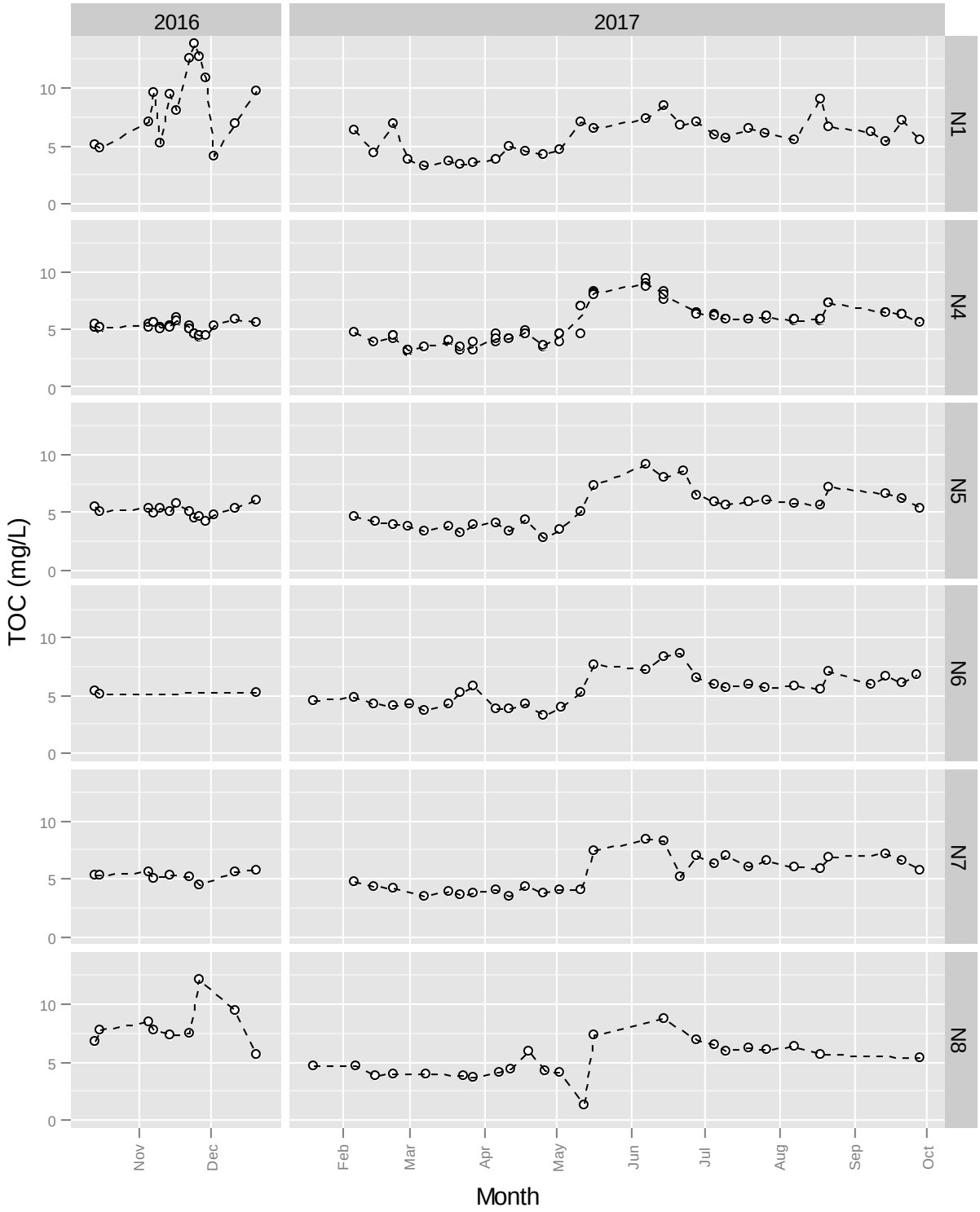


**Figure A4**. Time series for DOC by site

Notes: Red triangles indicate data points below MDLs. Dashed line shows the mean of daily samples.

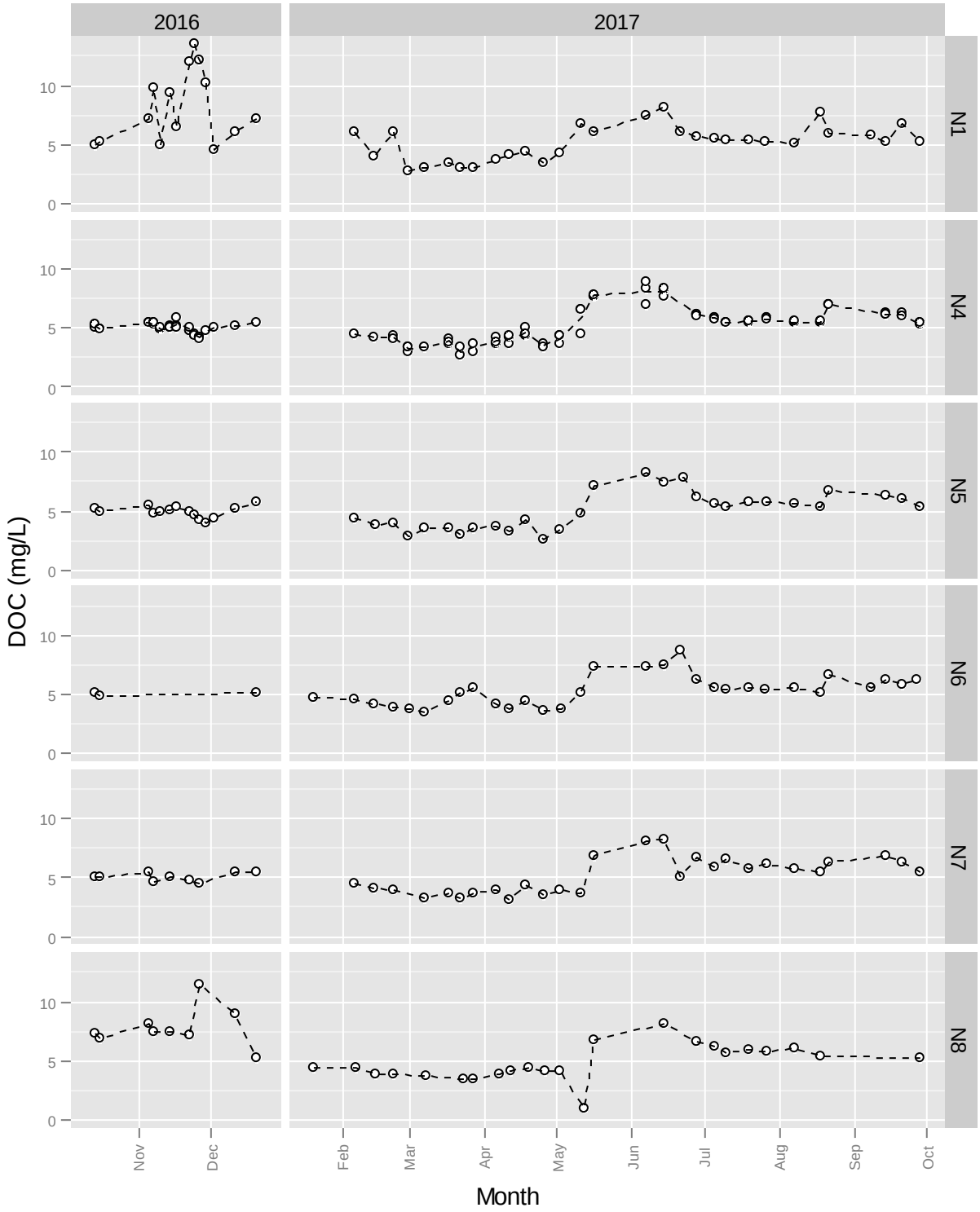


**Figure A5**. Time series for TMeHg by site

Notes: Red triangles indicate data points below MDLs. Dashed line shows the mean of daily samples.

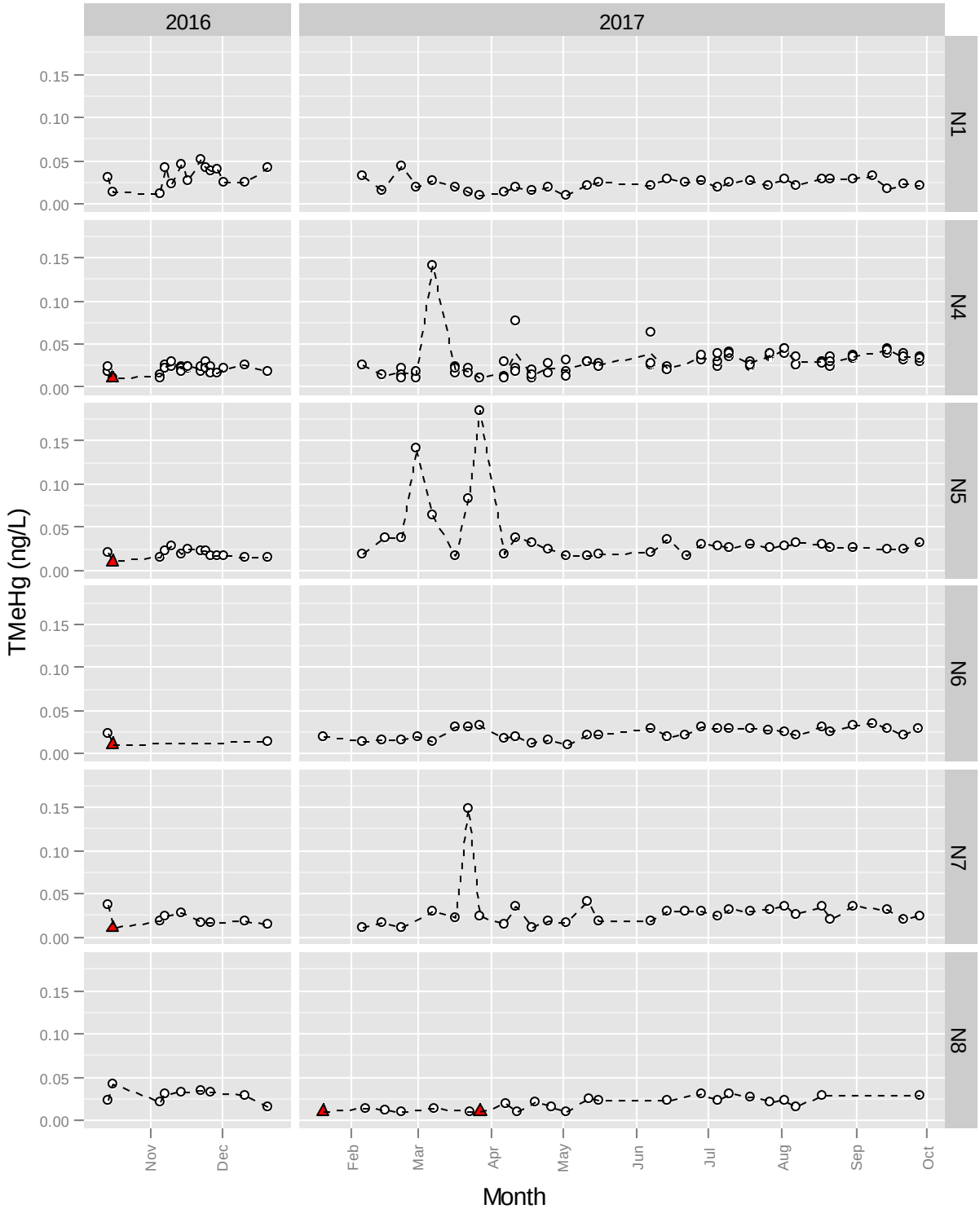


**Figure A6**. Time series for DMeHg by site

Notes: Red triangles indicate data points below MDLs. Dashed line shows the mean of daily samples.

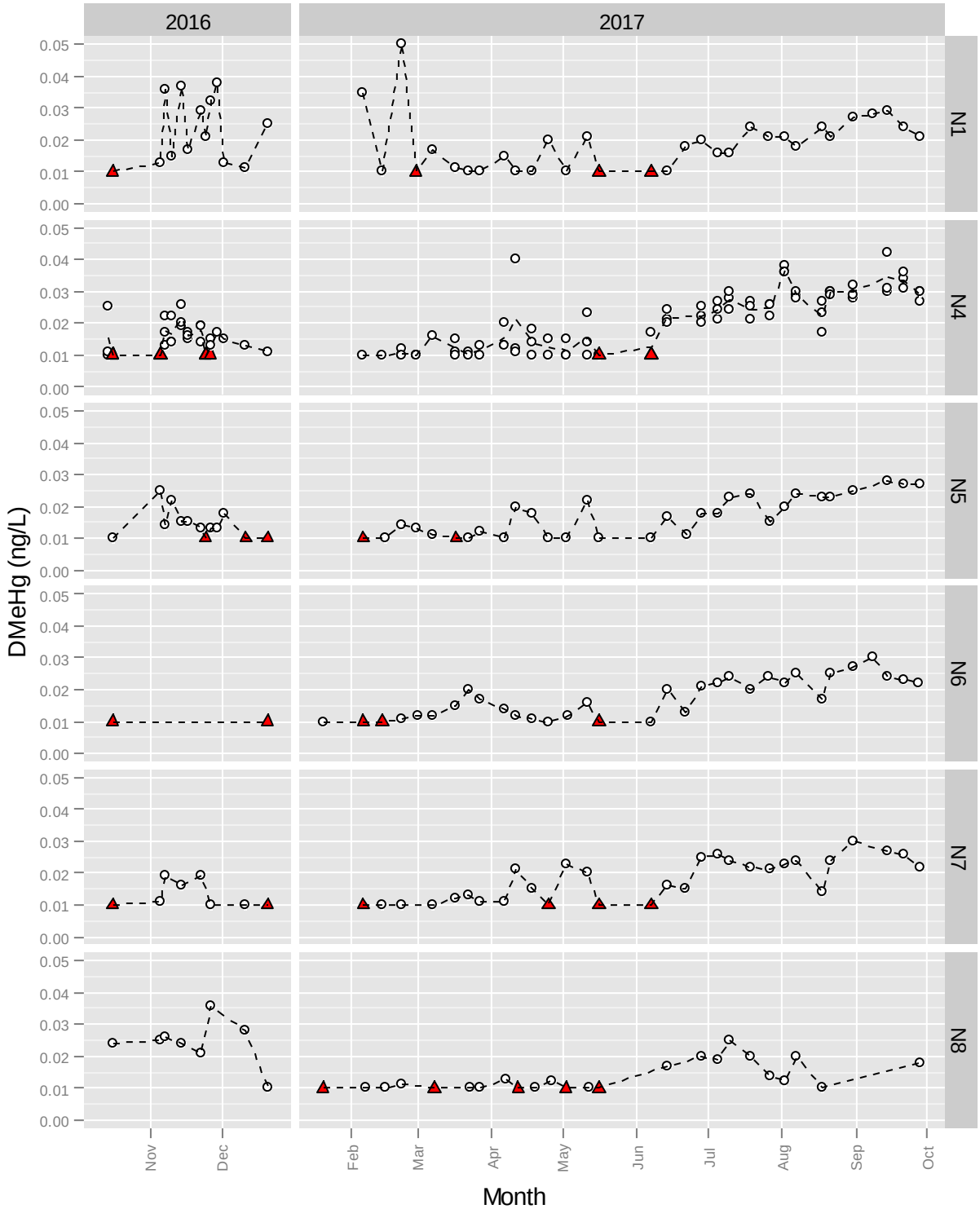


**Figure A7**. TMeHg versus TSS

Notes: Based on all data (including data below MDLs) and sites (N1, N4-N8). The highest four TMeHg points are identified: 1 = N5 on 27-Mar; 2 = N7 on 23-Mar; 3 = N5 on 28-Feb; 4 = N4 on 07-Mar.

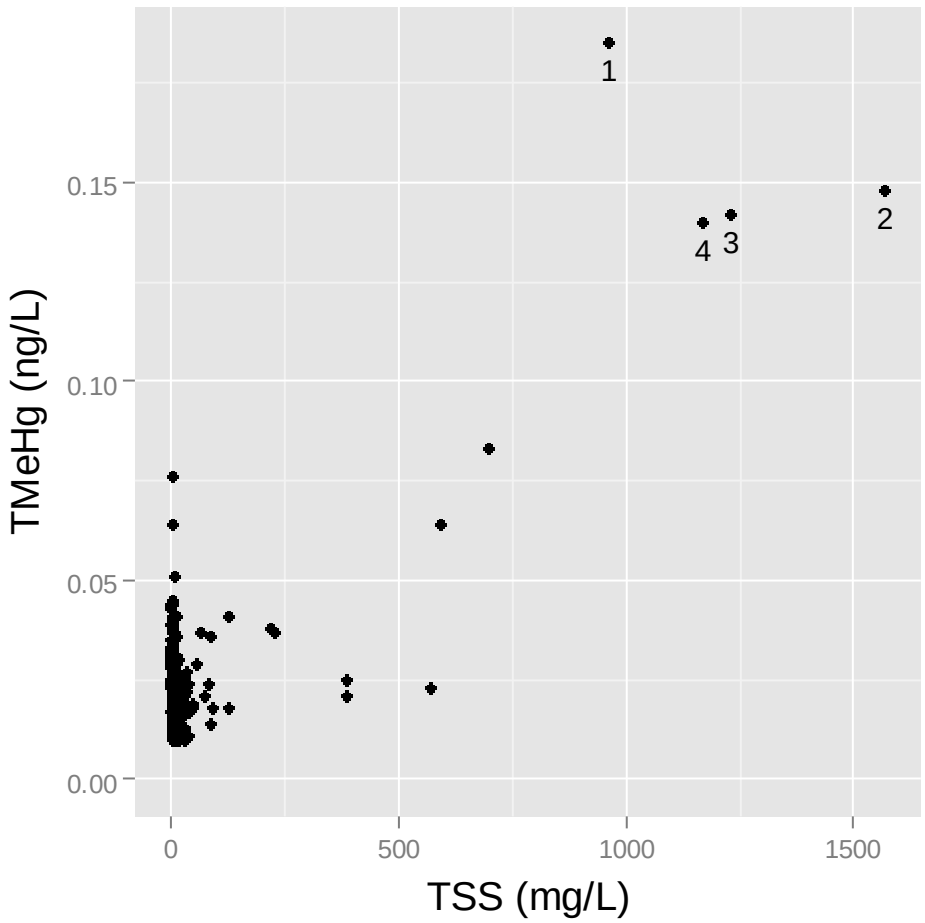


**Figure A8**. Bayesian posterior means and 95% credibility intervals for monthly means by site.

Notes: Data for October 2016 and January 2017 were omitted – see text for discussion. Dashed lines for the lower and upper 95% "credibility interval" for means correspond to the 2.5th and 97.5th percentiles of the posteriors.

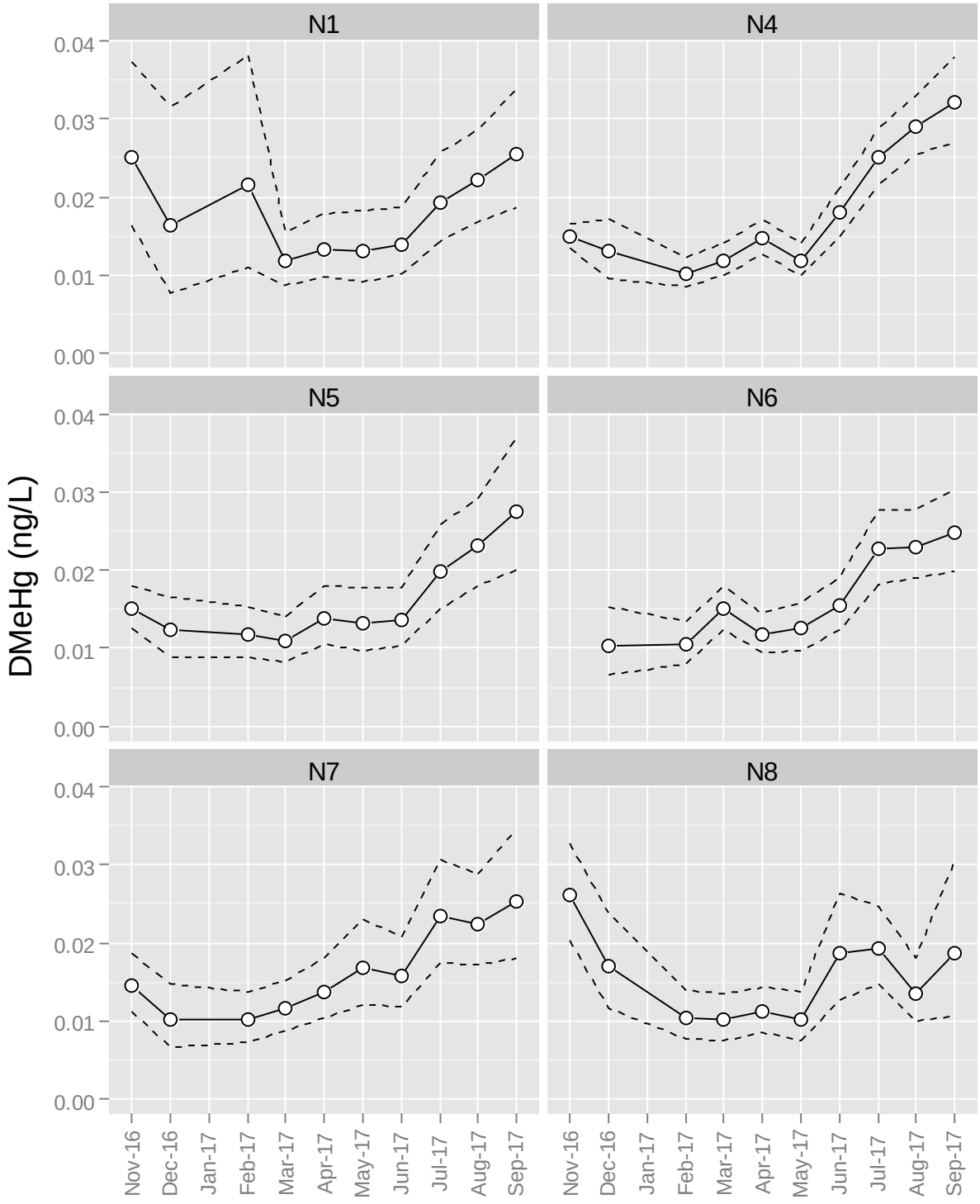


**Figure A9**. Standardized residuals of DMeHg (in log scale) for the Bayesian model of monthly means.

Notes: Red triangles indicate raw data points below MDLs. Points above the zero line indicate observed values higher than the monthly mean. Points below the zero line indicate lower values than the monthly mean.

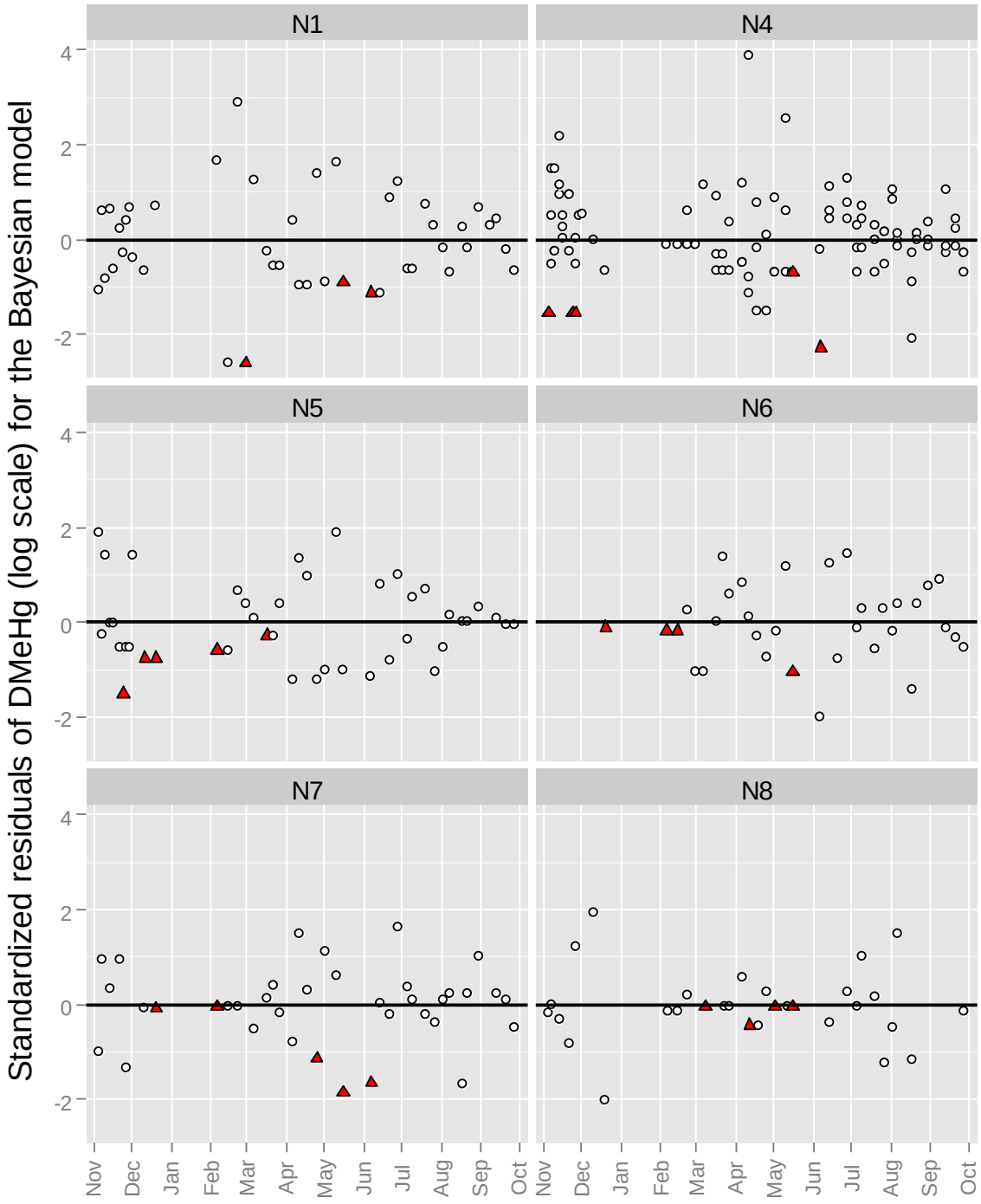


**Figure A10**. Ratios of the Bayesian posterior distributions for monthly means by site versus those for N1.

Notes: Red line at ratio of 1. Points above the line indicate higher monthly mean than N1. Points below the line indicate lower monthly mean than N1.

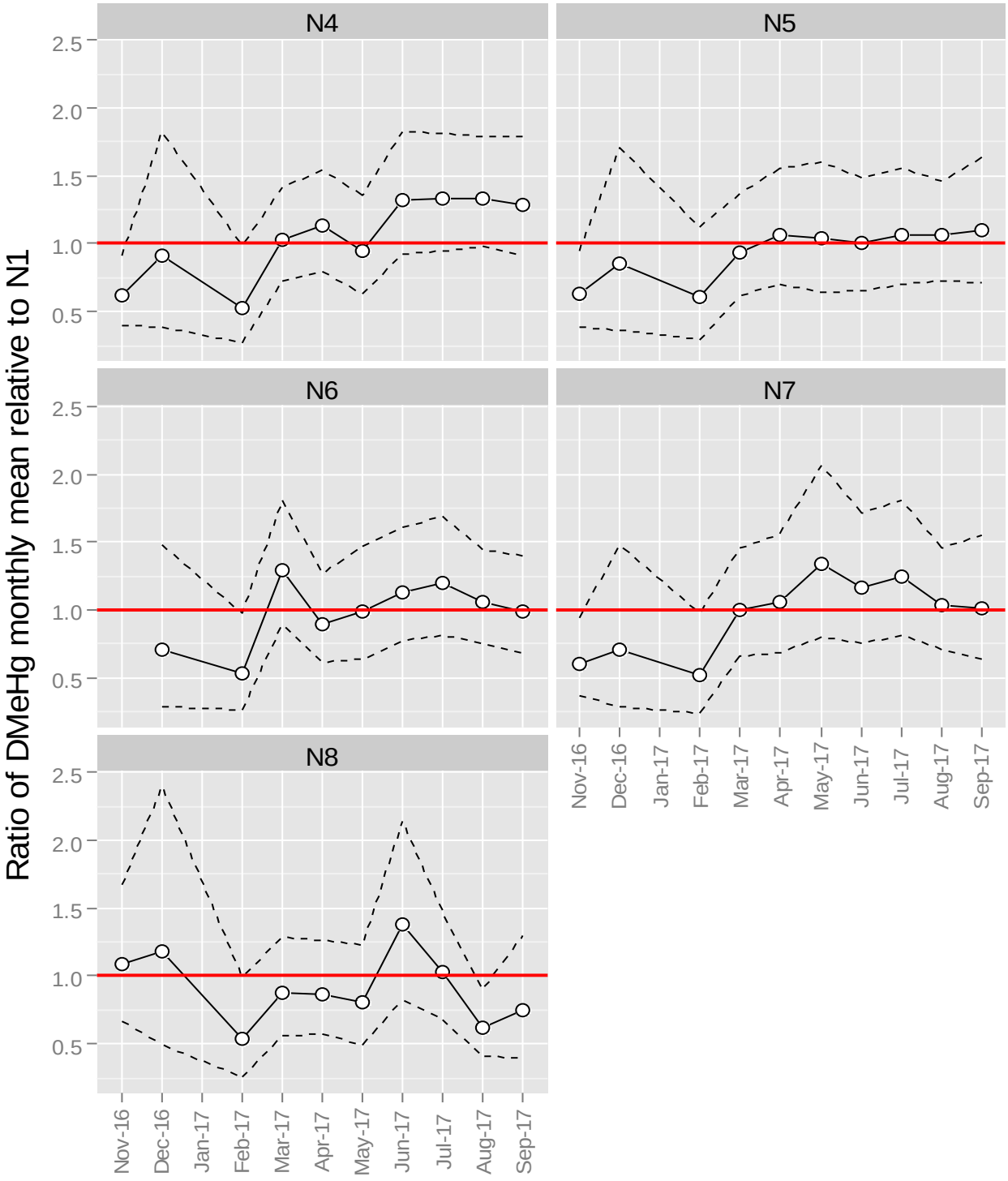


**Figure A11**. Standardized residuals of DMeHg (in log scale) for the mixed-effects trend models.

Notes: The residuals for N1 are shown for the model fit to sites N1 and N4. Red triangles indicate raw data points below MDLs. Points above the zero line indicate higher observed values than predicted by the model. Points below the zero line indicate lower values than predicted by the model.

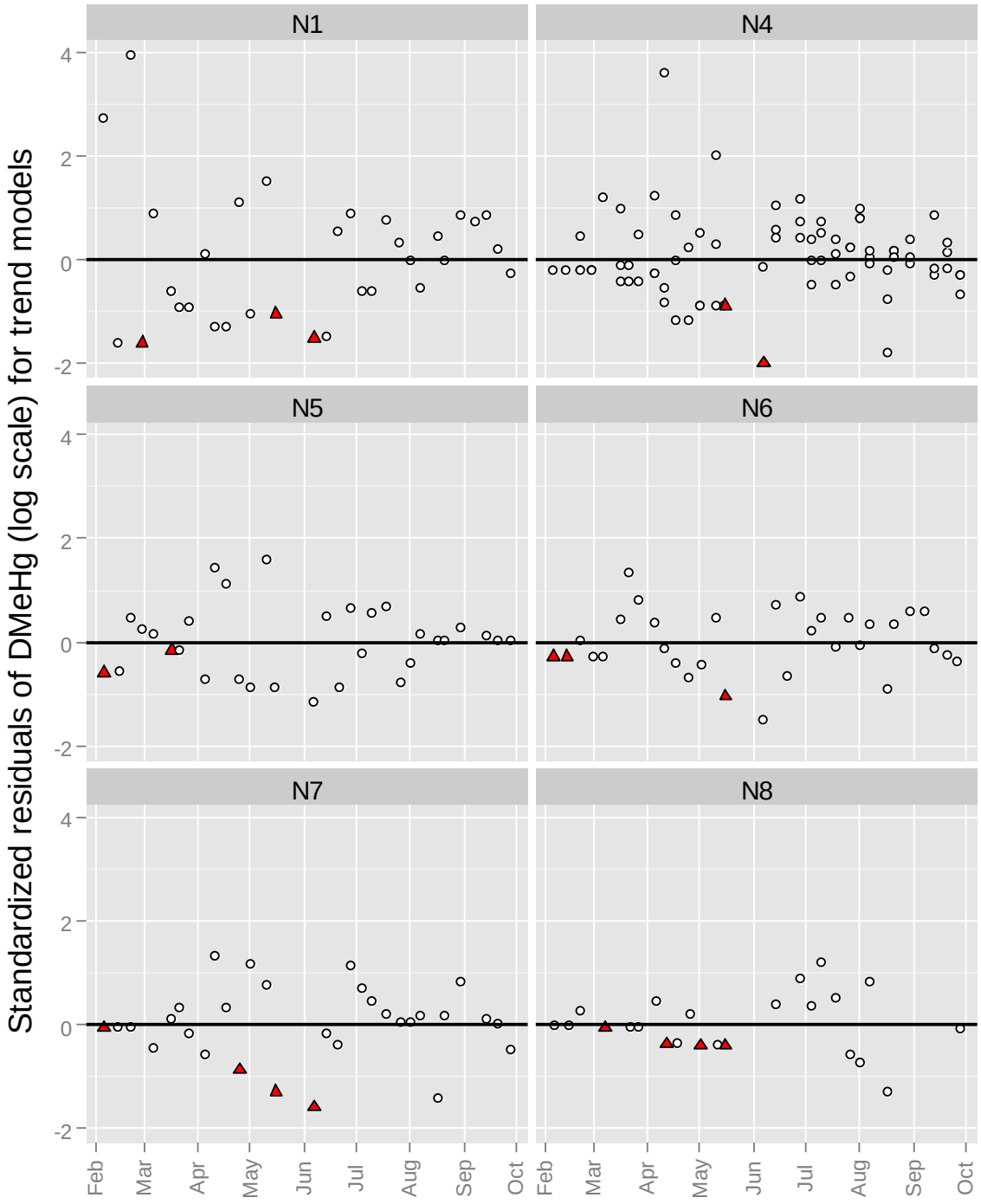
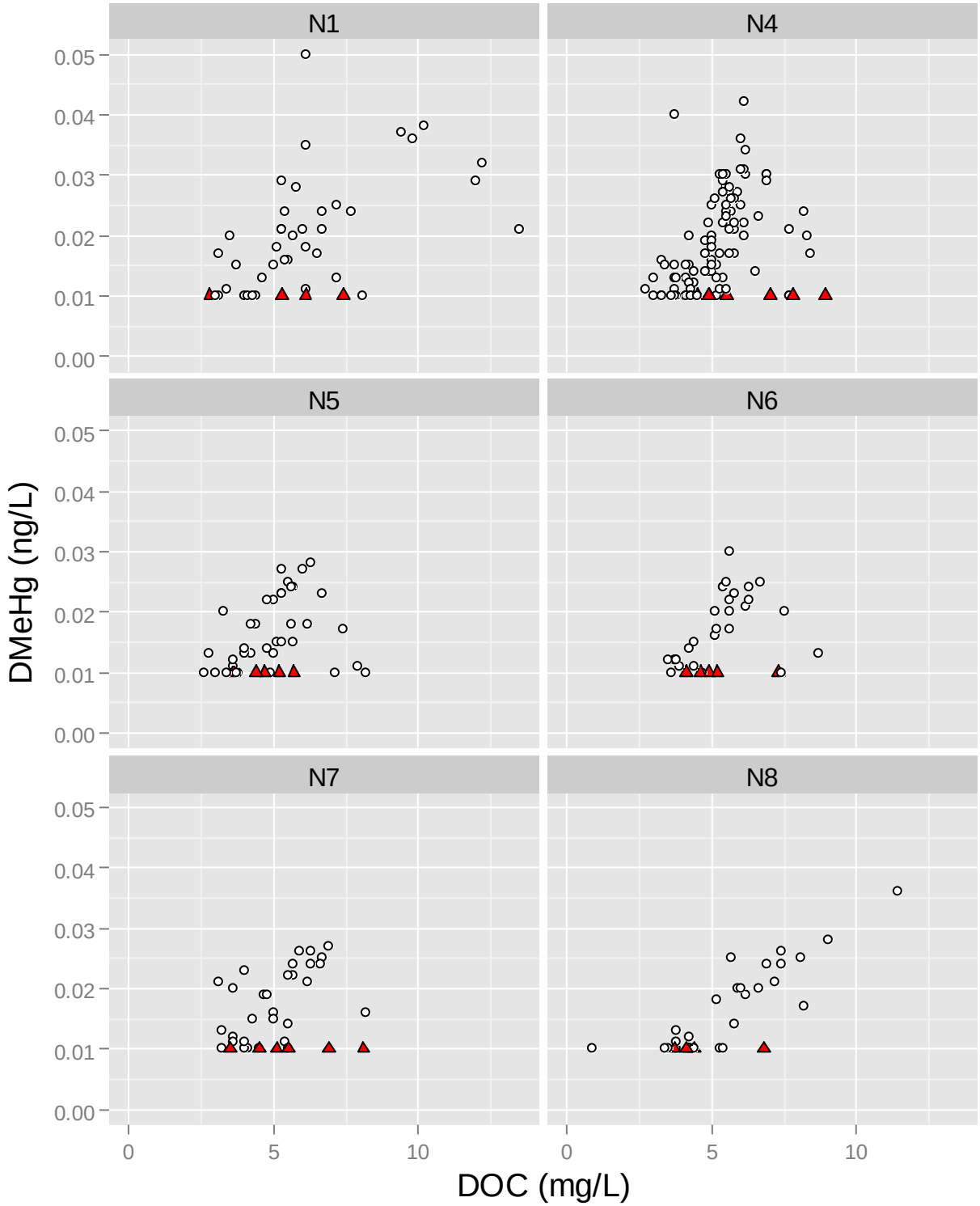


**Figure A12**. DMeHg versus DOC by site

Notes: Red triangles indicate data points below MDLs. Dashed line shows the mean of daily samples.