

# Effects of Stump Harvesting and Site Preparation on Mercury Mobilization and Methylation

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Cover: Runoff from the North catchment in the 277 Balsjö Catchment study site  
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## Abstract

Mercury (Hg) is an element of major concern in boreal freshwater ecosystems, due to high concentrations of Hg in fish. Forestry operations have been reported to increase the concentrations and loads of Hg to surface waters. In this thesis a series of catchment-scale experiments were used to determine forestry effects on total mercury (THg) and methyl mercury (MeHg) runoff concentrations caused by stump harvest, site preparation and antecedent logging.

The stump harvest did not increase Hg concentrations in runoff relative to traditional site preparation in either of the stump harvest studies. The lack of treatment effects caused by stump harvest and site preparation in one of the stump harvest studies focused attention on the antecedent logging. The question of whether the logging was of major importance when compared with the subsequent soil disturbance caused by site preparation was further investigated in the Balsjö catchment study. Contrary to the stump harvest study, the concentrations of THg and MeHg increased after both logging and site preparation by around 30-40 %, but no significant effect was detected after logging only. The more pronounced effect of site preparation in the Balsjö study might be due to more soil disturbance caused by site preparation that was carried out in early summer compared with the logging that was carried out in winter when snow protected the ground. The season and weather conditions present during forestry operations might therefore be of importance when considering possible treatment effects on Hg. The variation in forestry effects on Hg between catchments in this thesis, as well as in earlier studies, indicates that the catchment sensitivity to forestry operations varies. This variation could be due to differences in the biogeochemical status of soils and waters. It is thus vital to determine what factors influence THg and MeHg concentrations in different catchments. The importance of total organic carbon (TOC) was highlighted by a strong correlation between THg and TOC both within and between the study catchments in this thesis. The discharge was also found to have a positive influence on the THg and TOC concentrations, while temperature had a positive influence on the MeHg concentrations.

This thesis suggests that when and how forestry operations are implemented might be more important than the treatment type in some catchments. This thesis also identifies a variation in catchment sensitivity to forestry operations that requires further investigation.

*Keywords:* Forestry, Treatment effects, Boreal streams, Catchments, Methylation, Discharge, Organic carbon

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## List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

- I Eklöf, K., Fölster, J., Sonesten, L., Bishop, K. (2012). Spatial and temporal variation of THg concentrations in run-off water from 19 boreal catchments, 2000-2010. *Environmental Pollution*. 164, 102-109
- II Eklöf, K., Meili, M., Åkerblom, S., von Brömssen, C., Bishop, K., (2012). Impact of stump harvest on run-off concentrations of total mercury and methylmercury. *Forest Ecology and Management*. DOI:10.1016/j.foreco.2012.05.039
- III Eklöf, K., Kraus, A., Weyhenmeyer, G.A., Meili, M., Bishop, K. (2012). Forestry influence by stump harvest and site preparation on methylmercury, total mercury and other stream water chemistry parameters across a boreal landscape *Ecosystems*. DOI:10.1007/s10021-012-9586-3
- IV Eklöf, K., Schelker, J., Sørensen, R., Meili, M., von Brömssen, C., Laudon, H., Bishop, K. Impact of forestry on THg and MeHg in aquatic ecosystems; distinguish site preparation effects from logging effects. (manuscript).

Papers I-III are reproduced with the permission of the publishers.

The contribution of Karin Eklöf to the papers included in this thesis was as follows:

- I The respondent was the main person responsible for data handling, data analyses, interpretations, writing and publishing.
- II The respondent was the main person responsible for the logistics and development of the study design. The field sampling was partly done by the respondent. The data handling, data analyses, interpretations, writing and publishing were mainly done by the respondent.
- III The respondent was partly responsible for the design of the study and the field sampling. The data handling, data analyses and interpretation was partly done by the respondent. The writing and publishing was mainly done by the respondent.
- IV The respondent participated in the field sampling and the development of the study design. The data handling, data analyses, interpretation, writing and publishing was mainly done by the respondent.



## Abbreviations

Abs <sub>420</sub>	Absorbance at 420 nm
DOC	Disolved Organic Carbon
HCL	Highest Coast Line
Hg	Mercury
IRB	Iron Reducing Bacteria
K	Potassium
MANOVA	Multivariate Analysis of Variance
MeHg	Methylmercury
OM	Organic Matter
PHg	Particulate Mercury
PLS	Partial Least Squares
POC	Particulate Organic Carbon
Q	Discharge
RIA	Randomized Intervention Analysis
SRB	Sulfur Reducing Bacteria
THg	Total Mercury
TN	Total Nitrogen
TOC	Total Organic Carbon
TSS	Total Suspended Solids



# 1 Introduction

Forestry is an important industry in Sweden. With approximately 55% of Swedish land cover made up of productive forest land, forestry and the forestry products industry accounted for 2.2% (during the year 2008) of the country's gross domestic product (GDP) (Swedish Forest Agency, 2011). Taking into account the importance of forestry in Sweden and other boreal regions, possible environmental effects at a catchment level need to be carefully assessed. In an environmental perspective intensified forestry, such as removal of stumps after logging, could also be of benefit due to increased supply of biofuels and reduced consumption of fossil fuel (Egnell *et al.*, 2011). However, this environmental benefit has to be balanced against the ecological risks associated with soil disturbance created by forestry operations (Walmsley & Godbold, 2010). Forestry operations have been shown to increase loadings and concentrations of dissolved organic carbon (DOC), particles and nutrients (Kreutzweiser *et al.*, 2008) as well as mercury (Hg) (Bishop *et al.*, 2009).

## 1.1 Mercury contamination in Sweden

High mercury concentrations in freshwater fishes are a major concern in many regions in the northern hemisphere, including Sweden. Due to the increased mercury deposition since preindustrial time, the concentrations of mercury in fish in the south of Sweden is estimated to have increased by a factor of five during the last century (Johansson *et al.*, 2001). The Hg concentrations in the tissue of Swedish freshwater fish now exceeds the European Union threshold limit of 0.02 mg Hg kg<sup>-1</sup> (EU, 2008) in most of Sweden's hundred thousand lakes. Furthermore, the Hg concentrations in Swedish fish have been found to increase from the end of 1990 to 2006 (Åkerblom *et al.*, 2012).

The highest concentrations of Hg have been detected in south/central Sweden and along the Baltic Sea coast in northeastern Sweden in stream waters (Eklöf *et al.*, 2012a), fish and sediments (Munthe *et al.*, 2007). This

spatial pattern is possibly reflecting a north – south gradient of increasing Hg deposition caused by emission sources in central Europe (Munthe *et al.*, 2007). Hg contamination in Sweden is also attributed to a history of local point sources, such as chlor-alkali plants, metal production and fiber banks from timber industries (Lindqvist *et al.*, 1991) along the northeastern Baltic coast and in the south/central Sweden (Munthe *et al.*, 2007). However, the more widespread contamination of Swedish freshwater fishes is mainly attributed to diffuse anthropogenic deposition of long range Hg (Munthe *et al.*, 2007).

## 1.2 Sources and fate of mercury in the boreal landscape

### 1.2.1 Mercury emissions, deposition and soil storage

Mercury is a long-range transport pollutant widespread in remote areas. In Sweden about 80% of the mercury deposition originates from emission sources outside the country border (Johansson *et al.*, 2001). The fate of Hg in the atmosphere depends on the speciation of the emitted mercury where elemental Hg(0) can be transported for tens of thousands of kilometres, Hg(II) up to hundreds of kilometres, and particulate Hg (PHg) for shorter distances depending on the particle size and mass (Schroeder & Munthe, 1998). Natural mercury emissions are mainly attributed to volcano eruptions and volatilization from land and water surfaces whereas around half of the emitted Hg originates from anthropogenic sources such as fossil fuel combustion, metal production, cement production, waste disposal and old traditions of gold mining (Pacyna *et al.*, 2006). Due to the increased anthropogenic mercury emission during the industrialisation era the overall global deposition of mercury has increased by approximately a factor of three since preindustrial times (Lindberg *et al.*, 2007). In Europe the maximum mercury emission rate was found around 1960, and the mercury deposition in Sweden has slightly declined since then, with a more marked decrease in 1990 after economical and political changes in eastern Europe (Munthe *et al.*, 2001). Despite this decline in mercury deposition during recent decades, the mercury accumulations in soil are still increasing due to the high fraction of Hg retention in the soil (Johansson *et al.*, 2001). Newly deposited Hg is accumulated in the organic rich upper soil horizons and the highest mercury concentrations are thereby found in the mor layer and the upper organic-rich mineral layer (Bishop & Lee, 1997).

### 1.2.2 Mercury methylation

The organic form of Hg, methylmercury (MeHg), is the form of main concern due to its toxicity and bioavailability. MeHg is simultaneously created by methylation and degraded by demethylation. Measurements of MeHg in the

environment reflect the net methylation rate. Estimating the turnover time for MeHg has been more difficult since it requires separating the competing processes of methylation and demethylation. The transformation of inorganic Hg to MeHg, is a microbial process mainly carried out by sulfur reducing bacteria (SRB) (King *et al.*, 2001; Gilmour *et al.*, 1992). However, other bacterial communities, such as iron reducing bacteria (IRB), could contribute as well (Fleming *et al.*, 2005). The methylation rate is linked to factors controlling the abundance and activity of SRB such as suboxic microenvironment, the availability of sulfate (electron acceptor), high quality organic matter (electron donor), inorganic Hg and temperature (Drott *et al.*, 2007). In addition, the presence of neutral Hg sulphide species has been found to influence the passive transport of Hg across the cell membrane of SRB, and thereby also the methylation rate (Skylberg *et al.*, 2007). Whereas the methylation is a strictly biotic process the demethylation seems to be influenced both by biotic and chemical factors. Furthermore, the demethylation rate seems to be more stable than the methylation rate (Skylberg *et al.*, 2007). The factors controlling the methylation might thereby be of higher importance than the demethylation when considering the variability of net methylation rate.

### 1.2.3 Factors influencing mercury runoff from catchments

The mobilization of mercury from soils to water bodies is controlled by flow paths and the export of organic substances. Superficial flow path, through the upper humic and mercury rich soil horizons, usually result in high Hg stream concentrations (Bishop *et al.*, 1995). Mercury, as well as many other trace metals, is strongly attached to the reduced sulphur sites and oxygen/nitrogen-groups in the organic molecules (Skylberg *et al.*, 2006; Ravichandran, 2004). Strong correlations between Hg and organic matter (OM) in stream water have thereby been identified in many studies (e.g. Eklöf *et al.*, 2012a; Shanley *et al.*, 2005; Scherbatskoy *et al.*, 1998). The hydrological control of both OM and attached Hg results in a high runoff ratio of the yearly Hg load during periods of high flow events. However, for MeHg other factors which influence the methylation rate seem to be of superior importance for the runoff concentrations in many catchments. While MeHg has been found to be positively correlated to discharge in some areas (Shanley *et al.*, 2008; Branfireun *et al.*, 1996) flow has had a negative effect on MeHg concentrations in others (Eklöf *et al.*, 2012b; Sørensen *et al.*, 2009; Pettersson *et al.*, 1995). In addition to discharge and OM, particle stream concentrations and wetland abundance have been identified as factors controlling the THg concentrations in streams (Brigham *et al.*, 2009). Furthermore, factors controlling the THg and MeHg concentrations in the catchments have been found to be more important

for the stream concentrations than the atmospheric input (Munthe & Hultberg, 2004; Lee *et al.*, 2000). However, changes in deposition of Hg on open waters have been found to have a rapid effect on Hg fish concentrations (Harris *et al.*, 2007). Methylation of inorganic Hg also occurs in lakes, in the water sediment interface as well as in the water column (Matilainen & Verta, 1995).

### 1.3 Forestry effects on mercury contamination in aquatic ecosystems

Elevated concentrations of both THg and MeHg have been observed after forestry activities in runoff water (Munthe & Hultberg, 2004; Porvari *et al.*, 2003), downstream fishes (Garcia & Carignan, 2000), zooplankton (Garcia *et al.*, 2007) and periphyton (Desrosiers *et al.*, 2006). Based on forestry effect studies from boreal catchments Bishop *et al.* (2009) suggested that 9 – 23 % of the Hg accumulated in fish in Swedish inland water was a consequence of forest harvest. However, the catchment sensitivity to forestry seems to vary among sites and some recent studies have found no detectible, or just moderately, increased concentrations after various forestry operations (Eklöf *et al.*, 2012b; Allan *et al.*, 2009; Sørensen *et al.*, 2009a). It is therefore, vital to determine the effect of different kinds of forestry operations as well as sensitivity to disturbance in different types of catchments. This thesis focuses mainly on the disturbance caused by site preparation and stump harvest. The site preparation refers to the disturbance of the soils prior to the plantation of new trees. This mechanical soil treatment exposes the mineral soil and forms mounds or ridges where the new seeds or seedlings can be planted. Stump harvest is the extraction of the stumps after harvesting of the stands used to maximize the supply of biofuels from the harvest.

#### 1.3.1 Forest harvest

Increased discharge is commonly observed after logging. Removal of vegetation will lower the water losses from transpiration (Bosch & Hewlett, 1982) and more snow also accumulates in open areas (Murray & Buttle, 2003). Increased sunlight radiation on the open ground may offset the increases in discharge after logging by altering the soil temperature and increasing the evaporation of water from the soil surface. However, the increase in evaporation might only be of minor importance compared with the decrease in transpiration and increase in snow accumulation (Buttle & Murray, 2011). Despite this, a study in northern Sweden found that the direct evaporation from the snow surface was actually important for reducing the runoff during spring flood in open areas in some years (Schelker *et al.*, in review). Increased

groundwater recharge in logged areas in till soils of Fenno-Scandia results in more superficial groundwater path-ways though the organic carbon and mercury rich soil surfaces. Increased water discharge might not only increase the chemical loading of contaminants from the catchment but may also create more water logged anoxic environments which in turn provide good conditions for methylators such as SRB. Higher soil temperatures in open areas can further enhance the activity of the methylators as well as the addition of fresh organic carbon sources from decomposition of logging residual (Sørensen *et al.*, 2009a).

### 1.3.2 Forestry machinery operation

The operations of forestry machinery, both during logging, site preparation and stump harvest, can affect the soil physical properties, the hydrological regimes and the erosion rate. Significant increases in soil compaction are commonly observed after forestry operations but the magnitude of the disturbance caused by compaction varies with factors such as climate, soil properties and management practice (Greacen & Sands, 1980). The reduction of soil porosity might lower the infiltration capacity of water in the soil (Kozłowski, 1999). This could increase the superficial flow and result in flooded soils in logging tracks and cavities. Flooded soils can act as methylation hot-spots, with low redox potentials and good access to fresh organic carbon sources (Hall *et al.*, 2005; Porvari & Verta, 1995). Overland flow, connecting the methylation hot-spots and surface waters could then increase the load of MeHg to aquatic ecosystems (Bishop *et al.*, 2009). Increased erosion has also been found to be a consequence of forestry machinery operation (Kozłowski, 1999), which could also lead to increases in Hg loads, as the eroded particles and associated Hg are exported to streams and water bodies.

### 1.3.3 Stump harvest

An increased supply of forest biomass could be a way to meet the growing energy demand in Sweden, without increasing the use of fossil fuels. If more forest biomass is to be used for energy production we have to either increase the amount of harvesting areas or maximize the biomass production from each tree (Egnell *et al.*, 2011). The estimated biomass in stumps of the stem mass is around 20 % (Hakkila, 1989). The environmental benefits gained by also harvesting the stumps and increasing the supply of bio fuels and thereby decreasing the use of fossil fuel should be compared with the ecological costs caused by stump harvest. These ecological costs include a possible impact on soil carbon storage and greenhouse gas emission, increased compaction and soil erosion, changes in nutrient cycling and loss of substrate for vegetation and

biota (Walmsley & Godbold, 2010). One of these consequences may also be increased load of THg and MeHg to aquatic ecosystems.



*Figure 1.* Stump extraction in the stump harvest catchment study (paper II). Photo: Kevin Bishop

Stump harvest is performed by forestry machinery that extracts the stumps and then cuts and shakes them to remove excess soil from the root system (Figure 1). The mineral soil removed from the roots can then be used as a substrate for planting new trees or seeds. Extracted stumps are then transported to a landing area for storage for up to one year to allow rain and snow to wash out stones and soil particles from the roots (Walmsley & Godbold, 2010).

Removal of stumps might disrupt the physical structure of the soil, but the magnitude of the soil disruption depends on the architecture of the roots (Walmsley & Godbold, 2010). The removal of roots can result in disruption of soil structures. Forestry machinery operations on soils where the roots are extracted may thereby cause more soil compaction. Furthermore, more extensive operation of forestry machinery during stump harvest compared with conventional site preparation could result in even more compaction and disturbance of the soils. The stump harvest is often followed by traditional site preparation as well, although the stump harvest itself suffices as soil preparation in some sites. The higher risk of more severe soil disturbance



during stump harvest compared with conventional site preparation necessitates the careful assessment of the effect on Hg transport and methylation.

The current knowledge of forestry effects in boreal catchments is based on just a few available studies. In addition, these studies found a high level of variation in the ecological effects of forestry, possibly due to variation in catchment characteristics in the study sites. More research is necessary to understand the effects of forestry in different kinds of catchments and the factors responsible for the variation in the catchment sensitivity to forestry among sites. Furthermore, the influence of different kinds of forestry activities has to be identified. In particular, separating the effects of stand removal from the effects of site preparation and stump harvest.



## 2 Objectives

The overall aim of this thesis was to determine the effect of different forms of forest soil disturbance (site preparation and stump harvest) on Hg methylation and mobilization using a whole-catchment manipulation approach. The aim was also to understand the trends and factors controlling the Hg mobilization both in untreated and treated catchments. The specific objectives were:

- To investigate which catchment factors control the temporal and spatial variation of THg concentration and test for temporal trends of THg and associated factors in untreated reference streams distributed all over Sweden (paper I).
- To investigate whether the concentrations of THg and MeHg will increase after stump harvest in relation to the concentrations in catchments subjected to traditional site preparation and untreated reference forest (paper II).
- To investigate if the stump harvest caused higher THg and MeHg stream concentrations than the traditional site preparation as well as comparing both types of forest treatments to untreated reference catchments in a spatial dataset consisting of catchments from all over Sweden (paper III).
- To investigate if the disturbance caused by site preparation will increase the concentrations and loads of THg and MeHg in run-off water, as well as to determine whether the site preparation or the former logging is the more sensitive part of the forestry operations when it comes to treatment effects on mercury (paper IV).



## 3 Study sites

### 3.1 Monitoring of undisturbed watercourses in the Swedish environmental monitoring program (Paper I)

The data used in this paper are from the Swedish environmental monitoring program to study long-term trends of selected water chemistry variables. A selection of 19 watercourses spread across Sweden between latitudes N 55° 38' and N 68° 21' have been sampled for mercury (Figure 2). The catchments were characterised as reference catchments, not affected by intensive forestry, local industrial discharge or urban areas. The catchment sizes range from 0.93 km<sup>2</sup> to 9827 km<sup>2</sup>. The coverage of peatlands ranged between 0.2 % and 33.4 %. Influences of agricultural land were only significant in four of the catchments, all situated in the south of Sweden, with a spatial cover of agricultural land up to 64 %. The annual mean precipitation in the catchments (2000-2010) ranges from 650 mm to 1020 mm. The annual mean runoff ranges from 250 mm to 822 mm, and the annual mean air temperature ranges from 0.6 °C to 8.6 °C.

### 3.2 Stump harvest catchment study (Paper II)

The catchment study area for determining the effect of stump harvest and site preparation is situated in south-central Sweden (N 59° 10' 16" E 14° 34' 3"). The study site consists of five catchments subjected to logging/stump harvest (SH1 and SH2), logging/site preparation (SP), and untreated forest (R1 and R2) (Figure 2). Catchment SH2, a small ephemeral headwater stream heavily influenced (100 %) by the stump harvest, and R2, the inflow to the stump harvest area, are both situated upstream of SH1. The area undergoing treatment was 29 % in SH1 and 65 % in SP. The monitoring started in November 2006 after previous logging in the SH1, SH2 and SP catchments in August of 2006. In November 2007 the SH1 and SH2 catchments were stump

harvested. In January 2007 the SP catchment was site prepared. All catchments are defined as typical boreal forest, dominated by coniferous trees such as Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*). Neither of the catchments are dominated by peatlands (less than 6 %), but the riparian zones along the streams are rich in peat. The forested area in the region is dominated by podsollic soils.

### 3.3 Synoptic stump harvest study (Paper III)

The synoptic stump harvest study include 54 catchments spread across Sweden between latitudes N 56° 47' and N 65° 31' ranging 1000 km N-S and 400 km E-W (Figure 2). The 54 catchments were divided into three treatment groups; stump harvest (SH) (n=15), site preparation (SP) (n=21) and untreated references (Ref) (n=18). The percentage cover of treated areas in the catchments varied between 11–98 % for the SH catchments and 15–72 % for the SP catchments, with a median of 40 % for the SH catchments and 34 % for the SP catchments. All the treated catchments were subjected to stump harvest or site preparation within 3 years prior to the last sampling date in 2010. Each SP and Ref catchment was situated within a radius of 50 km from the SH catchments. The Ref catchments contained mature forest stands (over 40 years old) and were chosen to be similar to the SH and SP catchments in terms of vegetation and wetland cover. The catchment size for all catchments varied between 0.7 and 184 ha. All catchments were dominated by coniferous trees, mainly spruce and pine.

### 3.4 Balsjö catchment study (Paper IV)

The Balsjö catchment study, investigating effects of site preparation versus logging, is situated in the north of Sweden (N 64° 1' 37" E 18° 55' 43") approximately 70 km west of the Baltic Sea coast. The study site includes three catchments which have been monitored since 2005 for Hg (Figure 2). One was an untreated reference catchment, Ref-S, where the forest cover were left throughout the whole study period, The other two catchments were logged in March 2006 followed by site preparation by means of disk-trenching in May 2008. In one of the treated catchments, North, which was logged / site-prepared, a small (>5 m width on each stream side) discontinuous buffer strip of trees was left along the stream channel. No buffer zones were left along the stream in the other treated catchment, CC. The percentage cover of treated areas in the catchments was 35 % in North and 64 % in CC. The catchment size of CC was 40 ha, North was 40 ha and Ref-S was 24 ha. The Ref-S

catchment was a sub-catchment of North. All catchments were dominated by conifer trees, mainly spruce and pine. The bedrock was dominated by pegmatite with aplitic granite and aplite covered by well-drained till soils. Wetlands with organic rich peat were found in the valleys and along the streams.

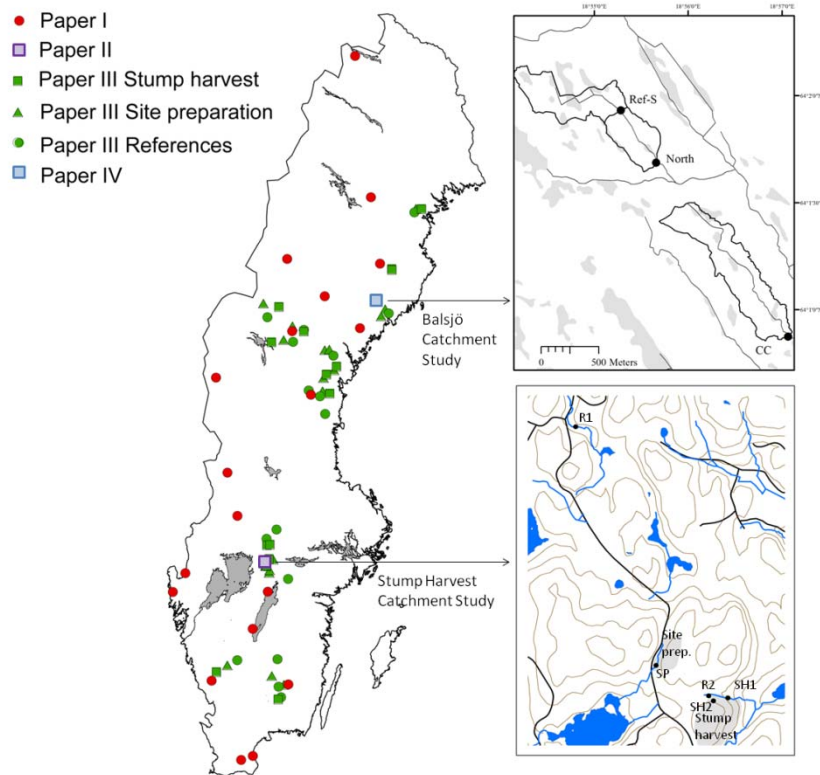


Figure 2. The location of the sample sites from all papers included in this thesis.





## 4 Methods

### 4.1 Sampling and chemical analyses

Water samples in the 19 watercourses which were monitored for trends in water chemistry during reference conditions (paper I) were collected throughout a ten year period, every second month from the summer of 2000. In the stump harvest catchment study (paper II) and the Balsjö catchment study (paper IV) the sampling was conducted every second week, and more frequently during high flow events. The synoptic sampling of stump harvested and site prepared sites all over Sweden (paper III) were done on two occasions, September 2009 and June 2010. The sampled water was, in all study sites (paper I-IV), analyzed for THg, MeHg, total organic carbon (TOC), total suspended solids (TSS), absorbance at 420 nm ( $Abs_{420}$ ) and other general chemistry variables. The concentrations of THg (paper I-IV) were detected by cold vapor atomic fluorescence spectroscopy after oxidation by BrCl and reduction to Hg (0) with SnCl<sub>2</sub> following the US EPA (Environmental Protection Agency) standards, method-EPA 1631 (2002). The analyses of THg were done at the Swedish Environmental Research Institute in paper I and at the Department of Applied Environmental Science at Stockholm University in paper II-IV. The concentrations of MeHg (paper II-IV) were detected by species-specific isotope dilution followed by mass spectrometry (Lambertsson & Björn, 2004) at the Department of Chemistry at Umeå University.

### 4.2 Discharge measurements

Discharge from the catchments in the stump harvest catchment study (paper II) and the Balsjö catchment study (paper IV) was measured using 90° V-notch weirs. Manual bi-weekly water level measurements and flow over a V-notch were used to calibrate hourly water level measurement by self-contained

capacitance loggers (Tru-Track) and pressure transducers (Druck). Furthermore, hourly discharge values were calculated by using the relationship in a rating curve of manual flow values versus manual water level measurements.

### 4.3 Data analyses and statistics

#### 4.3.1 Trend analyses

Paper I evaluated temporal trends of chemical variables using Seasonal-Kendall tests (Loftis *et al.*, 1991). The trends were quantified by their slope. This test evaluated if there was a continuous shift in the THg concentration and related variables over time. The Seasonal-Kendall is a non-parametric method which takes seasonal variation into account and is not sensitive to single extreme values.

#### 4.3.2 Flux calculations

Fluxes of various chemical variables were calculated in paper II and IV from daily discharge and bi-weekly concentrations. The daily discharge data were a mean of the hourly discharge data. The daily chemical concentrations were linearly interpolated from the analytical values sampled bi-weekly. During high flow episodes more frequent data were used for interpolating the daily concentrations.

#### 4.3.3 Randomized intervention analysis

Possible treatment effects in paper II and IV were evaluated by using Randomized Intervention Analysis (RIA) (Carpenter *et al.*, 1989). The RIA analyses determined if the mean (paper III) or median (paper IV) values of the difference in concentration between the catchments at each sample occasion changed significantly after treatment. The difference in exports of each parameter for each day was used when evaluating the loadings (paper IV). RIA simulates the distribution of the mean (paper II) or median (paper III) values by resampling the observed series and is therefore distribution-free. Instead of randomizing the observed values without restrictions as in the standard RIA method, the resampling of the observed values was done within the specified season in order to retain the seasonal variation in the data (Löfgren *et al.*, 2009). 2000 simulations were used in each RIA.

#### 4.3.4 Multivariate statistics

Multivariate methods were used in paper I-III to find major correlates for the THg and MeHg concentrations. Chemical variables and catchment information

variables (X) were used to explain the variance of THg or MeHg (Y) in partial least squares (PLS) regressions. PLS regression is a useful multivariate method for dealing with chemical variables which are linearly related to each other, as this method is robust against intercorrelations among X-variables (Wold *et al.*, 2001).

Another multivariate approach, multivariate analysis of variance (MANOVA), was used in paper III to test the influence of treatment (stump harvest and site preparation) on the THg and MeHg variation. This was tested in relation to categorical catchment properties that could influence the variation of these concentrations, such as the sample season, vegetation cover, soil category, latitude and the location of the catchment according to the highest coast line (HCL).



## 5 Results and Discussion

### 5.1 Forestry effects

#### 5.1.1 Stump harvest

In the stump harvest catchment study (paper II) neither the THg nor the MeHg concentrations increased after stump harvest. In fact, there was a significant decrease in THg concentrations by 11 % in the stump harvested (SH1) catchment relative to the reference (R2) (Figure 3). The MeHg concentrations decreased in both the stump harvested (SH1) and site prepared (SP) catchment relative to R2 by 15 % and 16 % respectively. The concentrations did not change significantly after stump harvest (SH1) as compared to site preparation (SP). Low concentrations of Hg in the soil (Allan *et al.*, 2009) and minimal soil disturbance due to frozen or snow covered soils (Sørensen *et al.*, 2009a) have been suggested to be a reason for only moderate, or non detectable, treatment effects after forest harvest in earlier studies. Neither of these explanations are valid for the lack of treatment effects after stump harvest and site preparation in these study catchments. The stump harvest and site preparation were carried out in a wet autumn/winter resulting in visible soil disturbance. In addition, the relatively high runoff concentrations of THg and MeHg from the catchments, including the references, suggests that the storage of Hg in the soil was high.

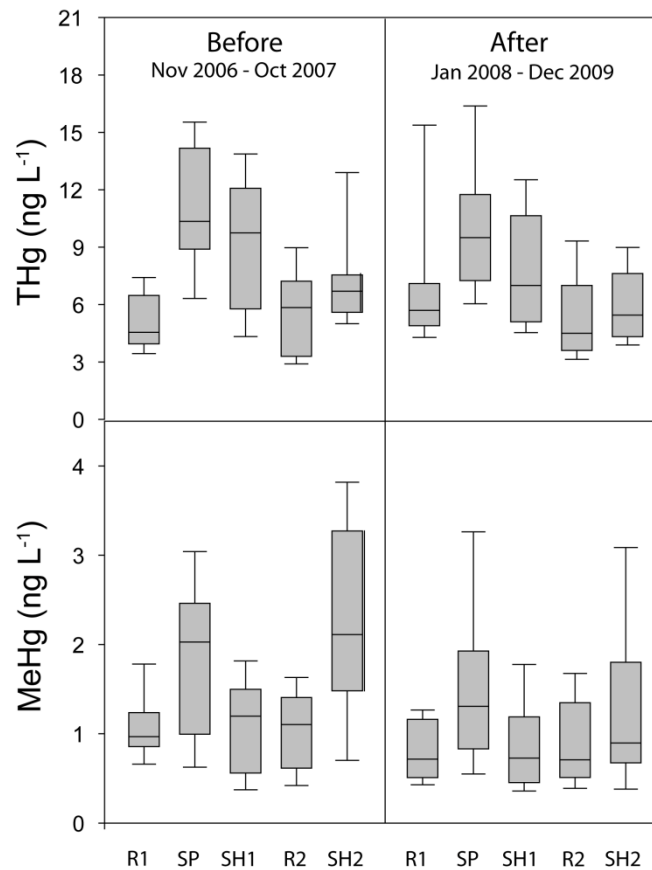


Figure 3. Boxplots (10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup> and 90<sup>th</sup> percentile) of the THg and MeHg concentrations in the stump harvested (SH1 and SH2), site prepared (SP) and the reference (R1 and R2) catchments before and after stump harvest and site preparation.

Stump harvest and site preparation did not cause any treatment effects in paper II, but the concentrations of THg and MeHg were generally higher in the treated areas than in the references both before and after stump harvest and site preparation (Figure 3). In the period before stump harvest and site preparation, the median THg concentrations in stump harvested (SH1) and site prepared (SP) catchments were almost 100 % higher than the median concentration in the two reference catchments, R1 and R2 (Wilcoxon-test,  $p < 0.05$ ). Also in the post-treatment period the THg concentrations were highest in the stump harvested (SH1) and site prepared (SP) catchments and lowest in one of the reference catchments (R2). The median concentrations of MeHg were highest in the site prepared catchment (SP) and the small ephemeral stream in the stump harvested area (SH2), both in the pre-treatment period and the post-

treatment period. The MeHg concentrations in SP and SH2 were around 69-118 % higher in the pre-treatment period and 40-85 % higher in the post-treatment compared to SH1 and the two reference catchments, R1 and R2. A PLS analysis indicated that the proportion of treated area in the catchments was one of the most important variables influencing the THg and MeHg concentrations before stump harvest and site preparation but not after. The higher concentrations of THg and MeHg in the treated areas, even when they were only logged and not subjected to stump harvest or site preparation, indicates that the logging operations may have already increased the THg and MeHg concentrations. This result is given strength by the PLS analyses which also highlighted the importance of treatment area in the PLS analyses before stump harvest and site preparation. The decrease in concentration after stump harvest and site preparation could be due to harvested areas still undergoing recovery from the logging in August 2006, one year prior to the stump harvest / site preparation treatments. This would imply that the logging effects overshadowed the impact from stump harvest and site preparation. However, the study was not setup to detect any effects of logging and it is not possible to evaluate the effects of the logging itself because the sampling started after the areas were logged.

An alternative explanation for the lack of treatment effects caused by stump harvest and site preparation in paper II is that there was a variation among sites in how they responded to forestry activities possibly owing to differences in the biogeochemical status of the soils and waters. This highlights why it is of such great importance to detect how the runoff of THg and MeHg is affected by different catchment variables, both in treated and untreated catchments.

In Paper III, no significant treatment effect from stump harvest or site preparation was detected either, when comparing the THg and MeHg runoff concentrations between the spatially distributed catchments subjected to stump harvest (SH), site preparation (SP) and no treatment at all (Ref), either in 2009 or in 2010 (nonparametric Wilcoxon-test,  $p>0.05$ ) (Figure 4). However, a treatment effect on potassium (K) and total nitrogen (TN) was identified, with highest concentrations in the SH catchments and lowest in the Ref catchments. This indicated that the stump harvest and site preparation had different effects on the surface water chemistry, albeit not on the THg and MeHg concentrations. Also, when the treated catchments were pooled, i.e. SH and SP into one group, the concentrations of THg and MeHg in the treated catchments were not significantly different from those in the Ref catchments, either in 2009 or in 2010 (Wilcoxon-test,  $p>0.05$ ). However, the variations in concentrations between the catchments were high, especially in the treated sites.

Although there was no significant difference in concentrations between the treated and untreated sites, a treatment effect on THg and MeHg concentrations became apparent (with SH and SP combined into one group) when the geographical location was taken into account in a MANOVA tests ( $p < 0.05$ ). Using MANOVA, variations in THg and MeHg were independent of vegetation and soil characteristics in the catchment but strongly dependent on the location according to the HCL and the latitudinal location. Location of sites in the southern cluster and below the HCL both had a positive influence on the THg and MeHg concentrations in the models. When just comparing the concentrations, the treatment effect might be over shadowed by the geographical variation in concentrations, mainly along the N-S gradient. Increased concentrations along the N-S gradient have also been indicated in earlier studies both in watercourses (Eklöf *et al.*, 2012a) and sediments (Munthe *et al.*, 2007).

A MANOVA test was performed on only the treated sites to identify possible differences in treatment effects caused by stump harvest and site preparation, while accounting for the background variation of THg and MeHg. When the Ref sites were removed from the analyses there was no significant effect of treatment on either THg or MeHg, indicating no difference in the magnitude of the treatment effect caused by stump harvest and site preparation. There was no correlation between the concentrations of THg and MeHg and the percentage of treated areas in the site prepared and stump harvested catchments. This could imply that the locations of the stream in direct connection with the treated area were of greater importance than the actual size of the treated area. Riparian zones (Bishop *et al.*, 1995) and newly formed discharge areas after logging (Skylberg *et al.*, 2009) have been pointed out as being of key importance for the Hg mobilization and methylation. Branfireun *et al.* (2005) also highlighted the role of wetlands as contributors to MeHg in aquatic ecosystems due to the rapid methylation of inorganic Hg observed in these ecosystems. Furthermore, Hintelmann *et al.* (2002) found that less than 1 % of Hg deposited in the watershed appeared in runoff within a year after deposition. The slow mobilization of Hg from the upper parts of the catchments, in addition to the possible rapid methylation in the wet near-stream zone would then suggest that the treatment effect in the upland recharge area is of minor importance compared with the effects in the discharge area, including the new discharge area formed after logging.



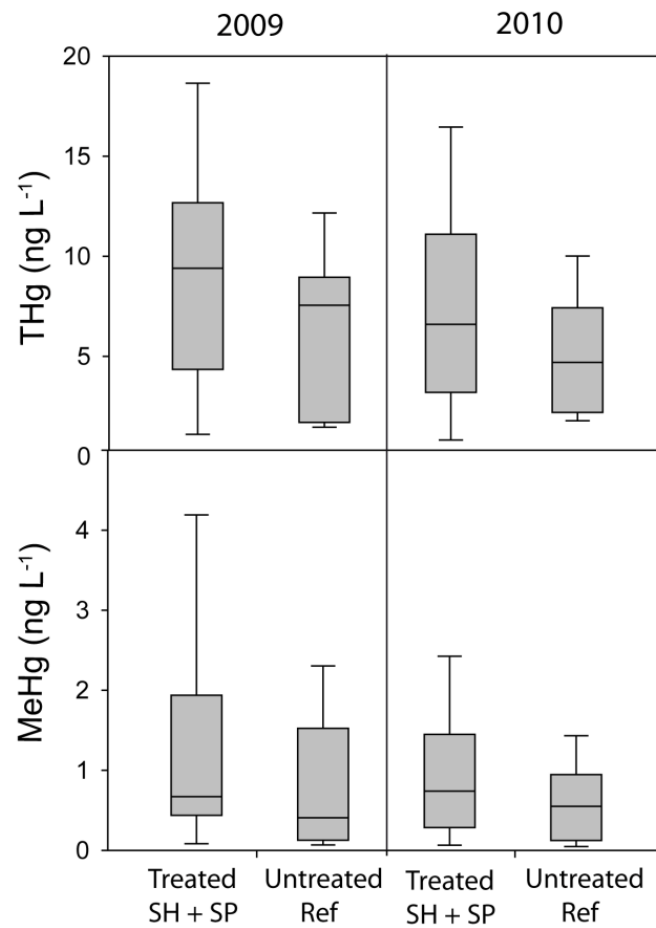


Figure 4. Boxplots (10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup> and 90<sup>th</sup> percentile) of the THg and MeHg runoff concentrations in paper III from the treated catchments subjected to stump harvest (SH) or site preparation (SP) and the reference catchments(Ref) in 2009 and 2010.

Neither of the stump harvest studies (paper II and III) detected any difference in the magnitude of treatment effects caused by stump harvest compared to traditional site preparation. As suggested in paper II, it could be that former logging of the areas led to higher concentrations in the treated sites compared with reference sites, and that the following disturbance caused by stump harvest and site preparation was of minor importance. The question of whether the logging or the following site preparation is the most sensitive part of the forestry operations were further studied in paper IV.

### 5.1.2 Site preparation versus logging

Contrary to the result in paper II, the results in paper IV, from the Balsjö catchment study, identified a more pronounced forestry effect on the THg concentrations caused by site preparation than from logging alone (Figure 5). After logging, the concentrations of THg increased slightly but not significantly in the treated catchments (CC and North) relative to the reference catchment (Ref-S). After site-preparation the concentrations of THg increased significantly by 16 % in both treated catchments relative to the concentrations in the reference catchment. The concentrations in the treated catchments also increased by 31 % (CC) and 27 % (North) relative to the reference when treatment effect from site preparation was added to that of logging by comparing the period after site preparation with the period before logging. A more pronounced effect after site preparation compared with after logging was also suggested in a study by Schelker *et al.* (2012) investigating the forestry effects on DOC in the same area.

The median MeHg concentrations did not increase significantly either after logging or site preparation when compared with the concentrations before the respective treatment. However, there was a significant increase by 49 % in the CC catchment after logging and site preparation together but not after logging only. This again highlights the importance of site preparation for possible treatment effects on Hg concentrations.

The natural variation of THg and MeHg in runoff water is large and the mobilization and methylation mechanisms are very complex. There is a possibility that the more pronounced effect of site preparation is also attributable to a delay in logging effects. It is possible that communities of methylation bacteria such as SRB, need some time to establish in newly formed discharge areas and flooded soils after logging. The fact that the logging was carried out in the winter on snow covered soils could also explain the relatively low concentration response from logging in this area (Sørensen *et al.*, 2009a). The site preparation was carried out in the early summer possibly causing more soil disturbance and compaction when compared with the winter logging on snow covered ground. The season and weather conditions during treatment might thereby be an important factor when considering possible treatment effects from forestry operations.

Although the treatment effects on the concentrations of THg and MeHg were stronger after site preparation than after logging, the exports of THg and MeHg increased more after logging compared to after site preparation. The 20-70 % increase of THg and MeHg exports after logging were strongly driven by the increased runoff after logging.

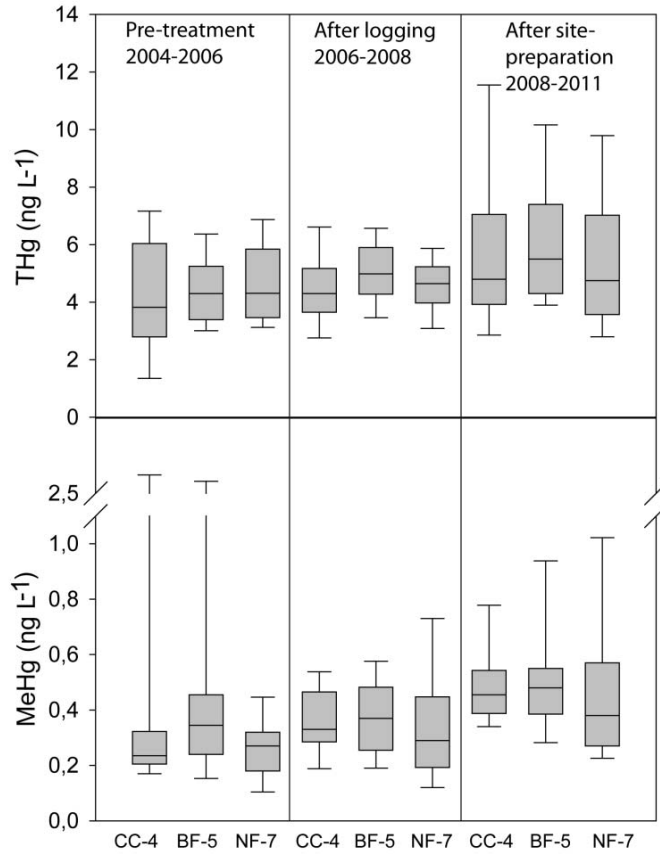


Figure 5. Boxplots (10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup> and 90<sup>th</sup> percentile) of the THg and MeHg runoff concentrations in the two logged and site prepared catchments, CC and North, as well as the reference catchment, Ref-S, in the pre-logging, after logging and after site preparation period.

### 5.1.3 The magnitude of treatment effects – comparisons with earlier studies

There is a great deal of variation not only in the actual concentrations of THg and MeHg, but also in the treatment effects among the studies included in this thesis, as well as in earlier forestry effect studies (Figure 6 and Table 1). Despite no forestry effects caused by stump harvest or site preparation in paper II, the concentrations of MeHg are remarkably high in all catchments, including the untreated references. Whereas the median concentrations of MeHg in the five catchments in paper II vary between 0.7-2.1 ng L<sup>-1</sup>, the median or mean values of the other studies did not range higher than 0.9 ng L<sup>-1</sup> which was the median concentration during one year in the site prepared

catchments in paper III. The highest THg concentrations were also found in the treated catchments in paper II and III, with median concentrations of up to 10 ng L<sup>-1</sup>. The concentrations of both THg and MeHg were lower in paper IV than in paper II and III, but the THg concentrations in paper IV were still around double those in paper I. The mean THg concentrations in the 19 reference watercourses in paper I ranged between 0.5-4.2 ng L<sup>-1</sup>. However, the catchments in paper I were generally much larger than those of the forestry effects studies (in paper II, III and IV), a factor which may have decreased the concentrations of DOC (Temnerud *et al.*, 2007) and possibly also THg.

Not only did the actual concentrations vary among studies, but also the magnitude in treatment effects. When the effect of site preparation was added to the effects of logging in paper IV, the magnitude of the treatment effect on the THg concentrations was around 30 %. This increase was similar to the median difference (around 10-34 %) in runoff concentrations from treated (stump harvested and site prepared) versus reference catchments in paper III. In addition, the treatment effects on MeHg were in the same range in these two studies. In Balsjö (paper IV) the MeHg concentrations increased by around 49 % after logging and site preparation, and in the spatial study (paper III) the concentrations were around 30-75 % higher in the treated catchments compared with the references. A more pronounced forestry effect on MeHg was identified by Skyllberg *et al.* (2009) in a spatial study in the north-east of Sweden where the MeHg concentrations more than doubled in catchments that were logged and site prepared (n=20) compared with untreated reference catchments (n=10). However, this forestry effect was only valid in catchments situated above the HCL. The latitudinal range was also about 7 times less in the study of Skyllberg *et al.* (2009) than in paper III, which may have reduced the background variation between the catchments and given a more pronounced forestry effect. The catchments in the study of Skyllberg *et al.* (2009) were also fully clear-cut and were generally smaller than those in paper III where the percentage of treated areas in the catchments ranged between 11 and 98 %, with a median of 40 % for the SH catchments and 34 % for the SP catchments. In Finland, Porvari *et al.* (2003) identified around 1.9 times higher MeHg concentrations after logging and site preparation than before logging. The loadings of THg and MeHg in the same study increased manifold in the 3 years following logging (Porvari *et al.*, 2003). A severe forestry effect on MeHg was also documented in south-west Sweden where forestry machinery driving disturbed the soil when passing a stream channel. The MeHg concentrations downstream of this disturbance increased by at least a factor of three (Munthe & Hultberg, 2004). The study of Munthe & Hultberg (2004), and the findings of paper IV, indicates that not only logging operations but also soil disturbance

from forestry machinery could result in significant forestry effects on Hg. Munthe & Hultberg (2004) suggested that increased MeHg concentrations were a consequence of changed water flow pathways that mobilized MeHg in the soil pool. On the other hand, the result in paper II indicated that soil disturbance caused by stump harvest and site preparation alone was not enough to result in any treatment effect on THg and MeHg in these areas. Instead, the logging alone might have had some effects on both THg and MeHg in these areas.

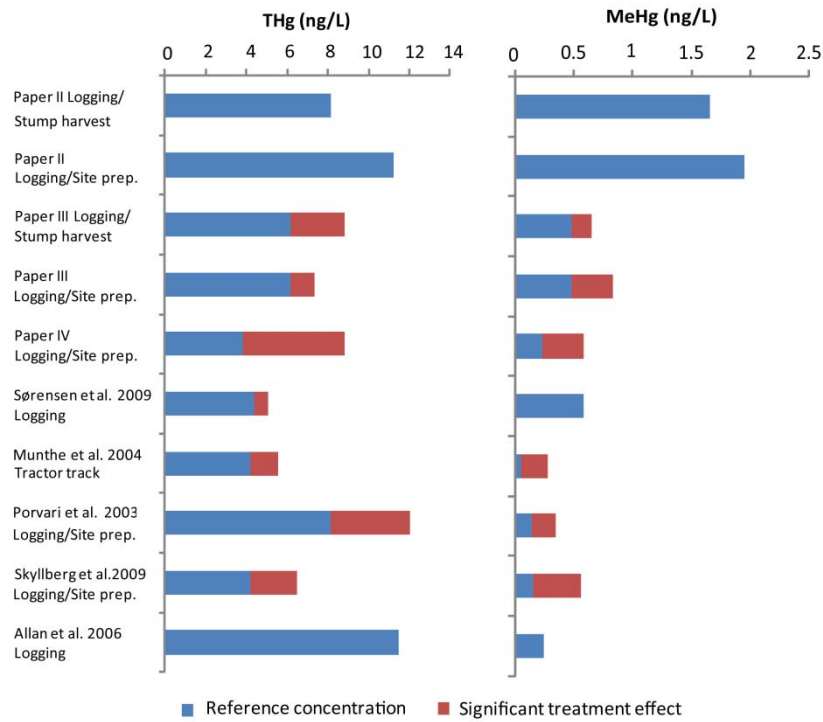


Figure 6. Reference concentrations and significant treatment effects, caused by different kinds of forestry activities, in various forestry impact studies in boreal catchments in Scandinavia and North America. Some values are calculated as mean and others as median, depending on what was used in the actual paper. The reference concentrations in paper II refer to the period when it was logged but not yet stump harvested or site prepared. The reference conditions in the other papers refer to the concentrations in untreated catchments.

## 5.2 Potential drivers for THg and MeHg stream concentrations

### 5.2.1 Organic carbon

It is well-known that OM accounts for much of the variation of THg in runoff, and strong correlations between the concentrations of THg and OM in surface waters have been reported in several studies (Shanley *et al.*, 2008; Ravichandran, 2004; Scherbatskoy *et al.*, 1998; Meili *et al.*, 1991). Paper I evaluated the THg-OM interactions in 19 catchments spread across Sweden during ten years of sampling. The fact that there was a strong correlation between THg and TOC, even when the whole dataset was used, indicates that the relationship between THg and organic matter exists independent of geographical variation in Hg deposition, geology, or any other factor evaluated in paper I. When compiling all the THg and TOC data from paper I-IV in Figure 7 the correlation of THg and TOC is actually stronger (Spearman's  $\rho=0.90$ ,  $p<0.0001$ ) than that when only using the data in paper I (Spearman's  $\rho=0.84$ ,  $p<0.0001$ ). However, this can be related to the larger range in concentrations when using data from all studies. The strong correlation of THg and TOC indicates that the differences in THg concentrations identified in section 5.1.3 are mainly driven by the variation in OM. Furthermore, the treatment effect on THg also often seems to be controlled by increased concentrations of OM. In paper III the ratio of THg and TOC was fairly constant between the treated sites and the references, suggesting that the slightly higher concentrations in the treated sites seem to be primarily controlled by concentrations of TOC during the two sampling occasions. In addition, when looking at other parts of the world the THg/TOC or DOC ratio seem to be fairly constant among sites. Shanley *et al.* (2008) found the THg/DOC ratio to be 0.24-0.37 ng mg<sup>-1</sup> in three watercourses across the US, and as high as 2.94 ng mg<sup>-1</sup> in the fourth watercourse. The 0.24 - 0.37 ng mg<sup>-1</sup> range in Shanley *et al.* (2008) is consistent with the 0.25-0.36 ng mg<sup>-1</sup> range (Table 1) of the studies in this thesis. Although within the range, the THg/TOC ratios in the treated catchments in paper II were slightly higher when compared with the references. Suboxic micro-environments in these areas might have favored the production of HS<sup>-</sup> which could increase the solubility and mobility of THg (Skylberg *et al.*, 2003). The THg/TOC ratio in the small headwater stream (SH2) which was heavily influenced by the treatment, were almost double that of the reference catchments (R1 and R2). This study did not take measurements that could prove any reducing conditions or a high production of sulphide, but the occasionally extreme concentrations of MeHg in SH2 indicate a high activity and abundance of SRB in this catchment. High particle concentrations in the treated catchments of paper II could also explain the high

THg/TOC ratios, since particles have been suggested to carry more Hg per unit organic C than the dissolved phase (Regnell *et al.*, 2009; Kolka *et al.*, 1999). However, while other studies pointed out the importance of particles for the export of Hg, the studies in this thesis found either no, or weak negative, correlations between THg and TSS.

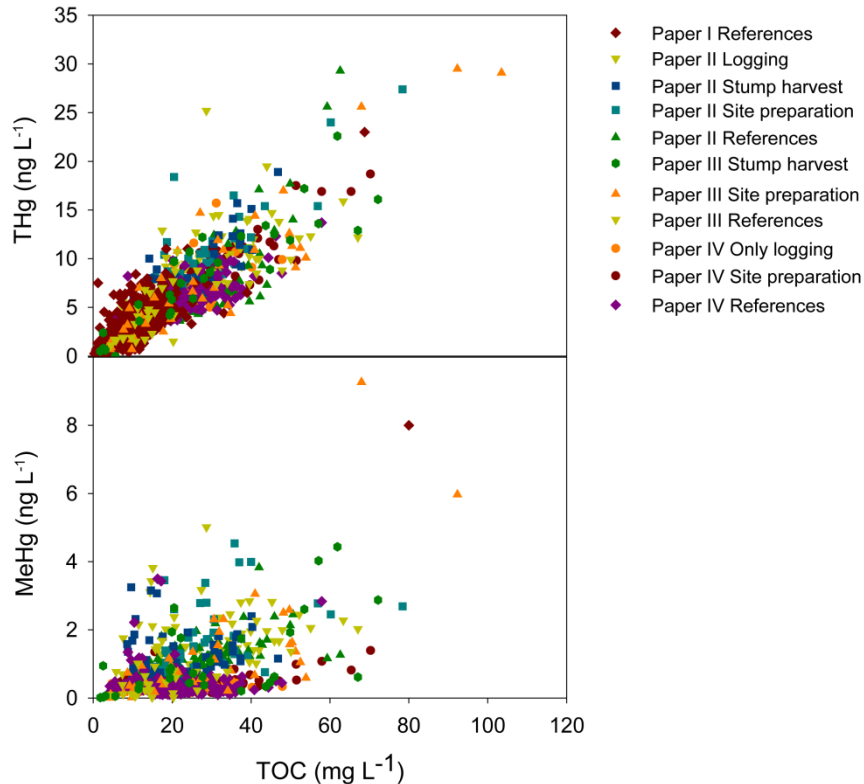


Figure 7. Relationship of THg-TOC, and MeHg-TOC using data from all sites included in this thesis. Data from all time periods and sites subjected to the same kind of treatment in each study were pooled.

The THg/TOC ratios were investigated in more detail in paper I. The results of paper I indicated that some fractions of TOC were more important for the mobilization of Hg than others. The THg concentrations in this study did not increase between 2000 and 2010, although TOC was increasing, and there was a corresponding decreasing trend for the THg/TOC ratio during this period. These results indicated that despite a strong correlation between THg and TOC, the increasing trends of TOC do not necessarily result in increasing THg concentrations. Furthermore, Abs<sub>420</sub> did not increase while TOC did, and there

were no trends in the THg/Abs<sub>420</sub> ratios during the period of 2000-2010. The fact that the trends of THg and Abs<sub>420</sub> coincided, but not the trends of THg and TOC, indicates that colored fractions of organic carbon, measured as Abs<sub>420</sub>, may be more important than other fractions of TOC in mobilizing THg. The only significant trend of increasing THg concentration from 2000-2010 also occurred in the same watercourse where there was a significant increasing trend of Abs<sub>420</sub>, namely Stormyrbäcken. Other studies have also found the more aromatic, hydrophobic and larger molecules of TOC, properties suggested to be identified along the absorbance spectra, to be better predictors for THg than TOC itself. Dittman *et al.* (2009) identified a stronger correlation between dissolved THg and absorbance at 254 nm (Abs<sub>254</sub>) ( $R^2 = 0.92$ ) than for THg and DOC ( $R^2 = 0.87$ ). They concluded that THg is, to a large extent, associated with the UV-absorbing fractions, measured as Abs<sub>254</sub>, of DOC. Burns *et al.* (2012) also identified specific absorbance at 254 nm (SUVA<sub>254</sub>) to be a better predictor for dissolved THg concentrations than DOC during the growing season in Fishing Brook in the north-eastern US.

Although there was a strong correlation between THg and TOC, the correlation between MeHg and TOC was much weaker (Spearman's  $\rho=0.36$ ,  $p<0.0001$ ). Factors other than the mobilization of OM seem to be of greater importance for the MeHg concentrations in runoff. Similar to the THg/TOC ratios, the MeHg/TOC ratios are highest in the treated catchments in stump harvested catchment study (paper II). This could again be an indication of a higher amount of reduced micro-environment in these areas compared with other study catchments.

Table 1. Median concentrations of THg (in  $ng L^{-1}$ ), MeHg (in  $ng L^{-1}$ ) and TOC (in  $mg L^{-1}$ ) as well as the median values of the ratios of THg/TOC and MeHg/TOC (in  $ng THg$  or  $MeHg / mg TOC$ ) from all studies included in the thesis. Data from all time periods and sites subjected to the same kind of treatment in each study are pooled.

Site	n	THg	MeHg	TOC	THg/TOC	MeHg/TOC
Paper I References	1094	2.1	-	7.8	0.29	-
Paper II Only logging	69	9.2	1.45	23.4	0.36	0.043
Paper II Stump harvest	80	6.0	0.86	16.8	0.34	0.040
Paper II Site preparation	48	9.5	1.34	24.7	0.36	0.056
Paper II References	219	5.3	0.83	21.4	0.25	0.039
Paper III Stump harvest	30	8.6	0.63	26.5	0.29	0.030
Paper III Site preparation	42	7.0	0.77	26.2	0.27	0.032
Paper III References	36	5.7	0.47	16.6	0.28	0.027
Paper IV Only logging	137	4.8	0.31	19.0	0.26	0.017
Paper IV Site preparation	143	6.2	0.43	22.6	0.28	0.018
Paper IV References	219	4.7	0.28	19.4	0.26	0.016



### 5.2.2 Hydrology and temperature

The concentrations of THg and TOC increased during high flow episodes both in paper II and IV (Figure 8 and 9). However, in paper II the temporal variation of THg and TOC were influenced both by flow and season (Figure 8), and the highest concentrations were actually found at low flow during the dry and warm summer months. Discharge was also one of the most important factors explaining the temporal variation of THg in the 19 watercourses in paper I. The positive correlation between THg and discharge, which has also been identified in other studies (e.g. Brigham *et al.*, 2009; Schuster *et al.*, 2008; Shanley *et al.*, 2008), was attributed to superficial flow paths during high flows through the organic carbon and Hg rich upper soil horizon (Bishop *et al.*, 1995).

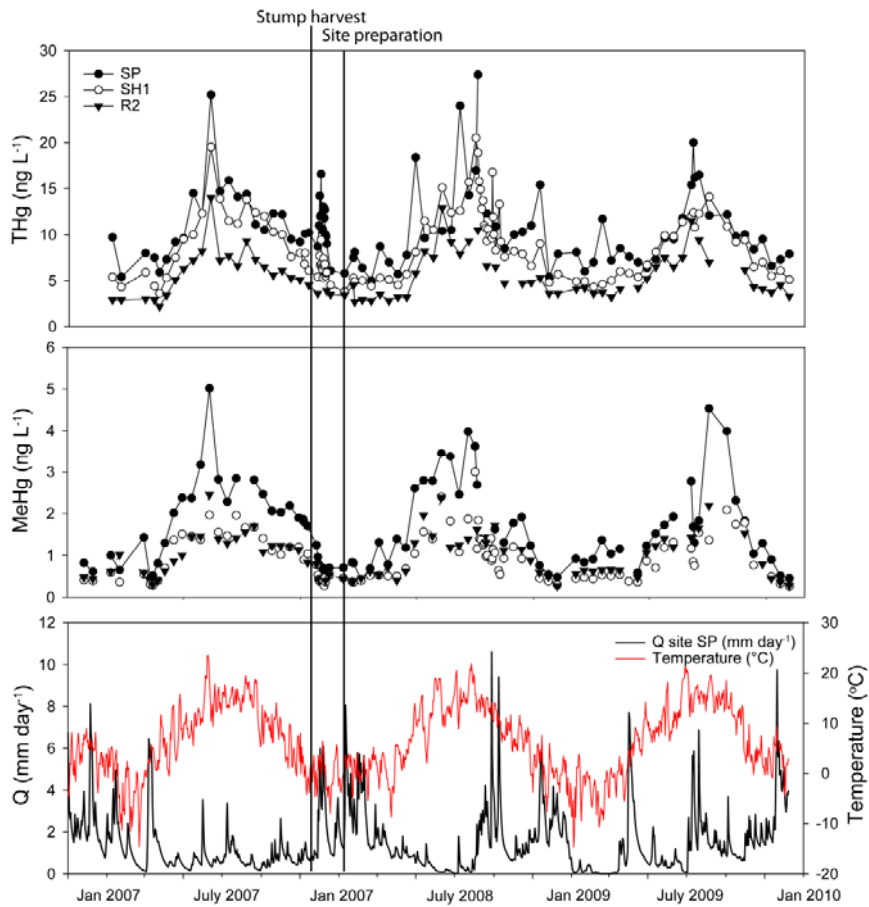


Figure 8. Time series of THg and MeHg concentrations as well as discharge and temperature from the stump harvested catchment study (paper II).

During high flow episodes in paper II, discharge not only increased THg concentrations, but also the THg/TOC ratio. In addition, there was a positive correlation between discharge and the temporal variation of the THg/TOC ratio in paper I. Fractions of TOC which have been suggested as stronger ligands for THg, such as hydrophobic acid fractions (HPOA) (Schuster *et al.*, 2008), have been found to increase with flow (Dittman *et al.*, 2009), possibly explaining the increasing THg/TOC ratios.

The influence of discharge on MeHg varies among sites in earlier studies. However, in this thesis MeHg and discharge were negatively correlated (paper II and IV). The concentrations of MeHg also peaked during summer in both paper II and IV (Figure 8 and 9) suggesting the importance of temperature for the net methylation of Hg.

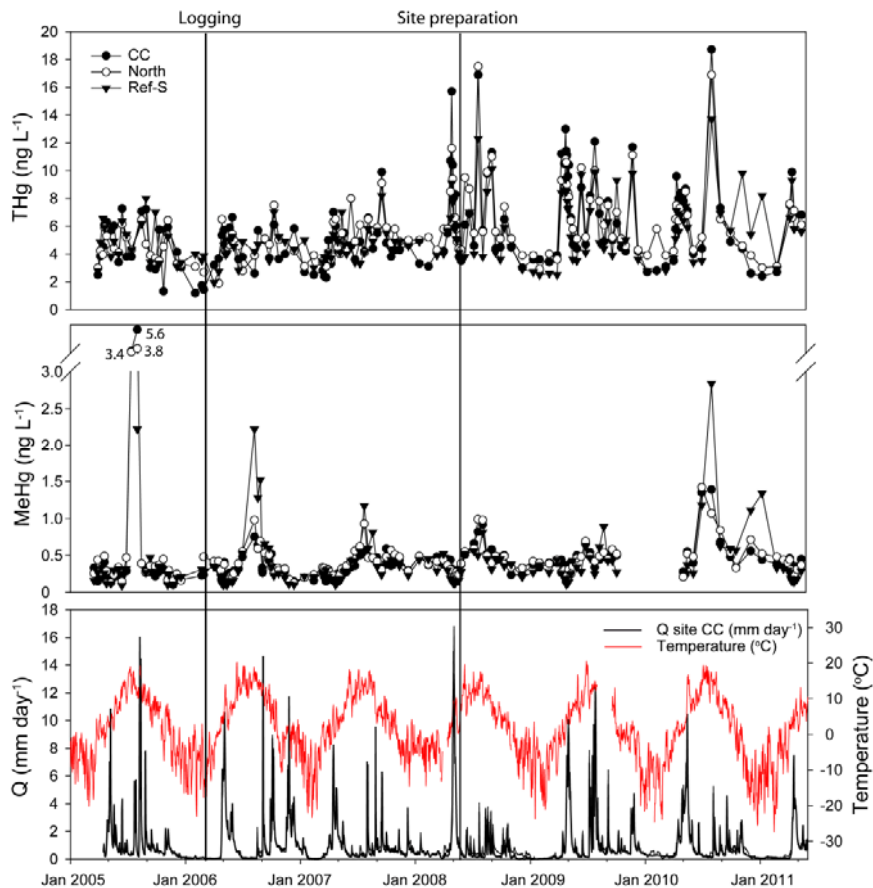


Figure 9. Time series of THg and MeHg concentrations as well as discharge and temperature from Balsjö catchment study (paper IV).

The influence of discharge on the THg concentrations, as well as temperature on the MeHg concentrations, implies that forestry activities influencing these factors should also influence THg and MeHg. In the Balsjö sites (paper IV) both discharge (Sørensen *et al.*, 2009b) and soil temperature (Schelker *et al.*, 2012) were found to increase after logging, but with just minor influence on the concentrations. The lack of treatment effect after logging in Balsjö was surprising and was possibly attributable to the minimal soil disturbance during the logging operations in winter harvesting conditions (Sørensen *et al.*, 2009a) as discussed earlier.



## 6 Conclusions and future perspectives

### ➤ **No differences in treatment effects caused by stump harvest compared to site preparation**

Although stump harvest was expected to cause more compaction and disturbance of the soils than traditional site preparation, no difference in treatment effect was identified between these two methods on THg and MeHg concentrations. However, a treatment effect on nitrogen and potassium was found in paper III, where concentrations were higher in the stump harvested catchments. This indicates that these forestry methods, although not affecting THg and MeHg concentrations, effect other aspects of surface water chemistry.

### ➤ **When and how the forestry operation are implemented might be more important than treatment type in some catchments**

The treatment effect on THg and MeHg caused by site preparation was more pronounced than that caused by logging in paper IV. However, the lack of treatment effect from stump harvest and site preparation in paper II, as well as the higher concentrations in the treated sites after logging only, suggests a more pronounced effect from logging than from stump harvest and site preparation in this study. The lack of logging effects in paper IV was also suggested to be a result of minimal soil disturbance during winter harvesting conditions. The season and weather conditions during the forestry operations were thereby suggested as an important factor influencing the magnitude of treatment effects.

➤ **Exports of THg and MeHg increased more after logging than after site preparation**

When considering the exports of THg and MeHg, the logging had a more pronounced effect than the site preparation. This was due to the increased runoff in the treated areas after logging.

➤ **Organic matter was strongly correlated to the THg concentrations and the THg/TOC ratio was similar among the study sites**

The similarity of the THg/TOC ratio among the study catchments included in this thesis (paper I-IV) suggests that the variation in THg concentrations is highly influenced by the variation in TOC. However, there are slightly higher THg/TOC ratios and higher MeHg/TOC ratios in some of the treated catchments (in paper II).

➤ **Abs<sub>420</sub> was a better proxy for THg than TOC itself**

Despite a strong correlation between THg and TOC, fractions of TOC, measured as Abs<sub>420</sub>, were found to be more important for Hg mobilization than other fractions of TOC.

*This thesis also raised some questions requiring further research:*

- What catchment factors are influencing the variation in sensitivity to forestry activities in boreal ecosystems?
- What are the drivers for the temporal variation of MeHg? Why are the MeHg concentrations negatively correlated to flow in some sites and positively in others? What are the processes behind the MeHg peak that appeared every summer in paper II and IV?
- How is the disturbance from forestry activities influencing the presence of methylation hotspots, and how does hydrology couple with the bacterial communities of methylators?
- How should we value the forestry effects on Hg and other water chemistry variables compared to other environmental costs such as effects on biota and soil C degradation? Furthermore, how should we value the environmental benefits gained by decreasing the use of fossil fuel due to increased biomass supply by stump harvest and intensified forestry, while accounting for environmental effects at a catchment level, such as effects on water quality?

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## Sammanfattning

Höga halter av kvicksilver (Hg) i fisk är ett stort problem i boreala sötvattens ekosystem. Skogsbruksaktiviteter har visat sig öka koncentrationer och belastningar av Hg till ytvatten. I denna avhandling utvärderas skogsbrukets effekter på avrinning av Hg efter stubbskörd, markberedning och den tidigare avverkningen, i ett antal försök på avrinningsområdesskala.

Stubbskörden ökade inte Hg koncentrationen i avrinnande vatten vid jämförelse med traditionell markberedning. Avsaknaden av en skogsbrukseffekt orsakad av stubbskörd samt markberedning i en av stubbskördsstudierna, riktade istället uppmärksamhet mot den tidigare avverkningen. Frågan om huruvida avverkningen är huvudorsaken till eventuella skogsbrukseffekter eller ej, i jämförelse med påverkan från den efterföljande markberedningen, undersöktes vidare i Balsjö försöksområde. I motsats till den tidigare nämnda stubbskördsstudien, ökade koncentrationerna av total Hg (THg) och metylkvicksilver (MeHg) med 30-40 % efter både avverkning och markberedning medan ingen signifikant skogsbrukseffekt gick att detektera efter enbart avverkning. Den större påverkan från markberedning än avverkning i Balsjö, skulle kunna orsakas av en kraftigare markstörning vid markberedningen som skedde under sommarförhållanden jämfört med den från avverkningen vilken genomfördes under vintern då ett snötäcke skyddade marken. Vilken årstid, samt vilka väderförhållanden, som råder då man brukar skogen, föreslås därför vara en möjlig faktor som kan påverka effekten av olika skogsbruksaktiviteter när det gäller Hg. Variationen i skogsbrukseffekter på Hg i denna avhandling, samt i tidigare studier, tyder på att avrinningsområdets känslighet för skogsbruk varierar. Denna variation skulle kunna orsakas av de olika biogeokemiska förhållanden som råder i mark och vatten i olika avrinningsområden. Det är därför mycket viktigt att utvärdera de faktorer som styr variationen av THg och MeHg koncentrationer i olika områden. Betydelsen av halter av totalt organisk kol (TOC) belystes genom starka

korrelationer mellan THg och TOC både inom avrinningsområden men också mellan avrinningsområden från alla de studier som ingår i denna avhandling. Flödet hade också en positiv påverkan, både på THg och TOC koncentrationerna, medan temperatur hade en positiv påverkan på MeHg koncentrationerna.

Denna avhandling föreslår att när och hur skogsbruk utförs är av betydelse för eventuella skogsbrukseffekter. Den identifierar även en variation i skogsbrukseffekter som föreslås bero på avrinningsområdets känslighet för skogsbruk. Något som bör följas upp med fortsatt forskning.

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