The influence of forestry activity on the structure of dissolved organic matter in lakes: Implications for mercury photoreactions

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Abstract

It is well known that dissolved organic matter (DOM) increases in lakes associated with forestry activity but characterization of the DOM structure is incomplete. Twenty-three lakes with a wide range of forestry activities located in central Quebec, Canada were sampled and analyzed for dissolved organic carbon (DOC) concentration, DOC fluorescence, and ultra violet–visible (UV–VIS) absorption spectra. The results show that DOC increases (as does the associated DOC fluorescence) with increased logging (slope = 0.122, \( r^2 = 0.581, p < 0.001 \); and slope = 0.283, \( r^2 = 0.308, p < 0.01 \), respectively) in the 23 lakes sampled however, the aromaticity of the DOM does not change with changes in logging (as found by UV–VIS ratios, absorbance slope in the UV region, and DOC normalized fluorescence (slope = 1.42 \times 10^{-6}, \( r = 0.331, p < 0.01 \)).

The DOM from four of these lakes was concentrated using reverse osmosis (RO) followed by freeze-drying. The structures of the concentrated dissolved organic matter (DOM) samples were analyzed using X-ray analysis of near edge structures (XANES), X-ray diffraction (XRD), and \(^{13}\text{C}\) solid-state nuclear magnetic resonance (\(^{13}\text{C}\) NMR) analysis. XANES analysis of functional groups in the four concentrated samples shows that there are significant differences in reduced sulphur between the samples, however there was no clear relationship with forestry activity in the associated catchment. XRD data showed the presence of amorphous sulhide minerals associated with the DOM concentrate that may be important sites for mercury binding. The \(^{13}\text{C}\) NMR spectra of these samples show that the percentage of carbon present in carboxylic functional groups increases with increasing logging. Such structures are important for binding photo-reducible mercury and their presence may limit mercury photo-reduction and volatilization. We propose a mechanism by which increased logging leads to increased carboxylic groups in DOM and thereby increased weak binding of photo-reducible mercury. These results, in part, explain the decrease in dissolved gaseous mercury (DGM) production rates with increased logging found in our previous work.

Keywords: Dissolved organic matter (DOM); Structure; Binding; Dissolved gaseous mercury; Photoreactions; Logging

1. Introduction

Trace metal speciation, movement and bioavailability are all heavily influenced by dissolved organic matter (DOM). Typically, the role of DOM is thought to be principally as a ligand. For example, researchers...
have suggested that increased total mercury in logged watersheds can be attributed to transport of DOM-bound mercury associated with increased DOM or particulate organic carbon inputs to lakes (Carignan et al., 2000; Garcia and Carignan, 1999, 2000; Roulet et al., 2000). However, for trace metals such as mercury the role of DOM is more complicated since DOM also acts as an important player in aquatic photochemical cycles. Dissolved organic matter is known to be involved in the production of dissolved gaseous mercury (DGM) (O’Driscoll et al., 2004). Yet, little is known about how structural changes in DOM influences its photochemical behaviour.

DGM in freshwater is principally composed of elemental mercury and is the form which can volatilize from a lake surface to the atmosphere (O’Driscoll et al., 2003). Previous research has indicated that mercury volatilization from water is a significant portion of global and regional mercury budgets (Rolfhus and Fitzgerald, 2001; Mason and Sullivan, 1997; Mason et al., 1994). The formation of DGM is an important pathway for reduction of the mercury burden of lakes.

DOM has been shown to be an important mediator of mercury photo-reactions (Xiao et al., 1995; Zhang and Lindberg, 2001; Amyot et al., 1997a,b,c; Nriagu, 1994; O’Driscoll et al., 2004; Zepp, 1988). Its effectiveness as a mediator of photo-reactions is tied to its ability to attenuate (and transfer) solar radiation energy (Lean, 1998; Scully and Lean, 1994). However, the effectiveness of DOM in mercury photo-reactions may be complicated by its ability to bind metals (Ravichandran, 2004).

In our previous work we examined the relationship between dissolved organic carbon (DOC) concentration (a measure of dissolved organic matter (DOM)) and DGM formation in lakes with logged and non-logged watersheds. Our work indicated that DGM photo-production efficiency is positively related to DOC concentration when DOM structure and dissolved ions are held constant (O’Driscoll et al., 2004). We also found that the logged lakes had a lower DGM photo-production efficiency than the non-logged lakes (independent of DOC concentration) (O’Driscoll et al., 2004). We hypothesized that this difference may be due to differences in DOM structure that will affect binding of mercury to DOM as well as the attenuation of solar radiation by DOM. Characterizing the structure of DOM is an analytically challenging exercise. Here we evaluate that hypothesis using a variety of characterization methods on the natural water and several reverse osmosis concentrates, these included: DOC, DOC fluorescence (DOCF), UV–Visible absorption spectra (200–800 nm), X-ray Absorption of Near Edge Structures (XANES), X-Ray diffraction (XRD), and solid state 13C nuclear magnetic resonance (13C NMR). These analysis methods were used to obtain the following details about DOM structure: (i) DOCF, UV–VIS scans were used to provide information on aromatic structures and radiation absorption characteristics, (ii) XANES was used to provide detailed information on sulphur speciation, (iii) XRD was used to examine the presence of minerals and (iv) 13C NMR was used to provide detailed information on structures containing carbon atoms.

2. Methods

2.1. Extraction of DOM

While a number of different DOM extraction methodologies exist (including XAD extraction, liquid chromatography, and tangential ultrafiltration), reverse osmosis is the only methodology that can efficiently concentrate 300 L of lake water without requiring drastic pH changes or the addition of chemicals that may affect DOC structure (Clair et al., 1991; Sun et al., 1995; Weber, 1988; Town and Powell, 1993; O’Driscoll and Evans, 2000). Surface water was sampled from a series of 23 lakes in central Quebec using 50 mL polypropylene tubes. Of these lakes 4 were chosen for detailed analysis of DOM structure. Three hundred liters of water from Lakes K2, K3, N70, and DF9 was sampled using acid washed 25 L high density polypropylene (HDPE) containers. Using the method of Sun et al. (1995), this water was then concentrated using a portable reverse osmosis system PROS/1S with 0.5 µm glass fibre pre-filter.

For the detailed structural analysis the lakes were chosen primarily to represent high and low levels of logging activity, but also to provide a range of dissolved organic carbon concentrations. The 4 lakes chosen provide the widest ranges of logging and DOC. Table 1 lists some of the physical and chemical characteristics of the 4 lakes studied in detail. Lakes N70 and K2 have catchments where very little logging has occurred (0% and 2% of basin, respectively), and have DOC concentrations of 6.7 and 3.2 mg L⁻¹, respectively. In contrast, lakes K3 and DF9 have logged catchments (26% and 67% of basin, respectively) and DOC concentrations of 4.9 and 13.7 mg L⁻¹, respectively. All lakes are relatively small (<1.5 km²) and are well saturated with oxygen (>94%). The date of logging is relatively recent.
Table 1

Physical and chemical characteristics of the 4 lakes sampled for DOM and their associated drainage basins

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>N70</th>
<th>K2</th>
<th>K3</th>
<th>DF9</th>
</tr>
</thead>
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<tr>
<td>Latitude</td>
<td>o o °</td>
<td>48°05'12&quot;</td>
<td>48°7'56&quot;</td>
<td>48°18'26&quot;</td>
<td>48°42'31&quot;</td>
</tr>
<tr>
<td>Longitude</td>
<td>o o °</td>
<td>75°29'09&quot;</td>
<td>75°10'08&quot;</td>
<td>75°16'18&quot;</td>
<td>75°01'03&quot;</td>
</tr>
<tr>
<td>Altitude above sea level</td>
<td>m</td>
<td>439</td>
<td>415</td>
<td>414</td>
<td>406</td>
</tr>
<tr>
<td>Lake area</td>
<td>km²</td>
<td>0.654</td>
<td>1.421</td>
<td>0.829</td>
<td>0.421</td>
</tr>
<tr>
<td>Average catchment slope</td>
<td>%</td>
<td>9.2</td>
<td>4.6</td>
<td>4.6</td>
<td>3.3</td>
</tr>
<tr>
<td>Maximum lake depth</td>
<td>m</td>
<td>20.4</td>
<td>12.2</td>
<td>7.2</td>
<td>10.5</td>
</tr>
<tr>
<td>Lake volume</td>
<td>m³</td>
<td>4.4E+06</td>
<td>6.1E+06</td>
<td>2.3E+06</td>
<td>1.4E+06</td>
</tr>
<tr>
<td>Percentage of wetlands in catchment</td>
<td>%</td>
<td>2.5</td>
<td>4.4</td>
<td>11.0</td>
<td>3.2</td>
</tr>
<tr>
<td>Cumulative percentage of basin logged</td>
<td>%</td>
<td>0</td>
<td>2</td>
<td>26</td>
<td>67</td>
</tr>
<tr>
<td>Shoreline</td>
<td>km</td>
<td>4.04</td>
<td>11.85</td>
<td>5.37</td>
<td>2.95</td>
</tr>
<tr>
<td>Oxygen saturation</td>
<td>%</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Secchi depth</td>
<td>m</td>
<td>3.5</td>
<td>1.7</td>
<td>3.1</td>
<td>1.0</td>
</tr>
<tr>
<td>pH in situ</td>
<td>pH units</td>
<td>6.4</td>
<td>5.7</td>
<td>6.1</td>
<td>6.3</td>
</tr>
<tr>
<td>Dissolved organic carbon</td>
<td>mg L⁻¹</td>
<td>6.7</td>
<td>3.2</td>
<td>4.9</td>
<td>13.7</td>
</tr>
</tbody>
</table>


2.2. UV–VIS absorbance and DOC fluorescence

142 Twenty-three lakes with varying amounts of logging 143 activity in the catchment basins were sampled in central 144 Quebec during three sampling campaigns (June 145 2001, August 2001, and June 2002). The following 146 lakes were sampled in duplicate using 50 mL polypropylene vials and refrigerated in the dark until analysis 148 of DOC concentration, fluorescence and UV–visible 149 absorption properties: AB34, AB35, AB40, AB220, 150 CSL2, CSL5, DA4, DA9, DF2, DF4, DF5, DF7, 151 DF9, K1, K2, K3, K4, K8 N35, N43, N55, N70, and 152 N89. All samples were pre-filtered through a 0.45 μm 153 Millipore filter with vacuum pump to remove particu- 154 lates. Relations between DOC, DOF and percentage 155 logging in the catchment were analyzed using SPSS 156 statistical package.

157 Absorbance between 200 and 800 nm (1 nm intervals) 158 was measured using a Varian Cary 100 Bio UV– 159 visible spectrophotometer and quartz cuvette (path 160 length = 1 cm). Absorbance reading was also calculated 161 for absorbance ratios E2/E3 (250 nm/365 nm) and E4/ 162 E6 (465 nm/665 nm) and the sum of absorbance 256– 163 312 nm. Fluorescence was measured in Turner Designs 164 Model 10 fluorometer, fitted with excitation filters #7- 165 60 and 5G (excitation wavelength 365 nm), emission 166 filter #47-B and reference filter 2A (emission wave- 167 length 437 nm) (Smart et al., 1976; Scully et al., 1996). 168 Calibration was achieved with quinine sulphate stand- 169 dards and all measurements were converted into quini- 170 nine sulphate units (qsu), where 1 qsu = 1 μg/L quinine 171 sulphate in 0.1 m H₂SO₄. DOC concentration of all 172 samples was determined using an IO Analytical 1010 173 total organic carbon analyzer (persulphate oxidation 174 method).

The slope (S) of the relationship and the intercept (I) was calculated for the relationship between the natural logarithm of the absorption and the wavelength (between 280 and 400 nm) was calculated for each of the lakes (Morris et al., 1995). All DOM quality vari- 180 ables were compared to percentage logging using correlation analysis (see Table 3).

We used a bivariate scattergram thus allowed us to 182 calculate unbiased values for the slope and intercept of the principal axis of the relationship between DOC, 185 DOCF, and forestry. The slope of the principal axis of the relationship between the observed and predicted values is:

\[
\text{Slope}_{\text{Principal Axis}} = \frac{\text{Covariance}}{\left(k_1 - \text{Variance} \left(\text{Observed Values}\right)\right)}
\]

where \( \lambda_1 \) is the first eigenvalue of the variance–covariance matrix. We estimated the uncertainty of the slope and intercept using the eigenvalues of the principal and secondary axes (Sokal and Rohlf, 1981). We evaluated the degree of association between the observed and predicted values using the product–moment correlation coefficient \( r \) and the coefficient of determination \( r^2 \) (Sokal and Rohlf, 1981). Note that in this case, because there was error associated with both the independent and dependent variables, it was necessary to calculate the coefficient of determination by multiplying the correlation coefficient by the ratio of the variance of the predicted values to the variance of the observed values. Tests of the significance of
203 the differences between the correlation coefficients
204 were preformed using the z transformation (55, 205 Section 15.5).

206 2.3. S XANES
207 S K-edge XANES spectroscopy was conducted at
208 the Canadian Synchrotron Radiation Facility (CSRF) at
209 the University of Wisconsin-Madison Synchrotron Ra-
210 diation Centre (SRC) using a double crystal monochro-
211 mator (DCM) beamline. The beamline was calibrated
212 using CuSO₄ powder to edge energy of 2483.5 eV. Data
213 reported were collected in total electron yield (TEY) 214 mode to minimize the effects of self absorption on the
215 spectra. XANES data was normalized with WinXAS
216 2.3 by fitting a linear baseline to the pre-edge region,
217 subtracting that polynomial to remove the background,
218 and then normalizing to a step size of 1.0.

219 2.4. X-ray fluorescence (XRF)
220 When elements interact with X-rays of energy
221 equal to or greater than the binding energy of core
222 electrons, then the core electrons are ejected as a
223 photoelectron wave. Higher level electrons then
224 decay into the core hole vacancies due and release
225 their excess energy as fluorescence. Because the en-
226 ergy of this emission is element specific, X-ray fluores-
227 cence analysis is a rapid and non-destructive way to
228 probe the elemental composition of samples. The XRF
229 analysis of the DOM samples was done using PNC-
230 CAT beamline 20-BM at the Advanced Photon Source
231 at Argonne National Laboratory. The synchrotron’s
232 ring was operating at 4.5 GeV in top-up mode (100
233 mA) for all experiments. A Canberra 13 element solid
234 state detector was placed at a 90° angle to the incident
235 X-ray beam, and freeze-dried powder samples of
236 DOM were placed at a 45° angle in the beam to
237 optimize fluorescence geometry.

238 2.5. X-Ray diffraction
239 X-ray diffraction was conducted at room tempera-
240 ture on freeze-dried DOM samples with a Rigaku Rota-
241 flex spectrometer. Samples were evaporated onto a
242 glass slide with a small amount ethanol and then the
243 slide was placed into the instrument for analysis.

244 2.6. NMR
245 ¹³C CPMAS spectra were acquired on a Bruker
246 Avance 500 NMR spectrometer operating at 125
247 MHz for ¹³C. Samples were packed in 4 mm (outer
248 diameter) zirconia rotors topped with kel-F caps and
249 spun at a rate of 14 kHz at the magic angle. The
250 proton 90° pulses were 3.6 μs and a proton decoupling
251 field of 69 kHz was applied during acquisition. The
252 relaxation delay and contact time were 2 s and 2 ms,
253 respectively. All spectra were the result of at least
254 40,000 scans. The FIDs were processed with 60 Hz
255 of exponential line broadening prior to Fourier trans-
256 formation. The baseline was corrected with a polyno-
257 mial. All samples were treated identically prior to
258 integration of peaks. Since this is a semi-quantitative
259 technique, peak area was expressed relative to the total
260 spectrum area. Peaks were integrated using the MEST-
261 RE software package.

3. Results and discussion

3.1. UV–VIS absorbance and DOC fluorescence

The DOC concentration, DOC fluorescence (DOCF),
percentage logging of the catchment basin for each of the
24 lakes sampled are shown in Table 2. As previously
reported by Carignan et al. (2000), we observed a pos-
itive linear relationship between percentage logging of a
lake basin and DOC concentration (slope = 0.122, r² = 0.581, p < 0.001). A weak positive relationship
was also found between percentage logging and DOC flu-
orescence (slope = 0.283, r² = 0.308, p < 0.01). The weak
relationship between DOCF and logging can be attrib-
uted to a correlation between DOCF and the B-band (256–312 nm) absor-
bance in each of the samples (r² = 0.96, p < 0.01). This suggests
that logging does not significantly affect the DOC struc-
ture in a manner that would affect its fluorescence
properties. Fluorescence is a good measure of the UV
absorbing component of DOC (the aromatic portion)
(Lean, 1998). Significant correlations were observed
between DOCF and the B-band (256–312 nm) absor-
bance in each of the samples (r² = 0.520, p < 0.05). However, DOC normalized fluorescence (i.e.
DOCF/DOC) was not found to be significantly corre-
296 lated \((r = -0.266, p < 0.05)\). The percentage logging
297 was found to be significantly correlated with the
298 sum of absorbance between 256 and 312 nm
299 \((r=0.566, p<0.01)\) and absorbance at 256 nm
300 \((r=0.562, p<0.01)\) (Table 3). Absorbance in these
301 wavebands is largely due to the aromatic component
302 of the DOM, these results indicate that with increased
303 logging there is an increased input of DOM and
304 aromatic carbon. However this data shows that logg-
305 ing does not affect the percentage of aromatic groups
306 present in the DOM (as also shown by the \(^{13}\)C NMR
307 data).

The mean slope of the natural logarithm of the
309 absorbance between 280 and 400 nm versus wavelength
310 \(S_a\) was calculated (Table 2). The mean \(S_a\) for all
311 samples \((n=68)\) was \(-0.0155 (\sigma=0.0010)\) cm\(^{-1}\)
312 nm\(^{-1}\). Morris et al. (1995) observed a similar increase
313 in absorbance with decreasing wavelength. For a series
314 of 65 lakes in Alaska, Colorado, Pennsylvania, and
315 Argentina they determined that \(S_a\) was \(-0.0181\) m\(^{-1}\)
316 nm\(^{-1}\) (standard error=0.0004) for the same UV portion
317 (280–400 nm) of the spectrum (Morris et al., 1995). The
318 values observed in this study are lower than that ob-
319 served by Morris et al. (1995), however fall within the
320 range values reported for other lakes. Kirk (1994)
321 reported values ranging from \(-0.010\) to \(-0.020\) m\(^{-1}\) nm\(^{-1}\). \(S_a\) was correlated with DOCF \((r=0.481,\)
322 \(p<0.05)\) and highly negatively correlated with the
323 absorption ratio for E2/E3 \((r=-0.876, p<0.01)\)
324 (Table 3). A decrease in the E2/E3 ratio is indicative
325 of an increase in aromaticity and molecular size
326 (Peuravuori and Pihlaja, 1997). Therefore, an in-
327 crease in \(S_a\) suggests an increase in the aromatic
328 and size of the DOM. However no significant cor-
329 relation was observed between percentage logging
330 and \(S_a\), which again shows that logging does not
331 affect DOM aromaticity.

In several soil studies the E4/E6 absorbance ratio
333 was found to decrease as decomposition increases
334 (Kononova, 1966), therefore is an indicator of humi-
335 fication. In support of the findings of Peuravuori
336 and Pihlaja (1997) we found no correlation between any of
337 the measurements and the E4/E6 ratio, which suggests
338 that this measurement is not useful for freshwater DOM
339 analysis.

The intercept of the natural logarithm of the ab-
340 sorbance between 280 and 400 nm versus wavelength
341 \(I_a\) was calculated (Table 2). The mean \(I_a\) for all
342 samples \((n=68)\) was found to be \(2.86 (\sigma=0.48)\)
343 cm\(^{-1}\). \(I_a\) was significantly correlated with both
344 DOC concentration and fluorescence \((r^2=0.878,\)
345 \(p<0.01,\) and \(r^2=0.917, p<0.01,\) respectively) and
Table 3
Correlation matrix examining relationships between DOC, DOCF, percentage logging and various DOM absorbance parameters

<table>
<thead>
<tr>
<th></th>
<th>DOC</th>
<th>DOCF</th>
<th>DOC/DOCF</th>
<th>Percent logged</th>
<th>Sum ABS 256–321</th>
<th>E4/E6</th>
<th>E2/E3</th>
<th>ABS 254</th>
<th>$S_a$</th>
<th>$I_a$</th>
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<td>DOC</td>
<td>Correlation</td>
<td>1.000</td>
<td>.776</td>
<td>.305</td>
<td>.784</td>
<td>.772</td>
<td>.002</td>
<td>-.106</td>
<td>.846</td>
<td>.215</td>
</tr>
<tr>
<td>Sig. (2-tailed)</td>
<td>.000</td>
<td>.157</td>
<td>.000</td>
<td>.993</td>
<td>.632</td>
<td>.000</td>
<td>.338</td>
<td>.000</td>
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<td>DOCF</td>
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<td>.314</td>
<td>.520</td>
<td>.960</td>
<td>.048</td>
<td>.150</td>
<td>.481</td>
<td>.917</td>
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<td>.232</td>
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<td>.158</td>
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<td>.103</td>
<td>.964</td>
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Note: correlations in bold are significant at the 0.05 level (2-tailed).

3.2. S XANES

XANES has been used to examine sulphur speciation in DOM. Morra et al. (1997) found that standard aquatic humic acids (obtained from the IHSS) are dominated by sulphonates (+5 oxidation state) with small amounts of ester bonded sulphates (+6 oxidation state), while standard aquatic fulvic acids primarily contained sulphonic acids, with reduced sulphur present in both. Xia et al. (1998) found Suwannee River fulvic and humic acid standards to contain 35% and 46% respectively of the total sulphur in reduced form. Qian et al. (2004) found that the differences in DGM photo-production between lakes are due to increased DOM concentration and not differences in UV absorbing structures in the DOM. Therefore, these results show that attenuation of UV radiation is not the primary factor attributing to the DGM photo-production differences in logged and non-logged lakes. However, we cannot assess the importance of visible and infrared radiation at this time.
lakes N70 and DF9 have less sulphate and more reduced sulphur (Fig. 1). Some sulphur in the sulphonyl (+5) form can also be observed in samples DF9 and N70 but not in K2 or K3. While the amount of reduced sulphur in these samples may appear to be small, intensity of XANES features from reduced sulphur is far less than that of sulphate (e.g. elemental sulphur is almost a factor of 3 less than sulphate) (Sandström et al., 2002). When the reduced S in the DOM samples is examined more closely (Fig. 2), it can be seen that the form of reduced S in all samples is similar to thiol groups such as cysteine and methionine. One peak at 2473.5 eV is present in all samples, and sample DF9 also possesses a shoulder centered at 2472.4 eV that may be due to sulphide minerals (good agreement with the peak and the spec-

Fig. 1. S XANES data for extracted dissolved organic matter compared to oxidized standards. The large peak in all DOM samples at 2480–82 eV is due to sulphur in +5 and +6 oxidation states, while the smaller peak in the 2470–2475 eV region is due to reduced sulphur. More reduced sulphur is observed in DOM from lakes DF9 and N70. The dashed box is enlarged for comparison to standards in Fig. 2.

Fig. 2. S K-Edge XANES spectra of reduced S in DOM compared to standards.
tra of ZnS was found). Iron sulphides are the most likely phases, but the position of the XANES peak does not correspond with crystalline iron(II) sulphide standards such as pyrite (FeS$_2$) or mackinawite (FeS). Since the position of the XANES peak shifts from FeS (2470 eV) to FeS$_2$ (2472 eV), it is possible that the XANES feature in the DOM samples is due to amorphous iron sulphides containing octahedral iron in either +2 or +3 oxidation state. The possibility of iron sulphides being present in the DOM samples is strengthened by an X-ray fluorescence scan of sample DF9 (Fig. 3). It can clearly be observed that a variety of trace metals (Fe, Cu, Ni, Zn, and As) are present in the concentrated DOM sample.

### 3.3. X-Ray diffraction

One of the findings from S K-Edge XANES spectroscopy was that metal sulphides might be present in some of the DOM samples. To explore this possibility, X-ray diffraction was conducted on all samples to verify whether mineral phases were actually present (Fig. 4). If the DOM samples contained only organic phases, then there would be no substantial peaks observable with XRD. In samples K2, N70, and K3, this is generally the case, although there are some minor features attributable to the crystallization of a small amount of CaSO$_4$ salt during freeze-drying. These CaSO$_4$ peaks are not seen in sample DF9, and instead a single broad peak centered at 4.5 Å is observed. This broad feature is consistent with XRD spectra of pyrite produced by the sulphuration of iron films at low temperatures (Sanhueza et al., 1999). Other researchers (Herbert et al., 1997) reported a single broad XRD pattern with a spacing near 5 Å for poorly crystalline mackinawite. This XRD peak therefore seems consistent with a sulphide mineral phase, as organic compounds could not produce such an XRD pattern. Perhaps, the collection methods concentrated a sulphide mineral colloid from the water, but it is more likely that the sulphides are intimately associated with the DOM. Sulphides could oxidize rapidly during the concentration process in aerobic waters. Association with DOM is likely to affect the rate of this oxidation.

From both XANES and XRD results it is reasonable to conclude that amorphous sulphide minerals are present associated with these DOM samples in aerobic waters. The relationship, if any, between these sulphides and mercury cycling is still unclear and the XANES analysis does not find any indication of other dramatic changes in sulphur speciation in logged vs. natural lakes. Alternatively, it is possible that since reduced sulphur was relatively low in these DOM samples, other functional groups (e.g. carboxylic acids) are relatively more important to mercury dynamics.

![Fig. 3. X-ray fluorescence scan of sample DF9.](image-url)
3.4. NMR analysis

The $^{13}$C NMR analysis (Fig. 5) found that aliphatic carbon and carbohydrate carbon groups were predominant (ranging 38.5–47.6% and 38.1–53.8%, respectively) for the lake water extracted DOM. This compares well with Dai et al. (2001) who found that the predominant carbon groupings were aliphatic and carbohydrate ranging from 22–42% to 29–60% respectively of total carbon in stream water dissolved organic matter. Our results also show that the aromaticity of the lake DOM is quite low with 3.8–12.0% of the carbon in aromatic groups, which is similar to the 12–16% found by Dai et al. (2001). The percentage of carbon in carboxyl groups ranged between 3.8% and 4.8% and no significant carbon was found to be in carbonyl groups.

The $^{13}$C NMR analysis (Fig. 5) also indicated increases in percentage of aliphatics and decreases in carboxyls with increased logging activity. We find no clear trend with logging as is observed for the % C in aromatic groupings (since K2 is an outlier with the high aromaticity but low logging). In addition the DOC normalized fluorescence and UV absorbance data indicates that logging is related to DOC concentration but not percentage of aromaticity of the DOM in the larger set of 23 lakes. This is in contrast to the findings of Dai et al. (2001) who examined the effects of clear cutting on soil organic matter and dissolved organic matter extracted from adjacent streams using $^{13}$C NMR. The authors found that soil DOM showed 40% more carbon in aromatic groups at the clear-cut sites relative to pristine sites. The authors attribute this to increased leaching of highly decomposed organic matter with clear cutting.

While no changes were observed in the UV absorbing structures in the DOM, we did find that the amount of carbon in carboxyl groups increased 26% (from 3.8% to 4.8% of total carbon) with a 67% increase in logging. Preston et al. (1992) report that the standard deviation of a similar $^{13}$C NMR technique for DOM is <5% between samples (or <0.3% error on the measured carbon in carboxylic groups). This is particularly important to the availability of photo-reducible mercury since: (i) carboxylic groups are present in DOM in much larger numbers than reduced sulphur groups; and (ii) carboxylic groups bind mercury weakly (in contrast to reduced sulphur which binds strongly) (Drexel et al., 2002).Weakly bound mercury is likely more available for production of DGM than is strongly bound mercury. Therefore the binding of mercury to carboxylic groups is very important to determining the initial availability of photo-reducible mercury.

3.5. Relationship between forestry activity, DOM structure, and DGM photo-production

As previously shown by Carignan et al. (2000), we find that DOC concentration in lake water is positively related to the amount of recent logging in the lake’s catchment. In addition we observe that the aromaticity
of DOM in a lake is not related to the percentage logging of the lake’s catchment (as shown by UV–VIS and DOC normalized fluorescence data). The work of Haitzer et al. (2002, 2003) demonstrates the importance of reduced sulphur groups within DOM which may bind Hg(II). While reduced sulphur groups in the DOM likely play an important role in the mercury–DOM binding observed, our results show no apparent relationship between levels of reduced sulphur in the DOM extracts and percentage logging in the lakes. We do, however, find a pattern of increasing percentage of carbon in carboxylic groups in the DOM with increasing percentage logging. We currently have no data on the relative amount of Hg(II) bound to reduced sulphur groups in the DOM compared to carboxylic groups. However, it is likely that any carboxylic-bound mercury is more available for photo-reduction reactions as reduced sulphur groups have been shown to be strong binders of mercury (Hintelmann et al., 1997). It should be noted that the specific structural analysis in this study is based on a limited number of DOM samples (due to analysis constraints) and should be verified over a wide range of lakes in order to make a definitive statement on the role of forestry in DOM structure. However, given the complexity of obtaining representative DOM samples and performing specific structural analysis we feel that this study provides enough evidence to warrant future research on this mechanism.

Fig. 5. $^{13}$C NMR spectra for the DOM solids isolated from each lake site. Spectra arranged top to bottom from lowest to highest percentage logging in catchment. The percentage of total carbon in each carbon structure is displayed vertically on the figure for each sample.
While the exact link between logging and DOM structure is unknown there are several possible mechanisms that may result in these structural changes. Previous research has shown that logging of a catchment can result in significant water table fluctuations (generally rising with increasing logging) (Xu et al., 2002). Changes in the water table will affect the movement of DOM from soils as well as the amount of overland run off. This may affect the proportion of DOM (contained in the soil) and new DOM (released from recent plant decay on the surface) that is transported to the lake.

There is some evidence to suggest that logging may affect the aromaticity of DOM in an ecosystem. Ciesle-
wicz and Gonet (2004) found higher amounts of carbon and oxygen and lower hydrogen and nitrogen in DOM from the bottom sediments of lakes with primarily forested catchments versus lakes with primarily agricultural catchments. The authors also observed an increased presence of aromatic structures in DOM from lakes with forested catchments versus agricultural catchments. Similarly, Dai et al. (2001) observed in an experimental forest in New Hampshire that logging of watersheds resulted in changes in soil organic matter (SOM) structure and DOM in soil solutions. The authors observed that SOM chemistry did not change with logging, however, the aromatic portion of the DOM in soil solutions was higher in logged catchments. Due to the wide variation in seasonal DOM chemistry isolated from streams the authors concluded that seasonal hydrology has a greater effect on DOM structure than does disturbance by clear cutting. In lakes where hydrology has a lesser influence logging disturbances may have a greater impact on DOM structure than does disturbance by clear cutting. In lakes where hydrology has a lesser influence logging disturbances may have a greater impact on DOM structure than does disturbance by clear cutting. In contrast to the work of Dai et al. (2001) and Cieslewicz and Gonet (2004), we do not find a relationship between lake water isolated DOM aromaticity and logging in this study. If we assume that aromaticity increases in DOM soil solutions with increased logging (as shown by Dai et al. (2001)), these results would suggest that newly decomposed carbon is more important to the lakes observed in this study.

DOM derived from the decaying root masses of recently logged trees and abandoned tree limbs may contain more carboxylic functional grouping and less reduced sulphur than DOM that has been exposed to longer periods of microbial activity and diagenesis. The importance of seasonal variations in DOM transport and DOM structure was not examined in this study. Laudon et al. (2004) found that the percentage of DOM transported by spring snowmelt events is less important to total DOM movement in lakes with increasing wetlands in the catchment. This suggests that in forested sites spring snowmelt is a significant movement of the DOM to a lake. Since our sampling was conducted in early fall it is unclear what influence the spring snowmelt would play in DOM transport and the structural characteristics of DOM isolated from logged and non-logged sites.

We know from previous work that mercury species bind strongly with reduced sulphur groups in DOM, and less strongly to the more abundant carboxylic groupings (Hintelmann et al., 1997; Drexl et al., 2002; Ravichandran, 2004; Haitzer et al., 2002, 2003). Our recent work indicated that mercury reduction rates were slower in lakes with logged catchments. We suggest that one possible explanation may be that logged catchments have less photo-reducible mercury available for creation of DGM due to the increased percentage of carboxylic functional groups present. While the mechanism by which logging affects DOM structure is currently unclear we suggest that changes in the water table and the relative transport of both newly decomposed and older refractory organic material are key to determining aromaticity and the functional group content of DOM (Fig. 6). One possible scenario is that new inputs of DOM contain more carboxyl groups than old DOM present in the lake and that logging in this particular set of lakes has increased the presence of new DOM.

In summary, our results indicate: (i) that forestry does increase DOC concentrations in lakes and result in associated increases in DOC fluorescence, however forestry does not influence DOM aromaticity; (ii) that significant differences in reduced sulphur content of DOM are measurable but not related to forestry in this dataset; (iii) the concentrated DOM contained amorphous sulphide minerals which may be important sites for mercury binding; and (iv) the carboxylic acid content of DOM increased with increasing logging which may limit the availability of photo reducible mercury.

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References


