

Influence of the Forest Canopy on Total and Methyl Mercury Deposition in the Boreal Forest

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Abstract Atmospheric mercury deposition by wet and dry processes contributes mercury to terrestrial and aquatic systems. Factors influencing the amount of mercury deposited to boreal forests were identified in this study. Throughfall and open canopy precipitation samples were collected in 2005 and 2006 using passive precipitation collectors from pristine sites located across the Superior National Forest in northern Minnesota, USA. Samples were collected approximately every 2 weeks and analyzed for total (THg) and methyl mercury (MeHg). Forest canopy type and density were the primary influences on THg and MeHg deposition. Highest THg and MeHg concentrations were measured beneath conifer canopies

(THg mean=19.02 ng L⁻¹; MeHg mean=0.28 ng L⁻¹) followed by deciduous throughfall (THg mean=12.53 ng L⁻¹; MeHg mean=0.19 ng L⁻¹) then open precipitation (THg mean=8.19 ng L⁻¹; MeHg mean=0.12 ng L⁻¹). The greater efficiency of conifers at scavenging THg and MeHg from the atmosphere may increase the risk of mercury related water quality issues in conifer-dominated systems.

Keywords Atmospheric deposition · Canopy · Methyl mercury · Total mercury · Throughfall

1 Introduction

Loadings of atmospheric mercury (Hg) are of concern due to depositional pathways that result in Hg entering surface waters, where it becomes available for transformation to MeHg (Watras et al. 1994). MeHg is bioaccumulated in aquatic systems and poses a threat to the health of fish-eating humans and wildlife. Atmospheric Hg is present in three main forms: gaseous elemental Hg (Hg (0)), ionic Hg compounds, and particulate Hg (Schroeder and Munthe 1998). Hg (0) is characterized by a long atmospheric residence time of 0.5–2 years. Ionic Hg compounds are more soluble and have a shorter atmospheric lifespan than Hg (0), and include MeHg. Particulate Hg, which is associated with aerosols and dust and is present in the atmosphere for a few days to

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weeks (Schroeder and Munthe 1998). Particulate Hg that settles on forested canopies is washed off in throughfall during precipitation events becoming part of the total deposition in forested sites (Kolka et al. 1999). Particulate Hg represents a relatively small fraction (~10%) of total dry deposition (Grigal 2002; Rea et al. 1996; Lindberg et al. 1994). The bulk of dry deposition is controlled by Hg (II) adsorption and Hg (0) oxidation (Lindberg et al. 1994). Precise mechanisms for dry deposition and factors controlling the percent particulate Hg have not been definitively determined. Hg (II) also plays an important role in wet deposition of Hg. Due to the increased solubility of Hg (II), it is the main form of Hg in wet deposition even though Hg (0) is much more prevalent in the atmosphere (Grigal 2002; Fitzgerald and Mason 1996).

Iverfeldt (1991) identified the effective surface area of different vegetation types as important in Hg flux. Conifer canopies have been identified as having greater surface roughness, including more leaf hairs, and a canopy structure that slows air flow, increasing flux (Johnson et al. 2007; Rea et al. 2002). A previous study conducted in northern Minnesota found higher total mercury (THg) concentration in throughfall under conifer species than under deciduous species or in open precipitation, indicating that conifers are more efficient at scavenging Hg than deciduous trees (Kolka et al. 1999). Lindberg et al. (1991) also found higher concentrations of THg in throughfall under conifer species when compared to deciduous species in Tennessee, USA.

MeHg is present in precipitation and throughfall, albeit at much lower concentrations than THg. It has been suggested that wet deposition of MeHg is controlled by methylation of Hg (II) complexes in solution in the atmosphere and is not related to THg in precipitation (Hammerschmidt et al. 2007). Atmospheric washout processes have been identified for both THg and MeHg precipitation measurements, where Hg (II) and particulate Hg are removed from the atmosphere in the early stages of precipitation events (Hall et al. 2005; Bloom and Watras 1989).

Measurements of MeHg in throughfall have yielded a variety of results, with St. Louis et al. (2001) finding concentrations of MeHg in jack pine throughfall to be 2.2 times higher than that measured in open precipitation, but finding no difference in deposition between throughfall and open precipita-

tion. Lee and Iverfeldt (1991) and Munthe et al. (1995), found no difference in MeHg concentration when comparing open precipitation to throughfall collected under conifer canopies in Sweden.

The objectives of this study were to measure THg and MeHg concentrations and flux under conifer and deciduous canopies and in open precipitation to identify factors affecting Hg deposition in a boreal forest ecosystem in northern Minnesota, USA. Canopy type and density were hypothesized to be the dominant influences on THg and MeHg concentration and flux. More dense canopies, particularly conifer canopies, were hypothesized to be better able to scavenge Hg from the atmosphere because of higher leaf surface area.

2 Materials and Methods

2.1 Site Data and Description

Throughfall collectors and open precipitation counterparts were grouped in five separate locations in the USDA Forest Service's Superior National Forest (SNF) in northeastern Minnesota (Fig. 1). Each group had collectors for conifer throughfall and deciduous throughfall. Three groups had collectors for open precipitation (Fig. 1).

Forest types and tree species were similar among the groups. Quaking aspen (*Populus tremuloides*) and paper birch (*Betula papyrifera*) were the dominant species in deciduous canopies while white spruce (*Picea glauca*) and balsam fir (*Abies balsamea*) composed most of the conifer canopies. Canopy density ranged from 38% in 97%.

Temperatures in the SNF range from -43° to 38°C , with an average annual temperature of 3°C . The area receives an average of 71 cm annual precipitation, with nearly 75% occurring between May and October. In the two study years, annual precipitation was 85 cm in 2005 and 72 cm in 2006. Prevailing winds are from the west and southwest (Midwestern Regional Climate Center 2007).

2.2 Collector Description

Collector design was based on the Swedish IVL bulk collector described by Iverfeldt (1991), and consisted of a 7.63 cm diameter PFA Teflon funnel connected to a 1 L bottle with Teflon PFA tubing. An inverted

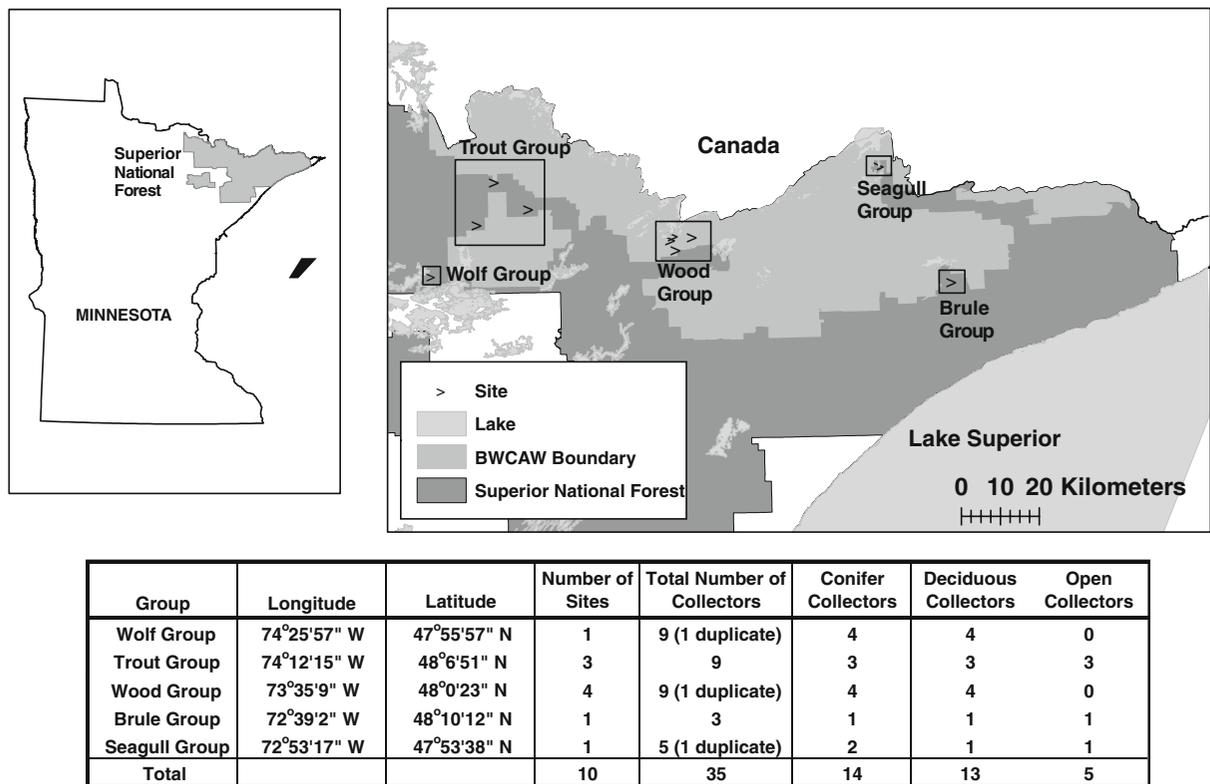


Fig. 1 Location of the Superior National Forest and sampling group locations with collector information

Teflon disc was placed in the bottom of each funnel to prohibit large debris from entering the sample train. All components in contact with samples were Teflon coated. The sampling apparatus was housed in a PVC shell that stood approximately 1 m tall, and was continuously open.

Canopy densities were measured with a convex densiometer and expressed as the fraction of the sky with canopy present (Korhonen et al. 2006; Lemmon 1956). Measurements were taken at the beginning (May/June) and middle (August) of the sampling year. Each value was the mean of four canopy readings per site; the values from the beginning and middle of the sampling season were averaged to determine the canopy density.

2.3 Sample Collection

Sample collection occurred approximately every 2 weeks from May to October of 2005 and 2006. THg samples were collected for 2005 and 2006; MeHg samples were only collected in 2006. Sampling was performed using PVC gloves and the ‘clean

hands, dirty hands’ method described by St. Louis et al. (1994) to minimize risk of contamination. All PFA Teflon components were acid washed overnight prior to deployment and between sampling years. Between individual sampling events, funnels and tubing were rinsed with de-ionized water. After each sampling event, a clean, acid-washed bottle replaced the bottle containing the sample. Each 1 L Teflon bottle contained 2 mL of low Hg concentrated HCl for sample preservation. After sample collection, they were placed on ice for transport back to the lab. Upon reaching the lab, samples from the 1 L bottles were transferred into 125 mL PFA Teflon bottles for THg analysis and 125 mL PETG bottles for MeHg analysis. Both sub-samples were refrigerated until analysis. Samples were unfiltered to quantify bulk deposition, and were not separated between the dissolved and particulate Hg fractions (St. Louis et al. 2001).

2.4 Lab Analysis

THg was analyzed using double amalgamation cold vapor atomic fluorescence spectroscopy as outlined in

EPA method 1631, Revision C (1999) and described by Gill and Fitzgerald (1987). A Brooks-Rand AFS Model III CVAFS equipped with Mercury Guru Software analyzed the samples. Samples for THg analysis received BrCl for digestion in BrCl: sample ratios from 1:100 to 1:20 depending on the amount of organic material present in the sample. Samples were then digested overnight in a 70°C oven. Hg was purged using N₂ gas following reduction by SnCl₂. Standard curves were run prior to each day's analysis. Standard reference materials (NIST #2976 mussel tissue and NIST #1515 apple leaves) averaged 92%±2% (SE) of the standard concentration while duplicate samples averaged 100%±6%. The method limit of detection for THg was 0.1 ng L⁻¹.

MeHg analysis was performed with a Tekran Model 2500 CVAFS Mercury Detector and gas chromatograph separation as described by Bloom (1989). Prior to analysis, samples were distilled using an aluminum heating block and ultra-clean nitrogen purge gas. Samples were ethylated with sodium tetraethyl borate, purged with nitrogen gas and collected onto a Carbotrap. Mercury species were then released from the Carbotrap by heating in an argon purge stream, separated on the GC column, converted to elemental Hg by pyrolysis, and analyzed by CVAFS. The limit of detection for MeHg was 0.07 ng L⁻¹, with mean MeHg concentration in analytical blanks of 0.008 ng L⁻¹. MeHg measured in distillation blanks was subtracted from concentrations measured during the sample analysis.

2.5 Collector Precision and Accuracy

Duplicate collectors in the Wolf, Wood, and Seagull groups (Fig. 1) and weekly field blanks were included as part of the QA protocol. Identical throughfall collectors were positioned less than 0.5 m from one existing collector per group (three total duplicates). Due to the close proximity of the duplicate and co-located collector, the canopy density for each collector was within 5%. Samples were collected at the same time from each collector, analyzed, and compared. THg and MeHg concentrations did not significantly differ between the duplicate and co-located collector ($p=0.88$, $n=10$ for THg; $p=0.46$, $n=7$ for MeHg).

Field blanks were also included as part of the QA/QC protocol. After distilled water was poured through the funnel and tubing as part of the sampling protocol

(Section 2.3), additional distilled water was poured through the funnel and tubing into a clean, acid washed 1 L bottle containing 2 mL of HCl. Blanks were collected from at least one site once per week and analyzed for THg and MeHg. Mean THg concentration in field blanks was 2.83 ng L⁻¹±0.31 ng L⁻¹ (SE). Mean MeHg concentration in field blanks was 0.005 ng L⁻¹±0.002 ng L⁻¹ (SE). THg and MeHg concentrations measured in the field blanks were subtracted from the sample concentrations collected during the same week.

To verify the ability of our relatively small 7.63 cm diameter funnel at collecting accurate precipitation volume, alternate collectors with larger diameter funnels (20.32 cm) were co-located with the IVL collectors at 15 of the 35 locations in 2005 and all 35 locations in 2006 for volumetric collection only. The funnel and bottle were secured to a wooden or PVC base at the same height as the IVL collectors. Volumes were measured in the alternate collectors when Hg samples were taken. Volumes collected by the 7.62 cm and the 20.32 cm diameter funnels were proportionally similar (Mann-Whitney test, $p=0.078$, $n=148$) to the surface area of the funnel. Consequently, no volume correction was needed for the mercury throughfall collectors.

2.6 Calculations and Statistical Analyses

Hg flux was determined by multiplying Hg concentrations by the volume of precipitation collected. Statistical analyses were performed using Minitab software, version 14.20. Prior to statistical comparisons, outliers were identified as values greater than 1.5 times the inter-quartile range. Paired t-tests were used to compare duplicate and co-located collectors for THg and MeHg concentration. When comparing sample volumes collected in the different collector types, the non-parametric Mann-Whitney test was used. One-way ANOVA was used to identify differences in volumes and THg and MeHg concentrations and flux based on canopy density, as well as to identify differences in MeHg:THg concentration ratio. Mann-Whitney tests were used to assess differences in Hg related to sample volume and canopy density. Two-sample t-tests were used to determine significant differences in THg concentrations and flux after logarithmic transformation to normalize the data. Regression analysis was used in determining relation-

ships between volume and THg and MeHg concentration as well as relationships between THg and MeHg concentration. Regression analysis was also used in determining relationships between co-located duplicate collectors.

3 Results

The data indicate that canopy type has the greatest influence on Hg concentrations and flux. Significant differences exist in THg and MeHg throughfall concentrations and flux based on the canopy type (Figs. 2 and 3).

THg concentrations were significantly higher under conifer canopies than under deciduous canopies ($p=0.002$, $n=143$) or in open precipitation ($p\leq 0.001$, $n=87$). Deciduous throughfall concentrations were also significantly higher than open precipitation concentrations ($p\leq 0.001$, $n=116$) (Fig. 2). Similar results were found when comparing event based THg flux; conifer throughfall flux was significantly higher than deciduous throughfall flux ($p=0.017$, $n=81$) and open precipitation flux ($p=0.01$, $n=59$), however, deciduous throughfall flux was not significantly different from open precipitation flux ($p=0.452$, $n=74$) (Fig. 2).

MeHg concentrations followed a pattern somewhat similar to THg concentrations. MeHg concentrations in conifer throughfall were significantly higher than in deciduous throughfall ($p=0.043$, $n=95$) and open

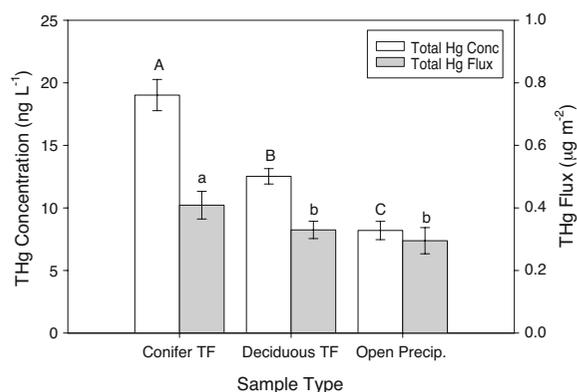


Fig. 2 Mean THg concentrations and flux by canopy type. Letters denote significant differences at the 0.05 level; error bars represent one standard error. THg concentrations varied among all three canopy types, while flux was different for conifer throughfall, but not between deciduous throughfall and bulk precipitation

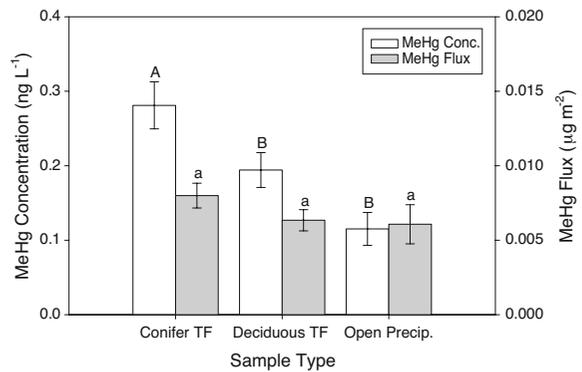


Fig. 3 Mean MeHg concentrations and flux by canopy type. Letters denote significant differences at the 0.05 level; error bars represent one standard error. MeHg concentrations differed between conifer throughfall and bulk precipitation, while MeHg flux was not significantly different among any of the three sample types

bulk precipitation ($p=0.003$, $n=64$). However, MeHg concentrations in deciduous throughfall were not significantly different from open precipitation concentrations ($p=0.171$, $n=71$). No significant differences were found in MeHg flux among canopy types, with conifer flux not different than deciduous deposition ($p=0.099$, $n=96$) or open precipitation flux ($p=0.131$, $n=67$). Also, deciduous flux was not significantly different from open precipitation flux ($p=0.692$, $n=73$) (Fig. 3).

Canopy density did have an effect on THg and MeHg concentrations (Figs. 4 and 5). THg concentrations measured in conifer throughfall under canopies with densities higher than 90% were significantly higher than concentrations measured under canopies with densities from 80–90% ($p=0.05$, $n=39$) and under canopies with less than 80% density ($p=0.008$, $n=41$). THg concentrations in deciduous throughfall under canopies with greater than 90% density were significantly higher than concentrations measured under canopies with densities less than 60% ($p=0.003$, $n=63$), but not significantly higher than concentrations measured under canopies with densities between 60 and 90% ($p=0.12$, $n=53$). Comparisons between equivalent canopy densities for conifer and deciduous canopies found conifer throughfall THg concentrations to be significantly higher than deciduous throughfall THg concentrations for canopy densities ranging from 60–90% ($p=0.03$, $n=40$) and for canopy densities greater than 90% ($p=0.001$, $n=60$).

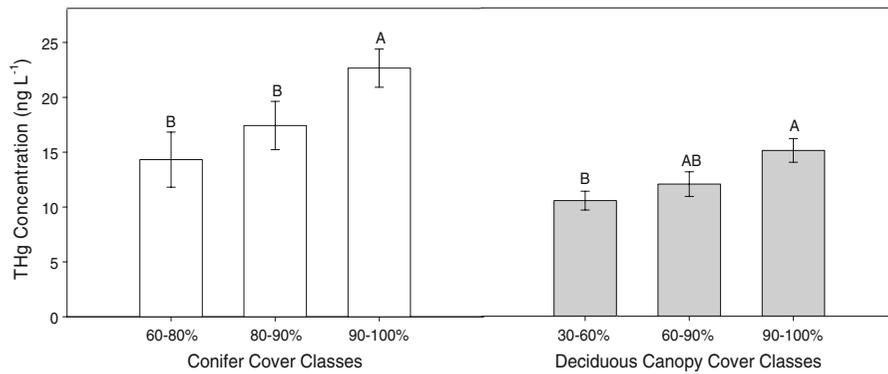


Fig. 4 Canopy effects on THg concentration. Significant differences were found among the different conifer throughfall cover classes ($p=0.02$, $n=52$); canopies with densities greater than 90% had significantly higher THg concentrations than canopies with densities less than 80% ($p=0.008$, $n=41$) and higher THg concentrations than canopies with densities between 80 and 90% ($p=0.05$, $n=39$). THg concentrations

The highest MeHg concentrations were measured in areas with conifer canopy densities greater than 90%, and were significantly higher than those measured under canopies with densities between 60 and 80% ($p=0.007$, $n=32$) and under canopies with densities between 80 and 90% ($p=0.06$, $n=32$). MeHg concentrations measured under deciduous canopies were not significantly different based on canopy density ($p=0.853$, $n=56$). Similar to THg concentrations, inter-canopy comparisons determined that for canopy densities greater than 90%, MeHg concentrations in conifer throughfall were significantly higher than MeHg concentrations in deciduous throughfall ($p=0.004$, $n=45$). No significant differences were

from deciduous throughfall were also significantly different based on canopy density ($p=0.004$, $n=84$). Samples from canopies with densities greater than 90% had higher THg concentrations than samples from canopies with densities less than 60% density ($p=0.003$, $n=63$), but were not different for canopy densities between 60 and 90% ($p=0.12$, $n=53$). Error bars represent one standard error

found between the two canopy types for canopy densities ranging from 60 to 90% ($p=0.78$, $n=33$).

THg flux was not significantly impacted by canopy density in either conifer or deciduous throughfall ($p=0.842$, $n=36$ for conifer canopies, $p=0.632$, $n=51$ for deciduous canopies). MeHg flux was also not impacted by canopy density ($p=0.136$, $n=44$ for conifer canopies, $p=0.858$, $n=56$ for deciduous canopies).

While THg and MeHg concentrations were both affected by canopy type, the ratio of THg present as MeHg was not different among canopy types ($p=0.44$, $n=93$). The proportion of THg present as MeHg ranged from 0–4.4% (concentration based), with an overall mean of 1.25%. For conifer throughfall,

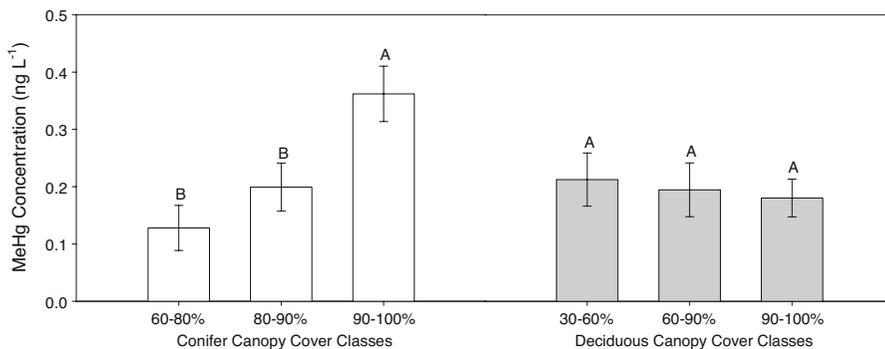


Fig. 5 Canopy effects on MeHg concentration. Significant differences were found in MeHg concentration in conifer canopy based on canopy cover ($p=0.005$, $n=42$). Canopies with densities greater than 90% had significantly higher THg concentrations than canopies with densities less than 80%

($p=0.007$, $n=32$) and higher THg concentrations than canopies with densities between 80 and 90% ($p=0.06$, $n=32$). No significant differences were found for deciduous throughfall based on canopy cover ($p=0.853$, $n=56$). Error bars represent one standard error

the mean MeHg content was 1.0% of THg, deciduous throughfall was 1.4%, and open precipitation was 1.2%. The correlations between THg and MeHg concentrations ($r^2=0.034$) were not significant. No significant correlations were found between THg concentrations and sample volumes ($r^2=0.032$) or MeHg and sample volumes ($r^2=0.058$).

Open precipitation volumes were not significantly different when compared to either deciduous ($p=0.269$, $n=95$) or conifer throughfall volumes ($p=0.223$, $n=80$). Using the y-intercepts of the relationships between canopies and open bulk precipitation as an estimate of interception, conifer canopies intercepted an average of 24.6 mm, with deciduous canopies intercepting an average of 7.9 mm per precipitation event.

4 Discussion

Canopy type was the dominant factor influencing concentrations of THg and MeHg, as well as THg flux in this system. Dense canopies resulted in increased THg and MeHg concentrations measured in throughfall. Our mean THg concentration for conifer throughfall of 19.0 ng L^{-1} measured in this study was similar to those reported by Munthe et al. (1995) (range: $22.8\text{--}24.9 \text{ ng L}^{-1}$) under mature Norway spruce in Sweden, St. Louis et al. (2001) in northwest Ontario for a mixed jack pine/birch forest (mean 20 ng L^{-1}), and by Lindberg et al. (1994) in Tennessee under a pine canopy (17.5 ng L^{-1}). Conifer throughfall THg concentrations were less than half of mean concentrations found by Iverfeldt (1991) in a Norway spruce stand located in Sweden (48.4 ng L^{-1}). Similar to results found by Kolka et al. (1999) and Iverfeldt (1991), we found conifer THg concentrations to be higher than THg concentrations in open deposition, which has been attributed to the leaf surface area of conifer canopies. THg concentration increased beneath conifer canopies as canopy density increased (Fig. 4), further evidence that the higher effective leaf surface areas of conifer species influence their greater dry deposition scavenging abilities.

THg concentrations in deciduous throughfall in this study (mean= 12.5 ng L^{-1}) were similar to values reported by Rea et al. (1996) of 12 ng L^{-1} measured beneath beech and maple forests in Vermont, and Johnson et al. (2007) of 14.2 ng L^{-1} measured in

beech and birch forests in Maine. We found THg throughfall concentrations to be 1.5 times higher than open concentrations, similar to the ratio measured by Kolka et al. (1999) in a deciduous forest in Minnesota. Rea et al. (1996) concluded that deciduous throughfall concentrations are significantly higher than open bulk precipitation THg concentrations due to dry deposition of Hg to the deciduous canopy (Rea et al. 1996).

THg concentrations in open bulk precipitation measured in this study (mean= 8.2 ng L^{-1}) were similar to those found earlier at a Minnesota site 100 km southwest of this study area (Grigal et al. 2000; 9.9 ng L^{-1}) and fell within the range of concentrations reported by Hall et al. (2005) measured in the Great Lakes region (mean= $2.4\text{--}24.0 \text{ ng L}^{-1}$ from six different sites). We found no significant differences in THg concentration measured in open bulk precipitation in this study and measurements made at the Mercury Deposition Network (MDN) site (MN 18) located approximately 60 km from the study site during the 2006 sampling period (two-sample t-test; $p=0.80$, $n=55$), where the collector is open only during precipitation events for wet-only fluxes. Similar concentrations between our open bulk collector and the MDN collector indicate that little dry deposition of THg occurs in openings.

Similar to results reported in other studies, MeHg concentrations in conifer throughfall were higher than MeHg concentrations in open bulk precipitation. The mean MeHg concentration measured under conifer canopy in this study was 0.28 ng L^{-1} , which falls between the 0.38 ng L^{-1} from Norway spruce throughfall measured in Sweden (Munthe et al. 1995) and 0.22 ng L^{-1} from a mixed jack pine and birch forest in northwestern Ontario (St. Louis et al. 2001). The 2.3:1 ratio of conifer throughfall MeHg concentrations to open precipitation MeHg concentrations was nearly identical to the ratio found by St. Louis et al. (2001), and contrasts with the findings of Johnson et al. (2007) and Munthe et al. (1995), neither of which found significant differences in MeHg concentrations between conifer throughfall and open deposition. Similar to results reported by Johnson et al. (2007) and Munthe et al. (1995), MeHg flux in conifer throughfall was not significantly higher than MeHg flux in either deciduous throughfall or open precipitation.

MeHg concentrations and fluxes in deciduous throughfall were not significantly different from open

bulk precipitation, and did not increase with increasing canopy density. Mean MeHg concentrations measured in deciduous throughfall for this study (0.19 ng L^{-1}) were higher than those measured by Johnson et al. (2007) in throughfall from a beech-birch-aspens-maple forest in Maine (mean= 0.07 ng L^{-1}), and in a beech-oak forest in Germany (median= 0.13 ng L^{-1}) (Schwesig and Matzner 2000). Similar to this study, significant differences in MeHg concentrations were not found between open bulk precipitation and deciduous throughfall in either of these two studies.

MeHg concentrations in open precipitation measured in this study (mean= 0.12 ng L^{-1}) were within the range of those reported by Lee and Iverfeldt (1991) in Sweden (range: $<0.05\text{--}0.6 \text{ ng L}^{-1}$) and by Hall et al. (2005) in the Great Lakes region (range: $0.01\text{--}0.85 \text{ ng L}^{-1}$), and were similar to concentrations measured in open bulk precipitation in Germany (0.10 ng L^{-1}) (Schwesig and Matzner 2000). Comparison of the open precipitation MeHg concentrations found in this study to MeHg concentrations measured at MDN site 18 during the same time period (mean= 0.13 ng L^{-1}) found no significant difference between the two locations (two-sample t-test, $p=0.658$, $n=28$). Additionally, we found no significant relation between MeHg concentrations and THg concentrations in open precipitation.

Increases in THg concentration based on canopy density have been found in both deciduous and conifer canopies in Minnesota (Kolka et al. 1999), similar to the increases in concentration with greater canopy densities found in this study. The fraction of THg present as MeHg did not differ between deciduous and conifer throughfall. These data suggest that the higher efficiency of conifer canopies at scavenging THg from the atmosphere extends to MeHg, and that dry deposition of MeHg is likely the source of MeHg in throughfall waters as opposed to methylation of absorbed THg on the leaf surface. These results show that dry deposition of MeHg is a previously unreported input to this system.

5 Conclusions

The largest influence on THg and MeHg deposition rate in the boreal ecosystem of northern Minnesota is canopy type. Conifer species are better able to scavenge Hg from the atmosphere, resulting in greater

THg and MeHg concentrations in conifer throughfall than in deciduous throughfall or open precipitation. Conifer canopy density also influenced THg and MeHg concentrations with higher-density canopies producing higher concentrations. Higher-density deciduous canopies are correlated with increased THg concentrations but not MeHg concentrations. Among canopy types, conifer canopies also had the highest THg flux but we found no statistical differences in MeHg flux among canopy types. Based on our results and others it appears that conifer-dominated systems may be at increased risk of mercury related water quality issues because of conifers' greater ability to scavenge dry deposition.

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