Effects of disturbance and vegetation type on total and methylmercury in boreal peatland and forest soils[☆]

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ABSTRACT

Mercury (Hg) concentrations in freshwater fish relates to aquatic Hg concentrations, which largely derives from soil stores of accumulated atmospheric deposition. Hg in catchment soils as a source for aquatic Hg is poorly studied. Here we test if *i)* peatland soils produce more methylmercury (MeHg) than forest soils; *ii)* total Hg (THg) concentrations in top soils are determined by atmospheric inputs, while MeHg is produced in the soils; and *iii)* soil disturbance promotes MeHg production. In two small boreal catchments, previously used in a paired-catchment forest harvest manipulation study, forest soils and peatlands were sampled and analysed for Hg species and additional soil chemistry. In the undisturbed reference catchment, soils were sampled in different vegetation types, of varying productivity as reflected in tree density, where historical data on precipitation and throughfall Hg and MeHg fluxes were available. Upper soil THg contents were significantly correlated to throughfall inputs of Hg, i.e. lowest in the tree-less peatland and highest in the dense spruce forest. For MeHg, top layer concentrations were similar in forest soils and peatlands, likely related to atmospheric input and local production, respectively. The local peatland MeHg production was documented through significantly higher MeHg-to-THg ratios in the deeper soil layer samples. In the disturbed catchment, soils were sampled in and just outside wheeltracks in an area impacted by forest machinery. Here, MeHg concentrations and the MeHg-to-THg ratios in the upper 5 cm were weakly significantly ($p = 0.07$) and significantly ($p = 0.04$) different in and outside of the wheeltracks, respectively, suggesting that soil disturbance promotes methylation. Differences in catchment Hg and MeHg streamwater concentrations were not explained by soil Hg and MeHg information, perhaps because hydrological pathways are a stronger determinant of streamwater chemistry than small variations in soil chemistry driven by disturbance and atmospheric inputs of Hg.

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1. Introduction

Elevated concentrations of toxic and bioaccumulative methylmercury (MeHg; Bloom, 1992) in fish have potential harmful effects on humans and animals with fish as part of their diet (WHO, 1991). The main source of mercury (Hg) in pristine Scandinavian environments is deposition of long-range transported atmospheric Hg released in other countries (Berg et al., 2006; Pacyna et al., 2010). Most of deposited Hg is stored in the soil, and a minor part is leached to surface waters as inorganic Hg or MeHg (Fitzgerald et al., 1998), where transport of Hg and production and transport of MeHg is driven by catchment processes (Ravichandran, 2004). The biogeochemical cycling of Hg in catchments is one of the keys to improve understanding of concentrations and bioaccumulation of Hg species in the aquatic environment.

For boreal catchment export of MeHg, wetlands appear to be an important methylation source, as reported both in Scandinavia (e.g. Tjerngren et al., 2012a) and North America (e.g. Mitchell et al., 2008; St. Louis et al., 1996). It is well established that production of MeHg is occurring primarily through methylation of inorganic Hg by sulphur reducing bacteria (SRB) under anoxic conditions (Morel et al., 1998), but other pathways are also evident (e.g. iron reducing bacteria; Gilmour et al., 2013). In addition to wetlands, forested catchments dominated by upland soils can also export large amounts of MeHg (Eklof et al., 2012, 2013). Forest soils receive more Hg and MeHg from the atmosphere than wetlands, because Hg is absorbed by forest canopies and subsequently deposited to soils by throughfall and litterfall (Mowat et al., 2011; Munthe et al., 1995b). Hence, forest soils can contain similar or higher

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concentrations of Hg and MeHg compared with wetlands (Graydon et al., 2008). Forest management (Bishop et al., 2009) and catchment disturbance (Munthe and Hultberg, 2004) has been shown to be a factor that promotes leaching of MeHg, although the mechanisms behind remain poorly understood (Eklof et al., 2016). For instance, where natural wetlands have been identified as principal sources of MeHg in northern boreal regions, a recent study shows how wetlands also can act as MeHg sinks (Tjerngren et al., 2012b) under certain conditions, e.g. continuous standing water exposed to sunlight (Kronberg et al., 2012).

Many studies demonstrate strong relationships between aquatic concentrations of Hg species and Hg in the aquatic food web (e.g. Braaten et al., 2014c; Chasar et al., 2009; de Wit et al., 2012). In areas where atmospheric inputs are the dominating source of Hg, it can be expected that Hg concentrations in streamwaters are co-determined by Hg contents in soils, and by conditions that promote the production of MeHg in catchment soils, such as presence of peatlands (Mitchell et al., 2008; Porvari and Verta, 2003) and disturbance (Porvari et al., 2003). While concentrations of Hg in fish (Fjeld, 2010), lake sediments (Fjeld et al., 1994; Rognerud and Fjeld, 2001), mosses (Berg et al., 2006) and surface waters (Braaten et al., 2014a) have been documented in many regions in Norway, data on Hg in soils in remote areas are scarce. More data on Hg in soils and wetlands are potentially valuable for a larger understanding of catchment MeHg production and transport of Hg and MeHg to surface waters.

In this study, our main goal was to document the local variation in total Hg (THg) and MeHg concentrations in different soils and explain this variation in relation to vegetation type, soil characteristics and catchment disturbance, in two boreal catchments previously included in a paired-catchment forest harvest manipulation (de Wit et al., 2014). We tested the following hypotheses: *i*) peatland soils have lower THg and higher MeHg concentrations than forest soils; *ii*) THg concentrations in top soils are determined by atmospheric inputs, while MeHg is produced in the soils; and *iii*) soil disturbance promotes production of MeHg.

2. Materials and methods

2.1. Site description

The Langtjern lake catchment area (4.8 km^2, 510–750 m.a.s.l.) is located in south east Norway (Fig. 1; outlet of lake at 60.37 N, 9.73 E). No direct human disturbance has taken place in the catchment since the 1930s, but the catchment was severely acidified during the 20th century with the loss of its trout population and damage to invertebrate populations. The catchment has been part of the Norwegian acid rain monitoring programme since 1972, which includes weekly monitoring of lake outlet chemistry (LAE01, Fig. 1, Garmo et al., 2013).

Vegetation in the lake catchment was mapped in 1974. Dominating vegetation types are, in declining order of % area cover, Scots pine forest (*Pinus sylvestris* L., heather (*Calluna vulgaris*)), northern bilberry (*Vaccinium uliginosum*), 63%), Norway spruce forest (*Picea abies* L., Karst., bilberry, 6%), swamp forest (5%), peatlands (poor fens and ombrotrophic bogs, 16%). Water (5%) and bare rock (2%) made up the remainder of the catchment. The vegetation types differ in productivity, which is reflected in tree density, where Scots pine has the lowest density (open forest, no closed canopy), and spruce forest has the highest density (dense forest, closed canopy). Swamp forest has an intermediate tree density. Scots pine is a lower productivity class forest than Norway spruce (Larsson, 2000).

The eastern lake inlet is from the LAE03 sub-catchment (0.8 km^2, Larssen et al., 2008), used as a reference catchment in an experimental paired catchment study where 30% of a small,

nearby catchment (outside the main catchment, LAE11, 0.3 km^2) was harvested in 2009 (Fig. 1, de Wit et al., 2014). Water chemistry in both LAE03 and LAE11 streams has been monitored in monthly intervals since 2008. Mean annual temperature and precipitation for the Langtjern catchment between 2008 and 2011 were 4.5 °C and 914 mm, respectively (de Wit et al., 2014).

2.2. Throughfall

In the summer season of 2009, six locations in the LAE03 catchment were selected for sampling of throughfall, i.e. the peatland near to the lake (P1), three locations in the most common vegetation type Scots pine forest (F1), one in the swamp forest (F2) and one in the Norway spruce forest (F3). At each location, three throughfall samplers were placed at randomly chosen places with 10–20 m distance of each other. Each sampler consisted of a slightly tilted 0.1 m^2 (0.8 × 0.125 m) Teflon-coated gutter, firmly attached to two wooden sticks driven into the ground, at an approximately height of 40 cm. The gutters led to a glass funnel on a 10-L acid cleaned (50 ml of 1 M hydrochloric acid, HCl) glass bottle which was packed in aluminium foil. The Teflon-coated gutters were washed with rain water prior to sampling. The sampling period covered May 30 2009 until October 20 2009. Four samplings took place (June 30, July 28, August 30 and October 20). At each sampling, the water volume in each bottle was noted, also when the bottle was full. At each site, a composite throughfall sample was taken by pouring ca 80 ml of each bottle (sampler) into a 250 ml Teflon bottle for analysis of MeHg and THg, in addition to taking a composite sample for chemical analysis of TOC (see below for a description of chemical water analysis). The 10-L bottles were emptied after removing the sample.

Throughfall element fluxes were calculated by averaging the sample volume in the three sample bottles in each site, multiplying with species concentration, and dividing by number of days in the sampling period. On August 30, all sample bottles were full and we estimated the expected volume by taking the ratio of measured precipitation at a nearby meteorological station in the sampling periods, to the measured throughfall volume in the other sampling periods. The THg/TOC and MeHg/TOC ratios were used to evaluate the quality of the concentration data, and the first sampling had significantly higher ratios than the other three. Although environmental explanations for this are possible (e.g. high pollen levels), it was thought to be related to insufficient cleaning of the Teflon coating after installation of the samplers. The first sampling was therefore not used in the flux calculations. Throughfall fluxes in the three Scots pine sites were averaged to give one flux for the Scots pine forest.

2.3. Soil sampling and sample preparation

All soils were sampled during a field campaign in September 2013 (sampling description and summary in Table 1). In the reference, undisturbed catchment (LAE03), soils were sampled at the same locations where throughfall was collected (sites P, F1 (pine forest), F2 (swamp forest), F3 (spruce forest), see Fig. 1). In LAE11, undisturbed open peatland (P) was sampled. In the disturbed catchment area, impacted by forest machinery (i.e. harvester and forwarder) and where the canopy was removed, three wheeltracks (WT1, WT2, WT3) were sampled, paired with sampling points less than 5 m distance outside the wheeltracks with no signs of damage from forest machinery (WT1a, WT2a, WT3a). For sampling points WT1a-3a we use the notation "non-wheeltrack samples" throughout the manuscript.

The soils were sampled by digging a hole of ca. 20 cm depth with a spade, visually characterising the different soil layers, and