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1 **Effects of disturbance and vegetation type on total and methylmercury in boreal peatland and**

2 **forest soils**

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28   **Highlights**

29   • [Hg] in boreal peatland and forest soils was related to atmospheric deposition

30   • [MeHg] and MeHg-to-THg ratios testifies to increased peatland methylation

31   • Soil disturbance increases production of MeHg

32

33   **Abstract**

34   Mercury (Hg) concentrations in freshwater fish relates to aquatic Hg concentrations, which largely

35   derives from soil stores of accumulated atmospheric deposition. Hg in catchment soils as a source for

36   aquatic Hg is poorly studied. Here we test if *i)* peatland soils produce more methylmercury (MeHg)

37   than forest soils; *ii)* total Hg (THg) concentrations in top soils are determined by atmospheric inputs,

38   while MeHg is produced in the soils; and *iii*) soil disturbance promotes MeHg production. In two

39   small boreal catchments, previously used in a paired-catchment forest harvest manipulation study,

40   forest soils and peatlands were sampled and analysed for Hg species and additional soil chemistry. In

41   the undisturbed reference catchment, soils were sampled in different vegetation types, of varying

42   productivity as reflected in tree density, where historical data on precipitation and throughfall Hg

43   and MeHg fluxes were available. Upper soil THg contents were significantly correlated to throughfall

44   inputs of Hg, i.e. lowest in the tree-less peatland and highest in the dense spruce forest. For MeHg,

45   top layer concentrations were similar in forest soils and peatlands, likely related to atmospheric input

46   and local production, respectively. The local peatland MeHg production was documented through

47   significantly higher MeHg-to-THg ratios in the deeper soil layer samples. In the disturbed catchment,

48   soils were sampled in and just outside wheeltracks in an area impacted by forest machinery. Here,

49   MeHg concentrations and the MeHg-to-THg ratios in the upper 5 cm were weakly significantly (p =

50   0.07) and significantly (p = 0.04) different in and outside of the wheeltracks, respectively, suggesting

51   that soil disturbance promotes methylation. Differences in catchment Hg and MeHg streamwater

52   concentrations were not explained by soil Hg and MeHg information, perhaps because hydrological

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53 pathways are a stronger determinant of streamwater chemistry than small variations in soil

54 chemistry driven by disturbance and atmospheric inputs of Hg.

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56 **Keywords**

57 Mercury, methylmercury, soil disturbance, forest harvest, methylation, boreal

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59 **Capsule**

60 Influences of atmospheric Hg input, peatland soil chemistry and harvesting operations on

61 total Hg and methyl Hg concentrations in different peatland and forest soils were tested.

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63 **Introduction**

64 Elevated concentrations of toxic and bioaccumulative methylmercury (MeHg; Bloom, 1992) in fish

65 have potential harmful effects on humans and animals with fish as part of their diet (WHO, 1991).

66 The main source of mercury (Hg) in pristine Scandinavian environments is deposition of long-range

67 transported atmospheric Hg released in other countries (Berg et al., 2006; Pacyna et al., 2010). Most

68 of deposited Hg is stored in the soil, and a minor part is leached to surface waters as inorganic Hg or

69 MeHg (Fitzgerald et al., 1998), where transport of Hg and production and transport of MeHg is driven

70 by catchment processes (Ravichandran, 2004). The biogeochemical cycling of Hg in catchments is one

71 of the keys to improve understanding of concentrations and bioaccumulation of Hg species in the

72 aquatic environment.

73 For boreal catchment export of MeHg, wetlands appear to be an important methylation

74 source, as reported both in Scandinavia (e.g. Tjerngren et al., 2012a) and North America (e.g.

75 Mitchell et al., 2008; St. Louis et al., 1996). It is well established that production of MeHg is occurring

76 primarily through methylation of inorganic Hg by sulphur reducing bacteria (SRB) under anoxic

77 conditions (Morel et al., 1998), but other pathways are also evident (e.g. iron reducing bacteria;

78 Gilmour et al., 2013). In addition to wetlands, forested catchments dominated by upland soils can

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79   also export large amounts of MeHg (Eklof et al., 2012; Eklof et al., 2013). Forest soils receive more Hg

80   and MeHg from the atmosphere than wetlands, because Hg is absorbed by forest canopies and

81   subsequently deposited to soils by throughfall and litterfall (Mowat et al., 2011; Munthe et al.,

82   1995b). Hence, forest soils can contain similar or higher concentrations of Hg and MeHg compared

83   with wetlands (Graydon et al., 2008). Forest management (Bishop et al., 2009) and catchment

84   disturbance (Munthe and Hultberg, 2004) has been shown to be a factor that promotes leaching of

85   MeHg, although the mechanisms behind remain poorly understood (Eklof et al., 2016). For instance,

86   where natural wetlands have been identified as principal sources of MeHg in northern boreal

87   regions, a recent study shows how wetlands also can act as MeHg sinks (Tjerngren et al., 2012b)

88   under certain conditions, e.g. continuous standing water exposed to sunlight (Kronberg et al., 2012).

89   Many studies demonstrate strong relationships between aquatic concentrations of Hg

90   species and Hg in the aquatic food web (e.g. Braaten et al., 2014c; Chasar et al., 2009; de Wit et al.,

91   2012). In areas where atmospheric inputs are the dominating source of Hg, it can be expected that

92   Hg concentrations in streamwaters are co-determined by Hg contents in soils, and by conditions that

93   promote the production of MeHg in catchment soils, such as presence of peatlands (Mitchell et al.,

94   2008; Porvari and Verta, 2003) and disturbance (Porvari et al., 2003). While concentrations of Hg in

95   fish (Fjeld, 2010), lake sediments (Fjeld et al., 1994; Rognerud and Fjeld, 2001), mosses (Berg et al.,

96   2006) and surface waters (Braaten et al., 2014a) have been documented in many regions in Norway,

97   data on Hg in soils in remote areas are scarce. More data on Hg in soils and wetlands are potentially

98   valuable for a larger understanding of catchment MeHg production and transport of Hg and MeHg to

99   surface waters.

100   In this study, our main goal was to document the local variation in total Hg (THg) and MeHg

101   concentrations in different soils and explain this variation in relation to vegetation type, soil

102   characteristics and catchment disturbance, in two boreal catchment previously included in a paired-

103   catchment forest harvest manipulation (De Wit et al., 2014). We tested the following hypotheses: *i*)

104   peatland soils have lower THg and higher MeHg concentrations than forest soils; *ii*) THg

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105   concentrations in top soils are determined by atmospheric inputs, while MeHg is produced in the

106   soils; and *iii*) soil disturbance promotes production of MeHg.

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108   **Materials and methods**

109   *Site description*

110   The Langtjern lake catchment area (4.8 km^2, 510-750 m.a.s.l.) is located in south east Norway (Figure

111   1; outlet of lake at 60.37 N, 9.73 E). No direct human disturbance has taken place in the catchment

112   since the 1930s, but the catchment was severely acidified during the 20th century with the loss of its

113   trout population and damage to invertebrate populations. The catchment has been part of the

114   Norwegian acid rain monitoring programme since 1972, which includes weekly monitoring of lake

115   outlet chemistry (LAE01, Figure 1, Garmo et al., 2013).

116   Vegetation in the lake catchment was mapped in 1974. Dominating vegetation types are, in

117   declining order of % area cover, Scots pine forest (*Pinus sylvestris* L., heather (*Calluna vulgaris*)),

118   northern bilberry (*Vaccinium uliginosum*), 63%), Norway spruce forest (*Picea abies* L., Karst., bilberry,

119   6%), swamp forest (5%), peatlands (poor fens and ombrotrophic bogs, 16%). Water (5%) and bare

120   rock (2%) made up the remainder of the catchment. The vegetation types differ in productivity,

121   which is reflected in tree density, where Scots pine has the lowest density (open forest, no closed

122   canopy), and spruce forest has the highest density (dense forest, closed canopy). Swamp forest has

123   an intermediate tree density. Scots pine is a lower productivity class forest than Norway spruce

124   (Larsson et al., 2000).

125   The eastern lake inlet is from the LAE03 sub-catchment (0.8 km^2, Larssen et al., 2008), used

126   as a reference catchment in an experimental paired catchment study where 30% of a small, nearby

127   catchment (outside the main catchment, LAE11, 0.3 km^2) was harvested in 2009 (Figure 1, de Wit et

128   al., 2014). Water chemistry in both LAE03 and LAE11 streams has been monitored in monthly

129   intervals since 2008. Mean annual temperature and precipitation for the Langtjern catchment

130   between 2008 and 2011 were 4.5 °C and 914 mm, respectively (de Wit et al., 2014).

132 *Throughfall*

133 In the summer season of 2009, six locations in the LAE03 catchment were selected for sampling of

134 throughfall, i.e. the peatland near to the lake (P1), three locations in the most common vegetation

135 type Scots pine forest (F1), one in the swamp forest (F2) and one in the Norway spruce forest (F3). At

136 each location, three throughfall samplers were placed at randomly chosen places with 10 to 20 m

137 distance of each other. Each sampler consisted of a slightly tilted 0.1 m^2 (0.8x0.125 m) Teflon-coated

138 gutter, firmly attached to two wooden sticks driven into the ground, at an approximately height of 40

139 cm. The gutters led to a glass funnel on a 10-L acid cleaned (50 ml of 1 M hydrochloric acid, HCl) glass

140 bottle which was packed in aluminium foil. The Teflon-coated gutters were washed with rain water

141 prior to sampling. The sampling period covered May 30 2009 until October 20 2009. Four samplings

142 took place (June 30, July 28, August 30 and October 20). At each sampling, the water volume in each

143 bottle was noted, also when the bottle was full. At each site, a composite throughfall sample was

144 taken by pouring ca 80 ml of each bottle (sampler) into a 250 ml Teflon bottle for analysis of MeHg

145 and THg, in addition to taking a composite sample for chemical analysis of TOC (see below for a

146 description of chemical water analysis). The 10-L bottles were emptied after removing the sample.

147 Throughfall element fluxes were calculated by averaging the sample volume in the three

148 sample bottles in each site, multiplying with species concentration, and dividing by number of days in

149 the sampling period. On August 30, all sample bottles were full and we estimated the expected

150 volume by taking the ratio of measured precipitation at a nearby meteorological station in the

151 sampling periods, to the measured throughfall volume in the other sampling periods. The THg/TOC

152 and MeHg/TOC ratios were used to evaluate the quality of the concentration data, and the first

153 sampling had significantly higher ratios than the other three. Although environmental explanations

154 for this are possible (e.g. high pollen levels), it was thought to be related to insufficient cleaning of

155 the Teflon coating after installation of the samplers. The first sampling was therefore not used in the

156   flux calculations. Throughfall fluxes in the three Scots pine sites were averaged to give one flux for

157   the Scots pine forest.

158

159   *Soil sampling and sample preparation*

160   All soils were sampled during a field campaign in September 2013 (sampling description and

161   summary in Table 1). In the reference, undisturbed catchment (LAE03), soils were sampled at the

162   same locations where throughfall was collected (sites P, F1 (pine forest), F2 (swamp forest), F3

163   (spruce forest), see Figure 1). In LAE11, undisturbed open peatland (P) was sampled. In the disturbed

164   catchment area, impacted by forest machinery (i.e. harvester and forwarder) and where the canopy

165   was removed, three wheeltracks (WT1, WT2, WT3) were sampled, paired with sampling points less

166   than 5 m distance outside the wheeltracks with no signs of damage from forest machinery (WT1a,

167   WT2a, WT3a). For sampling points WT1a-3a we use the notation "non-wheeltrack samples"

168   throughout the manuscript.

169   The soils were sampled by digging a hole of ca. 20 cm depth with a spade, visually

170   characterising the different soil layers, and separating these with a knife. Following this, ca. 5x5 cm^2

171   samples of each soil layer were cut at three sides in the soil pit, thus giving triplicate soil samples.

172   Each soil sample was put into a double zip-lock plastic bag, sealed and marked. Air was forced

173   manually out of the bag upon sampling and all samples were kept dark and cool until sample

174   preparation (< 48 h after sampling).

175   Prior to sampling the top soil layer, fresh plant material was removed. In the forest, L and F

176   layer of the organic horizon were lumped, while the H layer and the 0-5 and 5-10 cm of the mineral

177   soil were sampled separately (The Canadian System of Soil Classification, SCWG, 1998). According to

178   SCWG (1998) the L, F and H layer are characterised by accumulation of organic matter where the

179   original structure is easily discernible; by accumulation of partly decomposed organic matter where

180   some of the original structures are difficult to recognise; and by accumulation of decomposed

181   organic matter where the original structures are indiscernible, respectively. Where soil depth was

182   insufficient (i.e. not all the abovementioned layers were present), fewer samples were collected. In

183   the peatlands, the L and F layer were sampled separately based on a visual evaluation, and below the

184   F two more layers of 5 cm were sampled. The wheeltracks were all located in highly organic soils but

185   lacking differentiation according to soil depth, and here 0-5 and 5-10 cm soil layers were sampled.

186   The paired sampling points in the disturbed area were sampled similarly with 0-5 and 5-10 cm soil

187   depth.

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189   *Chemical analysis – soil*

190   For soil THg determination, subsamples were freeze dried prior to analysis. THg was determined by

191   thermal decomposition and direct atomic absorption spectrophotometry (AAS, Milestone Direct

192   Mercury Analyser DMA-80). For every 10 soil samples of Hg analysis (20 – 200 mg) quality assurance

193   and quality control (QA/QC) measures included method blanks sample duplicates (n = 2) and certified

194   reference material (CRM, MESS-3 marine sediment; n = 2). The certified Hg concentration of the CRM

195   used was 91 ± 9 μg/kg. The relative percent difference (RPD) of sample duplicates was always < 10 %

196   and recovery of CRM within 90 – 110 %.

197   MeHg was extracted from a wet subsample of soil by methods described in detail by (Bloom

198   et al., 1997). In short, the method include leaching of the Hg with potassium bromide (KBr; 18 %),

199   sulphuric acid (H_2SO_4; 5 %) and copper sulphate ($CuSO_4$; 1M) before extraction of the Hg in the

200   leachates into dichloromethane (DCM). The Hg was then back extracted into DI water (by use of

201   Whatman 1PS silicone treated filter paper) before heating (approximately 70 °C for 5 hours).

202   Determination follows the USEPA Method 1630 for determining MeHg by aqueous ethylation, purge

203   and trap, and cold vapor atomic fluorescence spectrometry as described in (Braaten et al., 2014a).

204   Analysis of a MeHg CRM (ERM-CC580; estuarine sediment) was within the reported range (75 ± 4

205   ng/g). Method Detection Limit (MDL) is 20 pg/g (3 standard deviations of blank extractions) based on

206   a sample weight of 0.05 g.

207   Total nitrogen (Tot-N) and total carbon (Tot-C) in the soil samples were determined using a

208   Flash 2000 Dynamic Combustion Automatic Element Analyser (Norwegian standard NS16168:2012).

209   Analysis was done on freeze dried sample material and MDL is 1.0 µg/mg for both Tot-N and Tot-C.

210   Phosphorous was determined by inductively coupled plasma – atomic emission spectrometry (ICP-

211   AES).

212   All soil analyses were performed at the Norwegian Institute for Water research (NIVA).

213

214   *Streamwater sampling and chemical water analysis*

215   Streamwater grab samples for general water chemistry is collected on a monthly basis in the

216   Langtjern catchments. Procedures for sample collection, preservation and analysis (including QC/QA)

217   is documented by Braaten et al. (2014b), with results from 2008 – 2012 being recently published by

218   de Wit et al. (2014).

219

220   *Statistics*

221   Properties of the datasets were reported using arithmetic means and one standard deviation (mean

222   ± one standard deviation, Table 2). The pools of Hg in the soil and other measured soil parameters

223   were compared across study sites (sample locations; vegetation and soil type) by use of non-

224   parametric Kruskal-Wallis test. To test for all possible individual comparisons between study sites, we

225   used student's t-tests. Multivariate correlations between selected variables (soil characteristics) and

226   Hg speciation were explored by Pearson's correlation coefficient, r. The wheeltrack and non-

227   wheeltrack samples from catchment LAE11 were compared using t-tests on paired samples, i.e. one

228   sample parallel was directly compared to another (i.e. WT1-WT1a, WT2-WT2a and WT3-WT3a).

229   All statistical analysis and calculations were done in JMP 9.0 (SAS) with a significance level α =

230   0.05, unless otherwise mentioned.

231

232 **Results**

Soil chemistry – carbon and nutrients

233

234 The forest soils from the undisturbed catchment LAE03 had thick organic layers (> 15 cm) on top of a

235 mineral soil, except for the soil under Scots pine where the O layer was only 9 cm deep (Table 2). The

236 L and F layer in the peatlands was thicker in LAE03 (15 and 10 cm, respectively) than in LAE11 (7 and

237 5 cm, respectively). In the disturbed soils from catchment LAE11, it was not possible to distinguish

238 between L and F layers and here we sampled by soil depth. All organic layers had a C-content around

239 45-53 % (Table 2, Figure 2a), whereas mineral soil layers had lower C (< 10 %). In the disturbed

240 catchment LAE11, the wheeltracks had more variable and on average slightly lower C-contents than

241 the non-wheeltracks (Table 2, Figure 2b).

242 All soils were low in N and P content (< 2 % and < 0.8 %, respectively, Table 2). The top layers

243 of the peatlands had lower N% and P% (< 1 % and < 0.4 %, respectively) than the disturbed soils

244 (wheeltracks 1.6 % and 0.7 %, respectively and non-wheeltracks 1.6 % and 0.6 %, respectively),

245 possibly because of release of nutrients in the disturbed catchments where the forest had been

246 harvested. The highest C/N ratios were found in the top layer of the peatlands (on average 68 and 59

247 for LAE03 and LAE11, respectively), which suggests a different litter quality from fresh sphagnum

248 than from forest vegetation. The decline of C/N ratio with peatland depth (Table 2) might indicate

249 preferential loss of C compared to N, or by microbial immobilisation of N. Peatlands are known to be

250 sinks for nitrogen (Wang et al., 2014).

251

Soil chemistry – mercury

252

253 Concentrations of MeHg and THg in the peatlands varied remarkably little with depth, in contrast to

254 the forest soils (Figure 2a). Top soil concentrations of MeHg in forest soils and peatland samples

255 were similar, i.e. on average 0.6 ± 0.6 ng/g. THg concentrations in the top layer of the forest soils

256 (143.8 ± 45.3 ng/g) were significantly higher than in the peatlands (40.6 ± 7.2 ng/g, $p < 0.001$). THg

257 increased going downwards in the organic layers, both for peatlands and forest soils, possibly as a

258 result of downward transport of dissolved organic matter (DOM), to which Hg is associated. Hence,

259   the low concentration of Hg measured in the mineral forest soil (< 50 ng/g) was likely due to its low

260   organic matter content (< 10 %). MeHg concentrations in the top soil from the wheeltracks (0.9 ± 0.7

261   ng/g) were higher than in the non-wheeltracks (0.1 ± 0.1 ng/g, p = 0.05), in the area disturbed by

262   forest harvest (catchment LAE11), while THg showed the opposite pattern (89 ± 19 ng/g and 147 ± 25

263   ng/g, respectively, p = 0.02).

264   The MeHg-to-THg ratio (shown as %MeHg, used as an estimate of the long-term net

265   production of MeHg in the soils) in top soil layer samples, was highest in the peatlands (on average

266   1.5 ± 1.4 %), and weakly significantly higher than in the forest soils (0.4 ± 0.5 %, p = 0.06). %MeHg did

267   not show a significant change with depth in peatlands or forest soils (Figure 2a), but maximum ratios

268   were observed in the deepest sample for both peatlands (3.1 ± 2.3 % and 1.1 ± 0.5 % for LAE03 and

269   LAE11, respectively). In the wheeltracks in the disturbed catchment area, %MeHg was comparable

270   with the peatlands while the non-wheeltracks had values more similar to the forest soils (Figure 2b).

271   Our first hypothesis – that peatland soils have lower THg and higher MeHg concentrations

272   than forest soils – was only supported for THg. The peatlands in our study had similar MeHg

273   concentrations as the forest soils in the top layer, whereas MeHg in the deeper soil layers was

274   highest in the peatlands.

275

276   *Soil mercury in relation to vegetation type and throughfall*

277   THg concentrations in the upper soil layers in the four vegetation types of the undisturbed LAE03

278   catchment were significantly related to throughfall fluxes of THg at each location respectively (Figure

279   3; linear regression, r^2 = 0.97, p = 0.02). Throughfall fluxes of THg were measured in the summer of

280   2009 and we assume that the pattern of different throughfall fluxes between vegetation types are

281   representative for the year of soil sampling (2013). In the peatland, no canopy was present and the

282   throughfall flux represents wet atmospheric THg deposition (1.3 µg/m^2). The difference between the

283   throughfall in the peatland and the forest types illustrates that the presence of canopy increases

284   input of Hg to the soil. The throughfall fluxes increase from the open pine forest (2.6 µg/m^2), to

285   denser swamp forest (3.5 μg/m^2) to the densest of the vegetation type, the spruce forest (3.9 μg/m^2),

286   suggesting that canopy density increases Hg deposition.

287   The pattern of MeHg fluxes in the different vegetation types was similar to that of THg fluxes

288   (Figure 3), and they were significantly related (r^2 = 0.96, *p* = 0.02). MeHg throughfall in the forest

289   vegetation types (from 72 to 104 ng/m^2) were from 3.8 to 5.5 times higher than MeHg inputs to the

290   peatland (19 ng/m^2), which suggests that the high soil MeHg contents found in the top layer of the

291   forest soils are at least co-determined by atmospheric inputs. The decrease in MeHg in the forest

292   soils with depth suggests that in-soil net production of MeHg is likely to be low in the forest soils,

293   opposite to the peatland soils where MeHg did not decline with depth (Figure 2a). The weakly

294   significantly higher %MeHg (*p* = 0.06), an indirect estimate for MeHg production, in the top soil layers

295   of peatlands versus forest soils also indicates that peatland soils produce more MeHg than forest

296   soils.

297   Our second hypothesis – that MeHg in soils is produced in soils, while THg is determined by

298   atmospheric inputs – was partially supported. MeHg in the top soil layer in the forest appeared to be

299   determined by atmospheric inputs, and strongly declined with soil depth. In peatlands, MeHg was

300   also found in the deeper layers suggestion local production, as indicated by the significantly higher

301   %MeHg. THg in the upper soil layers was strongly related to atmospheric inputs in all vegetation

302   types.

303

304   *The effect of soil disturbance*

305   The LAE11 catchment was harvested in January 2009, resulting in soil disturbance visibly evident as

306   deep wheeltracks. Soil was sampled in three wheeltracks, paired with soil samples in not visibly

307   disturbed yet harvested area within 5m distance ("non-wheeltracks"; Figure 1, Table1). In the top soil

308   layer from the wheeltrack locations, %MeHg was significantly higher (t-test on paired samples, *p* =

309   0.04) than in the non-wheeltrack locations while MeHg concentrations were weakly significantly

310   higher (t-test on paired samples, *p* = 0.07). THg concentrations was weakly significantly different (t-

311   test on paired samples, $p = 0.06$). Neither C/N ratios ($p = 0.23$) nor levels of C% ($p = 0.48$) in the

312   wheeltracks were significantly different from the non-wheeltracks, indicating similar organic matter

313   content and quality.

314   Our third hypothesis – that soil disturbance promotes methylation of inorganic Hg – was

315   supported by the significantly higher MeHg and MeHg-to-THg ratios in the wheeltracks as compared

316   to the non-wheeltracks.

317

318   **Discussion**

319   *Spatial variation of Hg in soils*

320   The range of soil THg concentrations in the present study (from 16 ± 2 to 300 ± 36 ng/g, Table 2) are

321   similar to what is previously documented for the Langtjern catchment (Larssen et al., 2008); 37 – 268

322   ng/g, and lower than proposed critical limits for Hg in soil organic matter (500 ng/g) (Meili et al.,

323   2003). Our observed concentrations are, however, low compared with a range reported in a study of

324   a peatland swamp in southern Sweden (Kronberg et al., 2012), i.e. 177 to 640 ng/g, but similar to

325   studies from further north in Sweden (Tjerngren et al., 2012a), i.e. 113 – 287 ng/g. The higher

326   concentrations in southern Sweden are also documented elsewhere (~250 – 400 ng/g in De Wit et

327   al., 2015) and are related to its location further south with possibly more influence from atmospheric

328   deposition of long range transported Hg. The differences fit the patterns of declines in environmental

329   Hg along a north-south gradient in Scandinavia, substantiated by studies of Hg in top sediments

330   (Munthe et al., 2007) and mosses (Berg et al., 2006; Steinnes et al., 2003).

331   There are not many studies available devoted to analysing environmental MeHg

332   concentrations in soils and peatlands from the boreal region based on non-manipulated soil data.

333   The few that exists from Scandinavia show higher concentrations than what is found in the present

334   study: 1.9 – 39 ng/g (Kronberg et al., 2012), 3.5 – 21 ng/g (Tjerngren et al., 2012a) and 0.11 – 13.4

335   ng/g (Skyllberg et al., 2003), but studies from boreal sites elsewhere show similar concentration

336   ranges (e.g. North America: 0.3 – 0.5 ng/g (St Louis et al., 2001). Variations in soil MeHg may be

337 driven partly by differences in atmospheric inputs from the canopy and partly by soil disturbance, as

338 discussed in the following.

339 We have not estimated the total soil pool of Hg in the present study as this is already

340 calculated for the Langtjern catchment by Larssen et al. (2008), demonstrating that the catchment

341 contains 17.4 mg Hg/m^2. This is less or similar to what is documented in other forested catchments,

342 examples including Gårdsjön, Sweden (28 mg Hg/m^2, Munthe et al., 1998), Lehstenbach (89.1 mg

343 Hg/m^2) and Steinkreuz (19.3 mg Hg/m^2), Germany (Schwesig and Matzner, 2000), Cedar River

344 watershed, Washington, US (25.8 – 29.2 mg Hg/m^2, Obrist et al., 2012) and northeastern US (mean of

345 n = 139 sites: 21.3 mg Hg/m^2, Yu et al., 2014). The soil pools are often several orders of magnitude

346 larger than the atmospheric input (including throughfall, litterfall and open precipitation), indicating

347 the significance of soil processes and soil pools of Hg on the biogeochemical cycling of Hg in remote

348 catchments.

349

350 *Catchment soil THg and MeHg concentrations in relation to throughfall*

351 Our data demonstrates a clear relationship between THg concentrations in throughfall and top soil in

352 the undisturbed catchment LAE03 (Figure 3). This pattern is previously documented by studies in

353 North America (e.g. Mowat et al., 2011; Witt et al., 2009) and Sweden (Lee et al., 2000; Munthe et

354 al., 1995a), where the great efficiency of conifers at scavenging THg and MeHg from the atmosphere

355 is highlighted. The importance of canopy scavenging is illustrated by the low concentrations of THg in

356 the peatland samples in our study (Table 2). Depending on forest type, Hg input to the forest floor is

357 shown to be typically 3-6 times greater than into open peatland sites (Demers et al., 2007; Demers et

358 al., 2013). This is a higher ratio than what is documented in the present study, probably related to

359 different forest types between the North American site (Demers et al., 2013) and Langtjern (de Wit

360 et al., 2014).

361 Our depth profiles of THg demonstrated increasing concentrations going downwards in the

362 organic layers for both peatlands and forest soils (Table 2). As mentioned, this testifies to the strong

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363   Hg-OM relationship in soils (Richardson et al., 2013), but could also indicate evasion of Hg from the

364   top soil layers to the atmosphere (Fu et al., 2010; Pannu et al., 2014). Graydon et al. (2012)

365   estimates, through spike studies in the experimental lake area (Ontario, Canada), that as much as

366   45% and 71 % of the added Hg is lost to the atmosphere from the upland forest soils and wetlands,

367   respectively. Although processes and factors affecting the evasion of Hg from soils, including

368   temperature, moisture and sterilization (Pannu et al., 2014), could lead to increased Hg loss from

369   peatlands compared to forest soils (Graydon et al., 2012), it cannot explain the large difference

370   between top layer Hg concentrations in our peatland and soil samples (Table 2, Figure).

371   For MeHg, the correlation between throughfall and top soil concentrations was not

372   significant (Figure 3), which agrees with the commonly accepted view that MeHg is produced in the

373   soil (e.g. Mitchell et al., 2008b) and not only transported via wet or dry atmospheric deposition. This

374   is also evident through the not significant relationship between top soil horizon concentrations of

375   THg with MeHg (r^2 = 0.04, p = 0.67) and MeHg-to-THg ratios (r^2 = 0.37, p = 0.15). But similar to the

376   findings by Mowat et al. (2011) and Lee et al. (2000) our data shows that loading of MeHg with

377   throughfall and litterfall is higher than open area atmospheric deposition. Hence, the similar MeHg

378   concentrations in the upper layer of peatland and forest soil are consistent with inputs of MeHg from

379   the forest canopy to the forest floor.

380

381   *MeHg production in soils and peatlands*

382   We found that THg concentrations in the top layer of the forest soils (143.8 ± 45.3 ng/g) were

383   significantly higher than in the peatlands (40.6 ± 7.2 ng/g, p < 0.001), indicating the patterns of

384   atmospheric input of Hg that we discuss below. For MeHg in top soils this pattern is different, with

385   similar concentrations observed for forest soils and peatland (both 0.6 ± 0.6 ng/g on average). As a

386   conclusion, our first hypothesis is only partly confirmed, as peatland MeHg concentrations are not

387   significantly higher than those of forest soils (Figure 2a).

388   The variation of MeHg-to-THg ratio in the present study (as %MeHg, < 0.1 - 2.6 %, Table 3),

389   indicates a heterogenic environment where methylation hotspots (as defined in McClain et al., 2003;

390   Mitchell et al., 2008) are likely present. If the %MeHg is viewed as an estimate of the long-term net

391   production of MeHg in the soils (as in Tjerngren et al., 2012a), our data suggest that peatland soils

392   are more effective areas for net methylation than forest soils, which is most clearly shown in the soil

393   layers below the top layer (Figure 2a). Although %MeHg did not show a significant change with depth

394   in peatlands or forest soils, MeHg-to-THg ratio maximums were observed in the deepest sample for

395   both peatlands, while the ratio in the deeper layers in the forest soils were markedly lower than for

396   the deeper peatland layers (Table 2, Figure 2a). We found that, on average, top layer peatland

397   samples had weakly significantly (p = 0.06) higher %MeHg (1.5 ± 1.4 %) than top layer forest soil

398   samples (0.4 ± 0.5 %). Together these patterns are consistent with both significant atmospheric

399   inputs of MeHg from throughfall in forest soils (Mowat et al., 2011, see further below) and

400   methylation in deeper peatland layers (Mitchell et al., 2008).

401   Literature suggests that top soil layers (0-10 cm) are home to the bacterial activity

402   responsible for methylation and de-methylation processes, indicating that most of the soil MeHg

403   pool is present there (Kronberg et al., 2012; Mitchell and Gilmour, 2008). Our data reveal no

404   significant difference in MeHg concentrations or MeHg-to-THg ratios in the top 10 cm compared to

405   the deeper layers (Figure 2a, Table 2), possibly indicating that de-methylation processes are

406   important in our top soil layers. Photo de-methylation is documented as a process significantly

407   affecting the lake MeHg budget in the Langtjern catchment by Poste et al. (2015) and could very well

408   be of significance in top layer soil as well. However, given that we interpret MeHg-to-THg ratios as

409   the long-term net production of MeHg in our samples, the de-methylation or degradation pathways

410   are beyond the scope of our study.

411   It should be mentioned that in previous studies from Sweden, variations of MeHg-to-THg

412   ratios were much larger than at Langtjern: 0.5 – 18.7 % (Kronberg et al., 2012) and 2.3 – 16 %

413   (Tjerngren et al., 2012a). In addition, streamwater concentrations of THg (13 – 18 ng/L) and MeHg

16

414   (1.4 – 5.9 ng/L) in southern Sweden (Kronberg et al., 2012) were higher than what is documented for

415   Langtjern (de Wit et al., 2014). Streamwater MeHg concentrations in LAE11 were significantly higher

416   than in LAE03 (0.15 ± 0.09 ng/L and 0.06 ± 0.03 ng/L, respectively; De Wit et al., 2014, monthly data

417   from 2010 - 2012). However, these differences were not consistent with catchment soil differences in

418   MeHg concentrations (Table 2). In fact we see the opposite pattern for MeHg in top layer peatland

419   samples, with concentrations (p = 0.01) and MeHg-to-THg ratios (p = 0.02) being significantly higher

420   in LAE03 (P, 1.0 ± 0.4 ng/g and 2.5 ± 2.3 %) than in LAE11 (P, 0.2 ± 0.1 ng/g and 0.7 ± 0.4 %, Figure

421   2a). We see no significant difference (p > 0.05) in THg concentrations (42 ± 6 ng/g and 40 ± 9 ng/g for

422   LAE03 and LAE11, respectively).

423   Demers et al. (2013) states that mobilisation of Hg from forest soils and wetlands are

424   dependent upon hydrological flow paths (in addition to decomposition dynamics). In the present

425   study our data show a lack of consistency between MeHg and THg concentrations in streamwater

426   and top layer peatland samples, which may be explained by soil heterogeneity or by lack of

427   hydrological connectivity between soil sampling points and streams.

428

429   *Net MeHg production in relation to soil disturbance*

430   A range of studies have previously aimed to document the effects of forest harvesting operations on

431   MeHg runoff and concentrations of MeHg in the aquatic biota (recently reviewed in Eklof et al.,

432   2016). In the other Scandinavian countries, Porvari et al. (2003, Finland) and Munthe and Hultberg

433   (2004, Sweden) have shown that soil disturbance following forest harvesting leads to increased

434   MeHg runoff. While catchment hydrology and changes in nutrient cycling are thought to play a role

435   for increases in MeHg runoff (Kreutzweiser et al., 2008; Lofgren et al., 2009), the detailed

436   mechanisms controlling the export of MeHg are not well known. In fact, the paired-catchment study

437   from the Langtjern area, our study location, revealed that harvest operations did not significantly

438   change THg or MeHg concentrations in runoff (de Wit et al., 2014). However, we observed a weakly

439   significant (p = 0.07) and significant (p = 0.04) difference between MeHg concentrations and MeHg-

440   to-THg ratios between the wheeltrack and non-wheeltrack samples, respectively (Table 2, Figure 2b).

441   Thus, we find an effect of soil disturbance on MeHg production, although this effect was not

442   reflected in MeHg concentrations in streamwaters in the disturbed and harvested catchment.

443   The support for disturbance effects on MeHg found in our soil samples, but not in the

444   streamwater chemistry, may relate to lack of hydrological connection between methylation hotspots

445   and the stream in the harvested LAE11 catchment. However, it is important to note that support for

446   harvest effects on MeHg in water remains ambiguous (Eklof et al., 2016), reflecting that factors

447   controlling MeHg production and leaching are still poorly understood. Possibly, a more extensive soil

448   sampling campaign would have been necessary to find relationships between soil and streamwater

449   chemistry. According to Tjerngren et al. (2012a), peatlands soils with a C/N ratio of approximately 20

450   produce significantly more MeHg (%MeHg of 16; MeHg yield 0.48 g m^{-2} yr^{-1}) than soils with lower or

451   higher C/N ratios (%MeHg < 7; MeHg yield 0.1 – 0.3 g m^{-2} yr^{-1}). The soils in our study had generally

452   considerably higher C/N ratios than 20 while MeHg-to-THg ratios were < 3% and the catchment

453   MeHg yields were 0.04 and 0.1 g m^{-2} yr^{-1} (De Wit et al., 2014). According to the patterns found by

454   Tjerngren et al. (2012a), Langtjern fits in as a low nutrient site with relatively low MeHg production.

455   However, we did not find any support for effects of soil nutrient status on MeHg concentrations or

456   MeHg-to-THg ratios in peatland or forest samples: no significant correlations were found between

457   indicators of soil nutrient status (Tot-N, C/N ratio, Tot-P) and MeHg-to-THg ratios, perhaps due to the

458   relatively small range in nutrient concentrations present at Langtjern.

459

460   **Conclusion**

461   Based on measurements of Hg in soil samples from two small boreal catchments, we conclude that

462   the lower THg concentrations in peatland soils as compared to forest soils are likely to be related to

463   higher inputs of THg from the forest canopy. The most important source of streamwater MeHg was

464   peatland soils, which had highest MeHg concentrations. However, we also found similar MeHg

465   concentrations in forest soils, as a result of canopy inputs of MeHg, suggesting that forest soils are

466   potentially significant contributors to MeHg in surface waters. The local production in peatlands was

467   documented through significantly higher MeHg-to-THg ratios in the deeper soil layer samples. Finally,

468   our finding support earlier hypotheses of soil disturbance promoting methylation of inorganic Hg,

469   suggesting that soil disturbance from forest harvest machinery may promote leaching of MeHg from

470   soils to streamwaters.

471

480

481   **Literature**

482   Berg T, Fjeld E, Steinnes E. Atmospheric mercury in Norway: Contributions from different sources.

483   Science of the Total Environment 2006; 368: 3-9.

484   Bishop K, Allan C, Bringmark L, Garcia E, Hellsten S, Hogbom L, Johansson K, Lomander A, Meili M,

485   Munthe J, Nilsson M, Porvari P, Skyllberg U, Sorensen R, Zetterberg T, Åkerblom S. The

486   Effects of Forestry on Hg Bioaccumulation in Nemoral/Boreal Waters and Recommendations

487   for Good Silvicultural Practice. Ambio 2009; 38: 373-380.

488   Bloom NS. On the chemical form of mercury in edible fish and marine invertebrate tissue. Canadian

489   Journal of Fisheries and Aquatic Sciences 1992; 49: 1010-1017.

490   Bloom NS, Colman JA, Barber L. Artifact formation of methyl mercury during aqueous distillation and

491   alternative techniques for the extraction of methyl mercury from environmental samples.

492   Fresenius Journal of Analytical Chemistry 1997; 358: 371-377.

19

493   Braaten HFV, de Wit HA, Fjeld E, Rognerud S, Lydersen E, Larssen T. Environmental factors
494   influencing mercury speciation in Subarctic and Boreal lakes. Science of the Total
495   Environment 2014a; 476: 336-345.

496   Braaten HFV, de Wit HA, Harman C, Hagestrom U, Larssen T. Effects of sample preservation and
497   storage on mercury speciation in natural stream water. International Journal of
498   Environmental Analytical Chemistry 2014b; 94: 381-384.

499   Braaten HFV, Fjeld E, Rognerud S, Lund E, Larssen T. Seasonal and year-to-year variation of mercury
500   concentration in perch (Perca fluviatilis) in boreal lakes. Environmental toxicology and
501   chemistry / SETAC 2014c; 33: 2661-70.

502   Chasar LC, Scudder BC, Stewart AR, Bell AH, Aiken GR. Mercury Cycling in Stream Ecosystems. 3.
503   Trophic Dynamics and Methylmercury Bioaccumulation. Environmental Science &
504   Technology 2009; 43: 2733-2739.

505   Demers JD, Driscoll CT, Fahey TJ, Yavitt JB. Mercury cycling in litter and soil in different forest types in
506   the Adirondack region, New York, USA. Ecological Applications 2007; 17: 1341-1351.

507   Demers JD, Yavitt JB, Driscoll CT, Montesdeoca MR. Legacy mercury and stoichiometry with C, N, and
508   S in soil, pore water, and stream water across the upland-wetland interface: The influence of
509   hydrogeologic setting. Journal of Geophysical Research-Biogeosciences 2013; 118: 825-841.

510   de Wit HA, Granhus A, Lindholm M, Kainz MJ, Lin Y, Braaten HFV, Blaszczak J. Forest harvest effects
511   on mercury in streams and biota in Norwegian boreal catchments. Forest Ecology and
512   Management 2014; 324: 52-63.

513   de Wit HA, Hettelingh J-P, Harmens H. Trends in ecosystem and health responses to long-range
514   transported atmospheric pollutants. Report 6946, Norwegian Institute for Water Research,
515   2015, pp. 92.

516   de Wit HA, Kainz MJ, Lindholm M. Methylmercury bioaccumulation in invertebrates of boreal
517   streams in Norway: Effects of aqueous methylmercury and diet retention. Environmental
518   Pollution 2012; 164: 235-241.

519 Eklof K, Kraus A, Weyhenmeyer GA, Meili M, Bishop K. Forestry Influence by Stump Harvest and Site

520   Preparation on Methylmercury, Total Mercury and Other Stream Water Chemistry

521   Parameters Across a Boreal Landscape. Ecosystems 2012; 15: 1308-1320.

522 Eklof K, Lidskog R, Bishop K. Managing Swedish forestry's impact on mercury in fish: Defining the

523   impact and mitigation measures. Ambio 2016; 45 Suppl 2: 163-74.

524 Eklof K, Meili M, Akerblom S, von Bromssen C, Bishop K. Impact of stump harvest on run-off

525   concentrations of total mercury and methylmercury. Forest Ecology and Management 2013;

526   290: 83-94.

527 Fitzgerald WF, Engstrom DR, Mason RP, Nater EA. The case for atmospheric mercury contamination

528   in remote areas. Environmental Science & Technology 1998; 32: 1-7.

529 Fjeld E. Environmental monitoring of mercury in perch, 2010 (in Norwegian). Report 2737,

530   Norwegian Environment Agency, 2010, pp. 33.

531 Fjeld E, Rognerud S, Steinnes E. Influence of environmental-factors on heavy-metal concentration in

532   lake-sediments in southern norway indicated by path-analysis. Canadian Journal of Fisheries

533   and Aquatic Sciences 1994; 51: 1708-1720.

534 Fu X, Feng X, Zhu W, Rothenberg S, Yao H, Zhang H. Elevated atmospheric deposition and dynamics

535   of mercury in a remote upland forest of southwestern China. Environmental Pollution 2010;

536   158: 2324-2333.

537 Garmo Ø, Skancke LB, Høgåsen T. The Norwegian monitoring program for long-range transported air

538   pollutants. Annual report - Water chemical effects 2012 (In Norwegian with English

539   summary). Norwegian Institute for Water Research, Norwegian Environment Agency, 2013,

540   pp. 72.

541 Gilmour CC, Podar M, Bullock AL, Graham AM, Brown SD, Somenahally AC, Johs A, Hurt RA, Bailey KL,

542   Elias DA. Mercury Methylation by Novel Microorganisms from New Environments.

543   Environmental Science & Technology 2013; 47: 11810-11820.

544   Graydon JA, Louis VLS, Hintelmann H, Lindberg SE, Sandilands KA, Rudd JWM, Kelly CA, Hall BD,

545   Mowat LD. Long-Term Wet and Dry Deposition of Total and Methyl Mercury in the Remote

546   Boreal Ecoregion of Canada. Environmental Science & Technology 2008; 42: 8345-8351.

547   Graydon JA, St Louis VL, Lindberg SE, Sandilands KA, Rudd JWM, Kelly CA, Harris R, Tate MT,

548   Krabbenhoft DP, Emmerton CA, Asmath H, Richardson M. The role of terrestrial vegetation in

549   atmospheric Hg deposition: Pools and fluxes of spike and ambient Hg from the METAALICUS

550   experiment. Global Biogeochemical Cycles 2012; 26.

551   Kreutzweiser DP, Hazlett PW, Gunn JM. Logging impacts on the biogeochemistry of boreal forest soils

552   and nutrient export to aquatic systems: A review. Environmental Reviews 2008; 16: 157-179.

553   Kronberg R-M, Tjerngren I, Drott A, Bjorn E, Skyllberg U. Net Degradation of Methyl Mercury in Alder

554   Swamps. Environmental Science & Technology 2012; 46: 13144-13151.

555   Larssen T, de Wit HA, Wiker M, Halse K. Mercury budget of a small forested boreal catchment in

556   southeast Norway. Science of the Total Environment 2008; 404: 290-296.

557   Larsson JY. Guidance for determination of forest vegetation types (in Norwegian). Report 11/2000,

558   Norwegian Institute of Bioeconomy Research, 2000, pp. 29.

559   Lee YH, Bishop KH, Munthe J. Do concepts about catchment cycling of methylmercury and mercury in

560   boreal catchments stand the test of time? Six years of atmospheric inputs and runoff export

561   at Svartberget, northern Sweden. Science of the Total Environment 2000; 260: 11-20.

562   Lofgren S, Ring E, von Bromssen C, Sorensen R, Hogbom L. Short-term Effects of Clear-cutting on the

563   Water Chemistry of Two Boreal Streams in Northern Sweden: A Paired Catchment Study.

564   Ambio 2009; 38: 347-356.

565   McClain ME, Boyer EW, Dent CL, Gergel SE, Grimm NB, Groffman PM, Hart SC, Harvey JW, Johnston

566   CA, Mayorga E, McDowell WH, Pinay G. Biogeochemical hot spots and hot moments at the

567   interface of terrestrial and aquatic ecosystems. Ecosystems 2003; 6: 301-312.

568 Meili M, Bishop K, Bringmark L, Johansson K, Munthe J, Sverdrup H, de Vries W. Critical levels of

569   atmospheric pollution: criteria and concepts for operational modelling of mercury in forest

570   and lake ecosystems. Science of the Total Environment 2003; 304: 83-106.

571 Mitchell CPJ, Branfireun BA, Kolka RK. Spatial characteristics of net methylmercury production hot

572   spots in peatlands. Environmental Science & Technology 2008; 42: 1010-1016.

573 Mitchell CPJ, Gilmour CC. Methylmercury production in a Chesapeake Bay salt marsh. Journal of

574   Geophysical Research-Biogeosciences 2008; 113.

575 Morel FMM, Kraepiel AML, Amyot M. The chemical cycle and bioaccumulation of mercury. Annual

576   Review of Ecology and Systematics 1998; 29: 543-566.

577 Mowat LD, St Louis VL, Graydon JA, Lehnherr I. Influence of Forest Canopies on the Deposition of

578   Methylmercury to Boreal Ecosystem Watersheds. Environmental Science & Technology 2011;

579   45: 5178-5185.

580 Munthe J, Hultberg H. Mercury and methylmercury in runoff from a forested catchment –

581   concentrations, fluxes, and their response to manipulations. Water, Air and Soil Pollution:

582   Focus 2004; 4: 607–618.

583 Munthe J, Hultberg H, Iverfeldt A. Mechanisms of deposition of methylmercury and mercury to

584   coniferous forests. Water Air and Soil Pollution 1995a; 80: 363-371.

585 Munthe J, Hultberg H, Lee YH, Parkman H, Iverfeldt A, Renberg I. Trends of mercury and

586   methylmercury in deposition, runoff water and sediments in relation to experimental

587   manipulations and acidification. Water Air and Soil Pollution 1995b; 85: 743-748.

588 Munthe J, Lee Y, Hultberg H, Iverfeldt Å, Borg G, Andersson I. Cycling of mercury and methylmercury

589   in the Gårdsjön catchment. In Hultberg H, Skeffington R (editors), Experimental reversal of

590   acid rain effects: The Gårdsjön roof project. Wiley & Sons Ltd, 1998.

591 Munthe J, Wängberg I, Rognerud S, Fjeld E, Verta M, Porvari P, Meili M. Mercury in Nordic

592   Ecosystems, Swedish Environmental Research Institute, 2007, pp. 45.

593   Obrist D, Johnson DW, Edmonds RL. Effects of vegetation type on mercury concentrations and pools

594   in two adjacent coniferous and deciduous forests. Journal of Plant Nutrition and Soil Science

595   2012; 175: 68-77.

596   Pacyna EG, Pacyna JM, Sundseth K, Munthe J, Kindbom K, Wilson S, Steenhuisen F, Maxson P. Global

597   emission of mercury to the atmosphere from anthropogenic sources in 2005 and projections

598   to 2020. Atmospheric Environment 2010; 44: 2487-2499.

599   Pannu R, Siciliano SD, O'Driscoll NJ. Quantifying the effects of soil temperature, moisture and

600   sterilization on elemental mercury formation in boreal soils. Environmental Pollution 2014;

601   193: 138-146.

602   Porvari P, Verta M. Total and methyl mercury concentrations and fluxes from small boreal forest

603   catchments in Finland. Environmental Pollution 2003; 123: 181-191.

604   Porvari P, Verta M, Munthe J, Haapanen M. Forestry practices increase mercury and methyl mercury

605   output from boreal forest catchments. Environmental Science & Technology 2003; 37: 2389-

606   2393.

607   Poste A, Braaten HFV, de Wit HA, Sørensen K, Larssen T. Effects of photodemethylation on the

608   methylmercury budget of boreal Norwegian lakes, Environmental Toxicology & Chemistry,

609   2015; 34(6): 1213-1223.

610   Ravichandran M. Interactions between mercury and dissolved organic matter - a review.

611   Chemosphere 2004; 55: 319-331.

612   Richardson JB, Friedland AJ, Engerbretson TR, Kaste JM, Jackson BP. Spatial and vertical distribution

613   of mercury in upland forest soils across the northeastern United States. Environmental

614   Pollution 2013; 182: 127-134.

615   Rognerud S, Fjeld E. Trace element contamination of Norwegian lake sediments. Ambio 2001; 30: 11-

616   19.

617   Schwesig D, Matzner E. Pools and fluxes of mercury and methylmercury in two forested catchments

618   in Germany. Science of the Total Environment 2000; 260: 213-223.

619 Skyllberg U, Qian J, Frech W, Xia K, Bleam WF. Distribution of mercury, methyl mercury and organic

620   sulphur species in soil, soil solution and stream of a boreal forest catchment.

621   Biogeochemistry 2003; 64: 53-76.

622 St Louis VL, Rudd JWM, Kelly CA, Hall BD, Rolfhus KR, Scott KJ, Lindberg SE, Dong W. Importance of

623   the forest canopy to fluxes of methyl mercury and total mercury to boreal ecosystems.

624   Environmental Science & Technology 2001; 35: 3089-3098.

625 St. Louis VL, Rudd JWM, Kelly CA, Beaty KG, Flett RJ, Roulet NT. Production and loss of

626   methylmercury and loss of total mercury from boreal forest catchments containing different

627   types of wetlands. Environmental Science & Technology 1996; 30: 2719-2729.

628 Steinnes E, Berg T, Sjobakk TE. Temporal and spatial trends in Hg deposition monitored by moss

629   analysis. Science of the Total Environment 2003; 304: 215-219.

630 Tjerngren I, Karlsson T, Bjorn E, Skyllberg U. Potential Hg methylation and MeHg demethylation rates

631   related to the nutrient status of different boreal wetlands. Biogeochemistry 2012a; 108: 335-

632   350.

633 Tjerngren I, Meili M, Bjorn E, Skyllberg U. Eight Boreal Wetlands as Sources and Sinks for Methyl

634   Mercury in Relation to Soil Acidity, C/N Ratio, and Small-Scale Flooding. Environmental

635   Science & Technology 2012b; 46: 8052-8060.

636 Wang M, Moore TR, Talbot J, Richard PJH. The cascade of C:N:P stoichiometry in an ombrotrophic

637   peatland: from plants to peat. Environmental Research Letters 2014; 9.

638 WHO (World Health Organisation). Environmental Health criteria 101, Methyl Mercury. Geneva,

639   Switzerland: International programme on chemical safety, 1991.

640 Witt EL, Kolka RK, Nater EA, Wickman TR. Influence of the Forest Canopy on Total and Methyl

641   Mercury Deposition in the Boreal Forest. Water Air and Soil Pollution 2009; 199: 3-11.

642 Yu X, Driscoll CT, Warby RAF, Montesdeoca M, Johnson CE. Soil mercury and its response to

643   atmospheric mercury deposition across the northeastern United States. Ecological

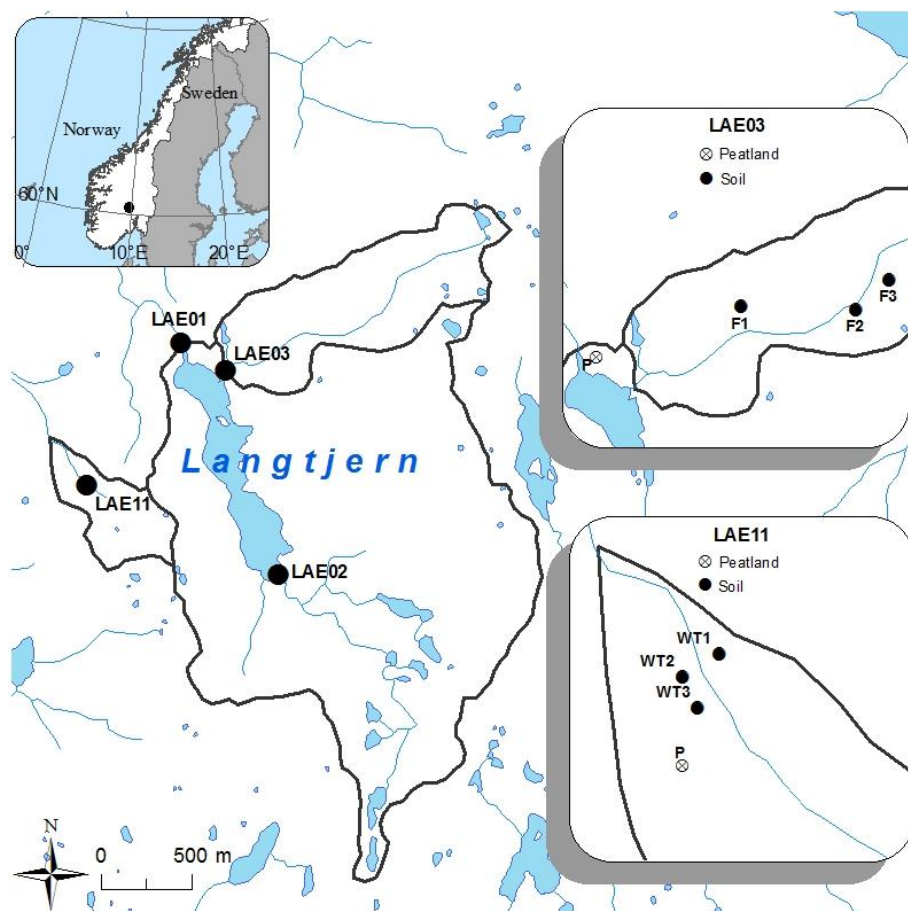644   Applications 2014; 24: 812-822.

Figures

Figure 1 Location of the study sites; the forest harvest impacted catchment (experimental catchment LAE11) and the gradient study catchment (undisturbed catchment LAE03). Sample ID's refer to the ID's used throughout the study and defined in Table 1. Shown are also sampling points LAE01 (lake outlet) and LAE02 and LAE03 (south and east lake inlets, respectively).
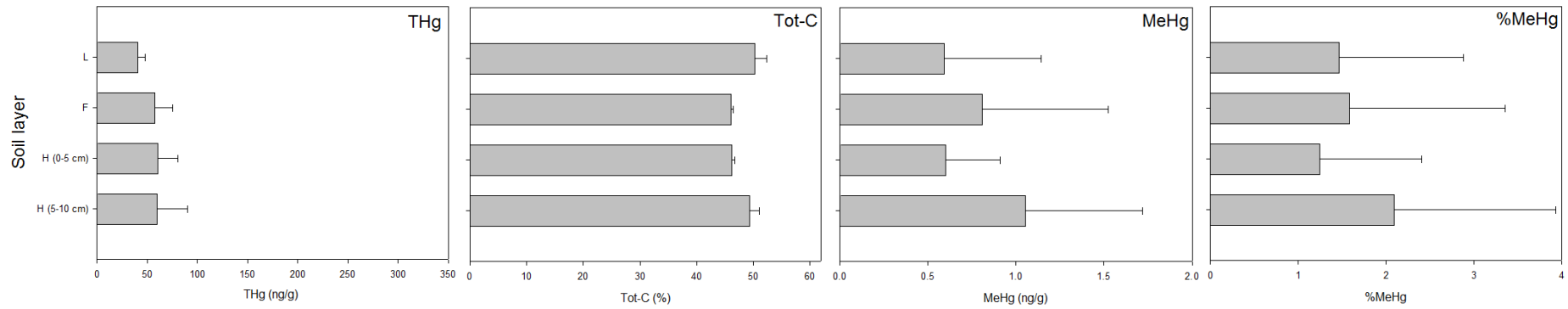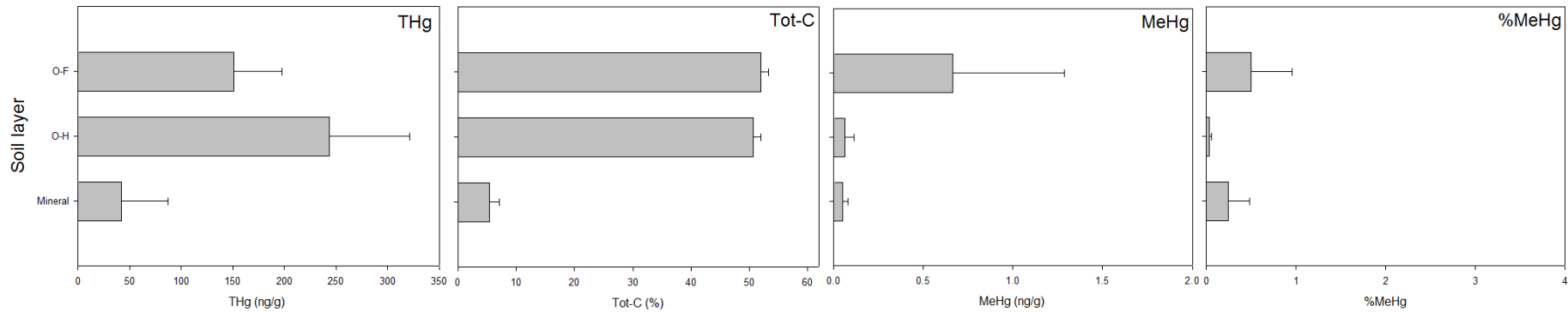
Figure 2a Depth profiles of (from left to right) THg concentrations (ng/g), Tot-C levels (%), MeHg concentrations (ng/g) and MeHg-to-THg ratios (as %MeHg) in peatland (top panels) and forest soil (bottom panels) samples. Shown are mean concentrations with error bars (± one standard deviation) for peatland samples LAE03-P and LAE11-P (n = 6 for each soil layer) and forest soil samples F1, F2 and F3 (n = 6 for each soil layer: O-F (F2 and F3), O-H (F2 and F3), Mineral (F1 and F3)). Soil layers follow the notation from Table 1.
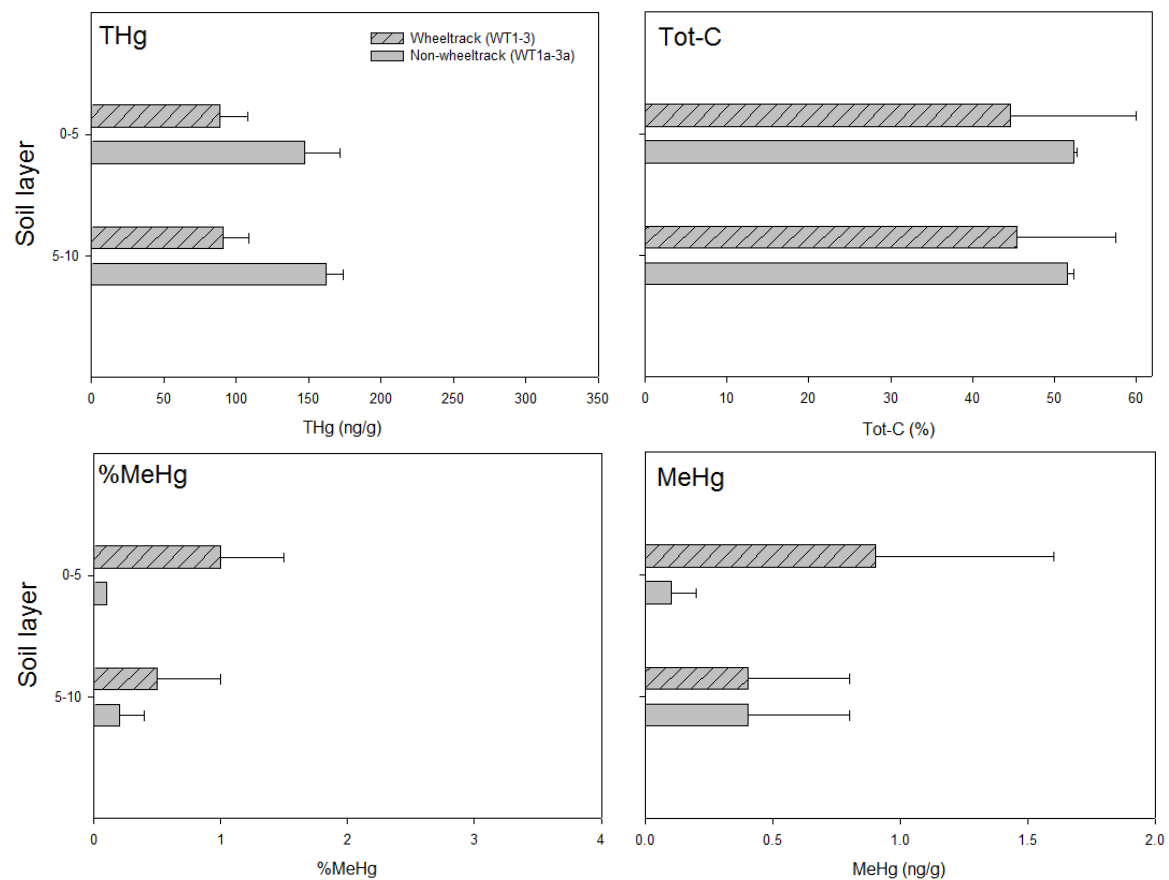
Figure 2b Depth profiles of (from top left and clockwise) THg concentrations (ng/g), Tot-C levels (%), MeHg concentrations (ng/g) and MeHg-to-THg ratios (as %MeHg) in wheeltrack (grey bars with pattern fill) and non-wheeltrack (grey bars without pattern) samples. Shown are mean concentrations with error bars (± one standard deviation) for wheeltrack samples WT1, WT2 and WT3 (n = 3 for each soil layer) and non-wheeltrack samples WT1a, WT2a and WT3a (n = 3 for each soil layer). Soil layers follow the notation from Table 1.
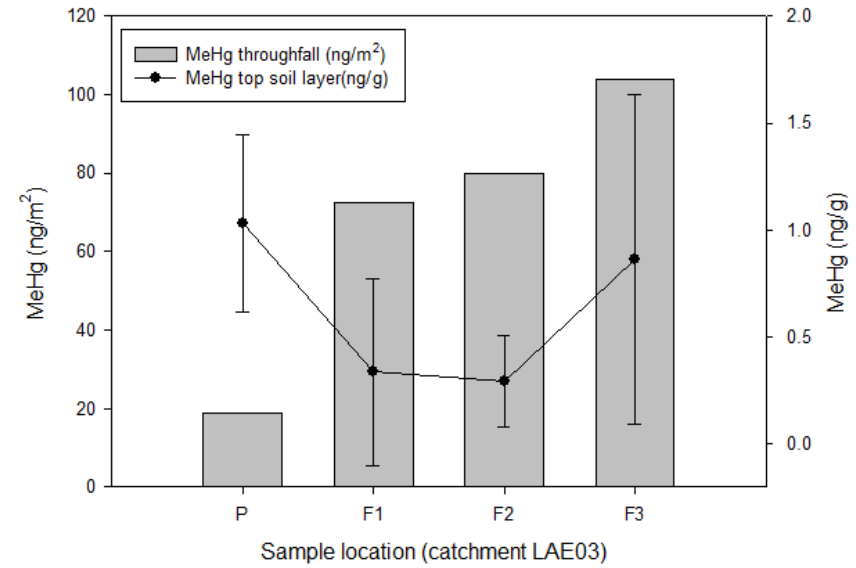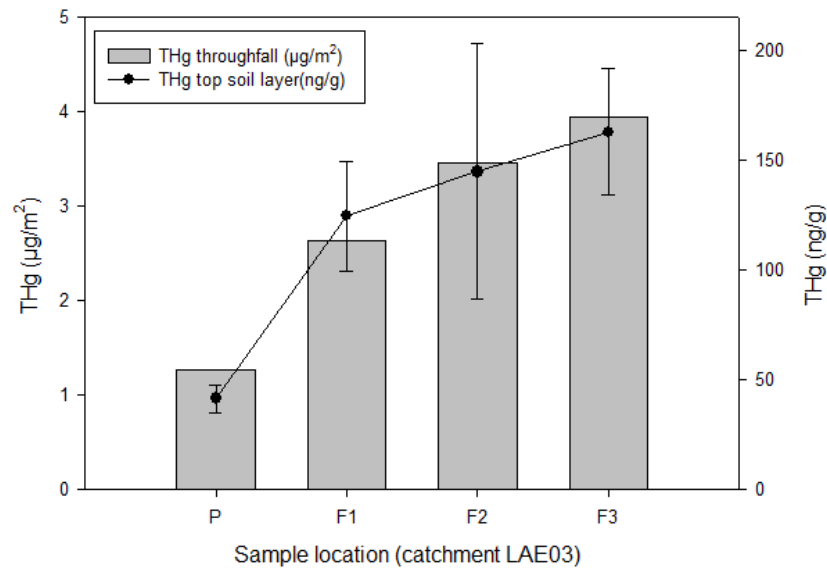
Figure 3 THg (left panel) and MeHg (right panel) concentrations in throughfall (left y-axes, grey bars) and the top soil layer (right y-axes, black circles, ng/g) from sample locations with different canopy density. Sampling location ID refers to canopy densities as described in Table 1. Throughfall concentrations are in $\mu g/m^2$ and ng/m^2 for THg and MeHg, respectively, while top soil concentrations are in ng/g for both THg and MeHg. Concentrations of THg and MeHg in top soil horizon are shown as mean $\pm$ one standard deviation.

Tables

Table 1 Sample ID's (used throughout the paper) with description of the samples collected; each sample ID was collected in triplicates giving 3 times the amount of samples indicated in the table. Indicated in the table is also where throughfall sample collectors were placed.

Catchment		Sample ID (sample location)	Location description	Soil/peatland layer sampled	Throughfall collectors
LAE03 Undisturbed catchment		**P**	Open peatland (sphagnum)	L, F, H (0-5 cm and 5-10 cm)	n = 3
		F1	Pine forest (open forest: > 20 m between individual trees)	O, mineral (0-5 cm)	n = 3
		F2	Swamp forest (intermediate dense forest:5-10 m between individual trees)	O-F, O-H	n = 3
		F3	Spruce forest (dense forest: < 5 m between individual trees)	O-F, O-H, mineral (0-5 cm)	n = 3
LAE11 Experimental catchment	**Undisturbed area**	**P**	Open peatland (sphagnum)	L, F, H (0-5 cm and 5-10 cm)	n.a.
	Disturbed area, harvested, impacted by forest machinery	**WT1, WT2, WT3**	Wheeltracks from forest machinery	0-5 cm, 5-10 cm	n.a.
		WT1a, WT2a, WT3a	<5 m away from wheeltracks, no sign of disturbance from forest machinery ("non-wheeltracks")	0-5 cm, 5-10 cm	n.a.

Table 2 Concentrations of selected environmental parameters determined in the soil samples: total carbon (Tot-C), total mercury (THg), methylmercury (MeHg), % methylmercury (%MeHg), total mercury to carbon ratio (THg/C), methylmercury to carbon ratio (MeHg/C), total nitrogen (Tot-N), total phosphorous (Tot-P) and carbon-to-nitrogen ratio (C/N ratio). Shown are mean concentrations ± one standard deviation (n = 3) for composite samples in each soil or peatland layer. Sample location corresponds to ID's presented in Figure 1 and Table 1.

Catchment	Sample location	Soil/ wetland layer	Layer thickness (cm)	Tot-C (%)	THg (ng/g)	MeHg (ng/g)	%MeHg	THg/C (ng/mg)	MeHg/C (ng/µg)	Tot-N (%)	Tot-P (%)	C/N (g/g)
LAE03	P	L	15	46.1 ± 0.6	42 ± 6	1.0 ± 0.4	2.6 ± 1.2	0.09 ± 0.01	2.2 ± 0.9	0.73 ± 0.25	0.30 ± 0.10	68 ± 20
		F	10	46.1 ± 0.8	47 ± 5	1.1 ± 0.9	2.5 ± 2.3	0.10 ± 0.01	2.4 ± 1.9	0.90 ± 0.07	0.37 ± 0.03	51 ± 3
		H (0-5 cm)	5	50.8 ± 0.8	51 ± 18	0.8 ± 0.3	1.9 ± 1.4	0.10 ± 0.04	1.6 ± 0.6	1.90 ± 0.25	0.54 ± 0.07	27 ± 4
		H (5-10 cm)	5	52.1 ± 0.6	35 ± 14	1.2 ± 0.9	3.1 ± 2.3	0.07 ± 0.03	2.2 ± 1.7	1.59 ± 0.37	0.46 ± 0.08	34 ± 7
	F1	O	9	53.2 ± 0.4	124 ± 25	0.3 ± 0.4	0.3 ± 0.5	0.23 ± 0.05	0.6 ± 0.8	1.11 ± 0.02	0.50 ± 0.05	48 ± 1
		Mineral	5	4.4 ± 0.3	68 ± 55	0.1 ± 0.0	0.2 ± 0.2	0.89 ± 0.69	1.4 ± 0.4	0.42 ± 0.52	0.27 ± 0.19	39 ± 5
	F2	O-F	8	50.8 ± 2.2	125 ± 57	0.2 ± 0.3	0.3 ± 0.4	0.24 ± 0.10	0.5 ± 0.6	1.44 ± 0.12	0.63 ± 0.10	35 ± 2
		O-H	8	50.0 ± 1.0	198 ± 57	0.1 ± 0.1	0.1 ± 0.0	0.40 ± 0.12	0.2 ± 0.2	1.75 ± 0.12	0.91 ± 0.08	29 ± 2
	F3	O-F	5	50.8 ± 0.8	163 ± 29	0.9 ± 0.8	0.6 ± 0.6	0.12 ± 0.11	1.7 ± 1.5	1.31 ± 0.09	0.66 ± 0.06	39 ± 3
		O-H	5	50.9 ± 0.2	300 ± 36	0.1 ± 0.1	0.0 ± 0.0	0.32 ± 0.06	0.1 ± 0.0	1.12 ± 0.15	0.49 ± 0.07	46 ± 6
		Mineral	5	6.0 ± 2.2	16 ± 2	0.1 ± 0.1	0.3 ± 0.3	0.59 ± 0.07	0.8 ± 0.6	0.13 ± 0.02	0.08 ± 0.02	50 ± 15
LAE11	WT1-3	0-5 cm	5	44.8 ± 15.4	89 ± 19	0.9 ± 0.7	1.0 ± 0.5	0.23 ± 0.15	2.7 ± 2.8	1.55 ± 0.51	0.68 ± 0.21	29 ± 1
		5-10 cm	5	45.4 ± 12.1	91 ± 18	0.4 ± 0.4	0.5 ± 0.5	0.21 ± 0.05	1.1 ± 1.3	1.63 ± 0.50	0.72 ± 0.20	28 ± 2
	WT1a-3a	0-5 cm	5	52.3 ± 0.5	147 ± 25	0.1 ± 0.1	0.1 ± 0.0	0.28 ± 0.05	0.2 ± 0.1	1.64 ± 0.13	0.64 ± 0.02	32 ± 3
		5-10 cm	5	51.6 ± 0.8	162 ± 12	0.4 ± 0.4	0.2 ± 0.2	0.31 ± 0.02	0.8 ± 0.8	1.59 ± 0.17	0.61 ± 0.11	33 ± 4
	P	L	7	46.1 ± 0.2	40 ± 9	0.2 ± 0.1	0.4 ± 0.1	0.09 ± 0.02	0.3 ± 0.2	0.80 ± 0.19	0.28 ± 0.10	59 ± 13
		F	5	46.3 ± 0.4	68 ± 22	0.5 ± 0.4	0.7 ± 0.4	0.15 ± 0.05	1.1 ± 0.9	1.00 ± 0.10	0.35 ± 0.03	46 ± 5
		H (0-5 cm)	5	47.8 ± 0.9	71 ± 18	0.4 ± 0.1	0.5 ± 0.1	0.15 ± 0.04	0.8 ± 0.2	1.30 ± 0.07	0.40 ± 0.02	37 ± 2
		H (5-10 cm)	5	48.5 ± 1.0	85 ± 18	1.0 ± 0.5	1.1 ± 0.5	0.17 ± 0.04	2.0 ± 1.2	1.37 ± 0.09	0.43 ± 0.05	36 ± 2