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Influence of Forest management on water quality and Hg dynamics – a synoptic research

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Abbreviations

DOC	**D**issolved **o**rganic **c**arbon
DOM	**D**issolved **o**rganic **m**atter
EC	**E**lectric **c**onductivity
EQS	**E**nvironmental **Q**uality **S**tandards
HCL	**H**ighest postglacial **C**oast**l**ine
IRB	**I**ron **r**educing **b**acteria
MeHg	**M**ethylmercury (**Hg**)
N_{tot}	total nitrogen
NOM	**N**atural **o**rganic **m**atter
PLS	**P**artial **L**east **S**quares
POC	**P**articulate **o**rganic **c**abon
P_{tot}	total phosphor
RGM	**R**eactive **g**aseous **m**ercury
SOM	**S**oil **o**rganic **m**atter
SRB	**S**ulfate **r**educing **b**acteria
STADEV	**Sta**ndard **dev**iation
THg	**T**otal inorganic mercury (**Hg**)
TOC	**T**otal **o**rganic **c**arbon
TSS	**T**otal **s**uspended **s**olids
VIP	**V**ariable **i**mportance in the **p**rojection

ABSTRACT

Forest management is hypothesized to increase the mercury (Hg) load towards aquatic systems. In this study a synoptic research was carried out assessing 55 sites across Sweden, whereby the sampling scheme was designed to compare reference (N = 18), stump harvested (N = 16) and site prepared (N = 21) areas. The influence of forest treatment irrespective the separation into stump harvest and site preparation on Hg export to surface water streams was evaluated with regard to water quality (TOC, suspended solids, TSS) and with special focus on Hg and MeHg levels. Furthermore, the parameters affecting THg and MeHg concentrations were determined.

Total phosphor (P_{tot}), total nitrogen (N_{tot}) and total organic carbon (TOC) concentrations were significantly higher in the treated areas compared to the reference sites ($p = 0.0465$, $p = 0.0251$ and $p = 0.0487$, respectively). THg revealed nearly significant higher concentration in the treated areas than in the reference site ($p = 0.077$). MeHg concentrations were not significantly differing between treated and reference areas, although a high standard deviation in the treated areas indicate that site specific catchment characteristics play an important role in the overall MeHg and THg mobilization.

The individual comparison of stump harvested and site prepared areas showed no statistical significant difference. This might indicate that in general the treatment methods did not differ regarding their effects of Hg mobilization as well as nutrient and ion leaching on surface water quality.

THg and MeHg correlated positive with TOC ($R^2 = 0.70$, $p < 0.0001$ and $R^2 = 0.48$, $p < 0.0001$). Furthermore, the quite strong significant correlation of THg and MeHg with absorption (unfiltered, 420 nm) that was $R^2 = 0.66$, $p < 0.0001$ and $R^2 = 0.60$, $p < 0.0001$, respectively, could favor the implementation of absorption measurement as a first estimate of Hg concentration in water.

This study could not confirm the indications in literature that forest harvesting is severalfold increasing THg and MeHg load to aquatic systems.

I INTRODUCTION

1. General Information

Heavy metals are ubiquitous contaminants of every industrial society (Padmavathiamma and Li, 2007). Unlike organic and even halogenated organic pollutants, toxic metal ions pose a serious environmental problem as they are non degradable (Rugh et al., 1996). The residence time of metals in the soil is in the magnitude of thousands of years (McGrath, 1987).

Mercury, named quicksilver by Aristotle, is present in two oxidation states in the environmental compartments (Hg^0 (reduced metallic) and Hg^{2+} (mercuric)) (Grigal, 2002; Clarkson, 1987). It is a transition metal showing exceptional physical and chemical properties. For example it is the only metal liquid at room temperatures, has a high surface tension, low electrical resistance and a high first ionization potential (241 kcal/mol) (Schroeder et al., 1991; Schroeder & Munthe, 1998). Due to its useful properties and manifold applications in industry its economic importance has grown (Schroeder & Munthe, 1998).

Mercury is entering the environment from a variety of natural and anthropogenic processes (point and non point sources) (Fitzgerald et al., 1998; Grigal, 2002). Human's interaction with nature due to e. g. mining activities and burning of fossil fuels has significantly elevated the atmospheric mercury (Hg) concentration since the start of industrialization. Long range atmospheric transport caused increased Hg deposition even in remote areas of Europe and North America exceeding natural concentrations and leading to the accumulation of Hg in the aquatic food chain (Fitzgerald et al., 1998). Hence, concentrations of Hg and especially its organometallic form MeHg (methylmercury) in fresh water fishes are often above the WHO recommendations (0.5 mg/kg) in Fennoscandia posing risks to the aquatic community as well as to humans (Hakason et al., 1990). The environmental quality standards (EQS) given by the European Union are more stringent and define the level at 20 µg/kg (Directive 2008/105/EC).

Most concern is focused on MeHg (methylmercury) as it is the most bioavailable species and can be concentrated more than a million-fold in living organisms (Schuster et al., 2008; Grigal, 2002). MeHg is a neurotoxin that is able to cross the blood-brain barrier and its ingestion via fishes is linked to e. g. the Minamata disease (Clarkson, 1987). However, neither the WHO nor the European Union separate the different levels of toxicity of mercury species (THg and MeHg) within their regulations and just refer to "mercury and its compounds" (Directive 2008/105/EC).

In boreal regions forestry is one of the dominant land uses. Elevated Hg concentrations in fishes in these regions are quite common due to various factors (Shanley & Bishop, in press). Several studies have revealed that forest disturbances might result in an increased THg and MeHg mobilization (Porvari et al., 2003; Munthe & Hultberg, 2004; Skyllberg et al., 2009). Porvari et al. (2003) assessed that clear-cutting and soil treatment significantly increases the mobility of THg and MeHg stored in forest soils. THg and MeHg concentrations increased significantly during 3 years after forest activities (logging, site preparation, replanting) from 8.13 ng/L and 0.15 ng/L to 12.02 ng/L and 0.35 ng/L, respectively. Skyllberg et al. (2009) found significantly elevated MeHg concentrations and MeHg/TOC ratios compared to reference sites in streams draining 0 – 4 year old clear cuts. Bishop et al. (2009)

suggested that 9 – 23 % of the mercury accumulated in fish in Swedish lakes could be attributed to forest activities. However, recent studies like the one of Sörensen et al. (2009) did not find the expected severalfold increase of Hg output to surface water streams after forest harvesting. This indicates the highly complex situation of mercury dynamics in relation to forest management. Furthermore, the findings of Sörensen et al. (2009) show that there is a need for increased research especially taking a broad spatial distribution of sampling sites into account in order to assess different site specific responses towards Hg mobilization. This kind of synoptic research, as carried out in this study, might help to understand the large variations of Hg output.

The export of THg is closely linked to hydrological effects of forest activities as well as the increased output of DOC (dissolved organic carbon). DOC is a major factor to control Hg mobilization and methylation and hence influences the Hg mobilization at the catchment level (Ravichandran, 2004). Besides, it is well known that logging of trees raises the water table and fluctuations in the water table between aerobe and anoxic conditions are likely to increase the overall methylation rate (Bishop et al., 2009).

However, the understanding of Hg behavior in terrestrial watershed and its subsequent release to aquatic systems is quite poor as it depends on a variety of complex interactions between biotic and abiotic processes (Grigal, 2002). For example specification of Hg^{2+} is very much depending on the pH, the strength of interaction with DOM, the concentration of DOM as well as the concentration of inorganic ligands (especially sulfide, S^{2-}) and the distribution between the solid and liquid phase (Haitzer et al., 2003).

Despite, the high uncertainties in measuring Hg fluxes and specification between the different environmental compartments the concern about the magnitude of the Hg problem and especially the contributions of forest activities are growing (Shanley & Bishop, in press; Grigal, 2002).

Forest management is not only affecting the Hg budget within a watershed but the water quality in general, e. g. by influencing nutrient cycling, temperature and total suspended solids (TSS). Forest harvest may lead to increased nutrient concentrations (P, N) due to reduced nutrient uptake by the terrestrial vegetation. This might increase the nutrient load to aquatic ecosystems for periods of 1 – 7 years for N and up to 10 years for base cations (Ca^{2+}, $Mg^{2+)}$ (Pike et al., 2009).

In this study the individual influence of site preparation and stump harvest on the water quality (e. g. TOC, suspended solids) with special focus on Hg and MeHg levels are assessed and compared. Furthermore, the influencing parameters on the Hg and MeHg concentrations will be determined. Upon our knowledge this is the first synoptic study that is carried out comparing 55 sampling sites with such a broad spatial distribution (latitude lowest – latitude highest).

2. Theoretical Background

2.1 Hg cycling in the environment

2.1.1 Input of Hg

Mercury is present in the atmosphere mostly as Hg^0 (relatively unreactive) and to a smaller portion as Hg^{2+} either as reactive gaseous Hg (RGM) or as particulate-phase Hg (Hg(p)). The spatial scale depends on the chemical and physical form of mercury and its rate of transformation among species. Elemental Hg is transported for several 10.000 km and has an average residence time in the atmosphere of 1 year. That is why nearly all of the atmospheric Hg is present in its reduced state (Hg^0). Hg^{2+} on the other hand is very reactive and is deposited within tens to a few hundreds of km (Schroeder & Munthe, 1998; Munthe et al., 2007)).

One of the most important characteristics differing from other metals found in the atmosphere is that Hg is able to be reemitted to the air after deposition and that its existence in the air occurs mostly in the vapor phase, not associated with aerosols (Schroeder & Munthe, 1998).

Atmospheric mercury enters the terrestrial and aquatic ecosystems via dry deposition, wet deposition in open areas (mostly Hg^{2+}) and wet deposition though forest canopy (thoughfall) (***Figure 1***). The deposition is much higher in forest areas due to the high amount of Hg attached on forest canopy and entering the soil by litterfall or thoughfall. According to Munthe et al. (2007) concentrations of Hg in wet precipitation (open deposition) are varying between 10 – 11 µg/m³ in southern Scandinavia and only 5 – 6 µg/m³ in the inland of northern Sweden (data from 1999 – 2002). This north-south gradient is strongly depended on the local precipitation amounts and emissions of mercury from central Europe.

Dry deposition occurs via the forest canopy’s foliar uptake (leaf stomata uptake of Hg^0) and is depending on the growing season (Rea et al., 2002; Miller et al., 2005). Further input processes of Hg to the terrestrial ecosystem involve dry deposition of RGM and Hg(p) on the external foliar surface, that is washed off by precipitation (throughfall) and forest litterfall (leaves, needles, branches) (Munthe et al., 2007). Grigal (2002) showed in his review that atmospheric deposition on forests is exceeding open precipitation by a factor of four.

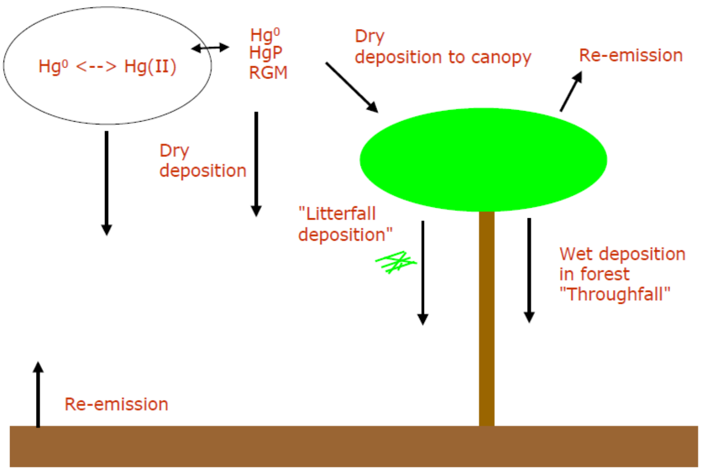

Figure 1: Atmospheric cycle of Hg in forested ecosystems (Munthe et al., 2007)

MeHg is assumed to mainly enter the terrestrial system via litterfall (Lee et al., 2000). According to the research of Lee et al. (2000) (Svartberget catchment, Sweden) the averaged annual input fluxes of THg are 7 g/km² (wet deposition), 15 g/km² (throughfall) and 17 g/km² (litterfall) compared to 0.08 g/km² (wet deposition), 0.17 g/km² (throughfall) and 0.3 g/km² (litterfall) for MeHg inputs. It can be noted that troughfall is as important as litterfall when it comes to the THg input, but litterfall is accounting for twice the input than troughfall when it comes to MeHg.

Most of the Hg deposited on the forest floor is in association with organic matter and accumulates in the soil (Munthe et al., 2007).

2.1.2 Output of Hg

As noted earlier the deposition and mobilization of Hg is closely linked to organic matter. Dissolved organic matter (DOM) is omnipresent in the aquatic and terrestrial environment and is known to bind metals, affecting their solubility and specification (Reuter & Perude, 1976). Hence, it is like a vehicle influencing the fate, transport, transformation (e. g. reduction) and bioavailability (e. g. methylation) of mercury. Hg most likely binds covalently to thiol (R-SH) and other sulfur containing groups within DOM. This complexation revealed the highest stability constant among other ligands (Ravichandran, 2004). Bishop et al. (1998) showed that the THg concentration declined from over 150 ng/L near the surface to about 20 ng/L at 50 cm. This gradient coincides with the decrease of DOC with soil depth.

The output of mercury from the terrestrial system is either via volatilization and/or solute transport (Grigal, 2002). The reduction of Hg^{2+} to Hg^0 occurs either biotic (microorganisms) or abiotic (photolysis, humic substances) and is very difficult to quantify. Hence, the estimates of the amount of mercury volatilized vary much and the error bars are large (Shanley & Bishop, in press). The reduction is influenced by the pH, concentrations of dissolved oxygen and chloride (Ravichandran, 2004). Especially, wetlands and areas next to the stream channels provide conditions for strongly reducing environments suitable for Hg volatilization (Grigal, 2002). It is assumed that volatilization is minor part compared to stream export of Hg (Krabbenhoft et al., 2005).

The export of THg via stream water is the dominant pathway in a lot of watersheds. THg and MeHg occur in dissolved and/or particulate form. Hurley et al. (1998) noted that landscape characteristics are found to control the Hg export to streams much more than Hg deposition. Features of the catchment that either release or accumulate DOC or POC (particulate organic carbon) are affecting the Hg mobility. The authors found that THg export from agriculture is more associated with particulate matter, whereas the THg export from forested watersheds (with wetlands) is dominated by the dissolved fraction. The export of particulate and dissolved THg is closely linked to high-flow events (e. g. storm, dam operation) (Hurley et al., 1998).

Wetlands with organic rich soil located next to streams have a much higher MeHg output than well drained forest or mineral soils (Bishop et al., 2009). Skyllberg et al. (2003) found that the ratio of MeHg/THg was decreasing from 1.2 – 17.2 % in peat soil close to the stream to 0.4 – 0.8 % in mineral soils further away from the stream. This is indicating that wetlands and riparian zones play an important role in the transformation process from THg to MeHg. Sörensen et al. (2009) showed a seasonal variety in MeHg concentrations peaking during summer low flow. The authors found no relationship between MeHg and TOC or suspended matter. This indicates that MeHg and TOC (DOC) on contrary to THg are not so strongly correlated and that the export of MeHg is probably more controlled by the net production rate (Shanley & Bishop, in press). The METAALLICUS study is investigating the mobilization of mercury with the help of isotope Hg (^{202}Hg). It was noted that the methylated Me^{202}Hg was more mobile than expected and was detected after 90 days outside the experimental plot (Banfireun et al., 2005). Grigal (2002) summarized in his review that THg and MeHg concentrations are highly variable in the soil solution with a MeHg/THg ratio ranging from about 0.15 to 15 %. Besides, MeHg being of great concern only a small portion of the available Hg (input, pools) is present as MeHg. On average about 4 % of THg flux is accounted to be MeHg. This is, however, an average on the bases of reviewed papers and the explanation for higher or lower fluxes of MeHg lie in catchment characteristics (Grigal, 2002)

The strong retention and hence the large pool of Hg in the soil is contributing to the uncertainty in the ongoing discussion whether industrial emission reduction have an immediate effect on the output of Hg from terrestrial systems (Shanley & Bishop, in press; Branfireun et al., 2005). Branfireun et al. (2005) (METAALLICUS) showed that experimentally applied ^{202}Hg is readily detectable (1 day after application) above the native pool. However, after 90 days the concentration of ^{202}Hg decreased implying increased sorption and/or volatilization. It was also found that “new” ^{202}Hg was converted into detectable concentrations of Me^{202}Hg and hence very fast enters the food chain.

The transport, fate and mobilization of Hg is a very complex process of biotic and abiotic factors, e. g. the catchment size, catchment topography, wetlands and possible disturbances (e. g. forest harvest) (Grigal, 2002). Hence, the chemistry of mercury is highly complex and this makes it difficult to predict its behavior and transport in the environment.

2.2 Hg methylation and demethylation

2.2.1 Hg methylation

The most dominant form of mercury in freshwater systems is Hg^{2+}, where as in >95 % of the mercury in fishes in the form of MeHg. Hence, the transformation process of inorganic mercury is linked to the bioaccumulation of mercury in the food chain and finally to the health risks for humans and wildlife (Ravichandran, 2004).

MeHg production is a cyclic and very dynamic process whereby Hg may be methylated and demethylated several times within a given system and the reactions are often taking place simultaneously. Methylation and demethylation are occurring in terrestrial as well as aquatic systems and are mediated by a variety of biotic and abiotic factors (Ullrich et al., 2001). Methylation rates are most likely controlled by the net methylation patterns as demethylation is thought to be less variable (Lambertsson & Nilsson, 2006). It is assumed that net methylation in the terrestrial watershed differs from those in the aquatic system regarding size (catchment vs. lake surface) and relative methylation strengths (e. g. wetlands) (Shanley & Bishop, in press).

The transformation of THg to MeHg occurs normally in semi-anoxic systems (e .g. riparian zones, sediments, water column). In the aquatic system mercury methylation occurs predominantly in the sediment and to a lesser extends in the water column (Furutani & Rudd, 1980). In terrestrial ecosystems wetland and peatland are the most important sources of MeHg (Skyllbert et al., 2003). Hydrologic factors within a wetland like the water flow, the residence time as well as the season of residence affect the production and transport of MeHg to the aquatic system (Grigal, 2002). Grigal (2002) documented an increase in MeHg concentration with increase of wetland area in the catchment.

DOM plays a very important role in the specification of Hg and hence influencing its volatilization rate and bioavailability (Ravichandran, 2004; Haitzer et al., 2003). A decrease in pH reduces the available sites for Hg binding (proton competition) and hence increases the bioavailability of Hg for methylating bacteria (Haitzer et al., 2003). Direct abiotic methylation by humic and fulvic acids (parts of DOM) is likely to be a minor factor compared to the biotic process but might be an important process in organic rich environments (Weber, 1993; Ullrich et al., 2001).

Methylation is dominantly a biotic process that may be enzymatic or non-enzymatic (Devereux et al., 1996; Ullrich, 2001). Obligate anaerobic sulfate reducing bacteria (SRB) are the primary methylators but recently the significant contribution of Iron reducing bacteria (IRB) has been shown (Devereux et al., 1996; Kerin et al., 2006). The methylation rate of SRB is largely controlled by sulfate (e- acceptor), high quality organic matter (e- donor), temperature and availability of THg (Drott et al., 2007). Hence, the methylation is not a simple factor of THg. Further environmental factors affecting the methylation are the bacterial activity and community structure, pH, redox conditions, and the presence of inorganic and organic complexing agents (e. g. formation of neutral HgS complexes). These parameters control net MeHg production and determine whether bacterial methylation or demethylation will dominate (Ullrich et al., 2001).

Hydrology is also very much influencing the methylation process by supplying solutes, influencing the redox condition and finally the transport of MeHg (Shanley & Bishop, in press). Besides, Hg methylation rates in terrestrial ecosystems are often limited by the availability of sulfate whereby sulfate is an unlimited source in marine sediments (Branfireun et al., 2003). However, high sulfate concentrations limit Hg methylation by the formation of less bioavailable Hg-S complexes (Benoit et al., 1999).

Drott et al., 2007 showed the importance of small neutral inorganic Hg-sulfide complexes in anoxic environments that are controlling the mercury uptake across the cell membrane of the SRB (passive diffusion mechanism). Furthermore this study highlighted the role of energy rich organic matter as e- donors for SRB. Sedlak & Ulrich (2009) demonstrated that the MeHg production in restored wetlands can be controlled by decreasing the bioavailability of inorganic Hg. In a laboratory study they found out that the addition of iron to sediment pore water decreased the sulfide concentrations by the formation of $FeS_{(s)}$ and hence decreased the pool of dissolved uncharged and bioavailable mercury complexes. The net MeHg production and flux to the surface water decreased by over 90 % when adding 720 g Fe/m^2 to the samples. They also noted that the transfer of inorganic Hg from the sediment to the surface water was not affected by iron addition. However, the influence of iron on Hg complexation as well as microbial activity (IRB) and therefore MeHg production need to be further assessed.

The terrestrial landscape is a significant store of Hg and is very much influenced by human activities which are on the other side affecting net methylation. This is especially important as it takes decades up to centuries until emission reduction will lead to a reduction in the Hg soil pool (Shanley & Bishop, in press).

The biological and chemical processes that control Hg methylation and bioaccumulation are highly complex and still poorly understood. Hence, further research is needed (Ullrich et al., 2001).

2.2.2 MeHg demethylation

Methylation is believed to be an accidentally process where as demethylation is regarded as a detoxification mechanism (Drott et al., 2007; Ullrich et al., 2001). In contrast to the methylation (primarily biotic) process demethylation is carried out both abotic and biotic. The redox potential plays an important role if the demethylation is carried out along the oxidative or reductive pathway (Lambertsson & Nielsson, 2006). Reductive demethylation is found to dominate in Hg contaminated aerobic waters whereby oxidative demethylation seems to occur mainly in unpolluted anoxic sediments (Lambertsson & Nielsson, 2006; Marvin-Dipasquale et al., 2000).

The reductive pathway is carried out by a variety of bacteria under aerobic and anaerobic conditions and is separated in the *mer*-operon and non-*mer*-operon mediated MeHg degradation (Lambertsson & Nielsson, 2006; Marvin-Dipasquale et al., 2000; Ruth et al., 1996). In the *mer*-operon mediated aerobic pathway (***Equation 1***) microbial volatilization is carried out encoding an organomercural lyase (*merB)* and an NADPH-dependent mercuric reductase (*merA*). *MerB* transforms organic mehtylmercury to less toxic Hg^{2+} (and methane) and *merA* reduces Hg^{2+} to the least toxic and volatile metallic Hg^0 (Rugh et al, 1996; Meagher, 2000). The *mer*-operon operated pathway can be seen schematically in ***Figure 2***.

$$CH_3Hg(I) \overset{MerB}{\rightarrow} Hg(II) \overset{MerA}{\rightarrow} Hg(0) \qquad \textbf{(1)}$$

In the anaerobic non-*mer*-mediated degradation process bacteria (e. g. SRB) form $(MeHg)_2S$ out of MeHg with microbial produced sulfide that decomposes to Me_2Hg and HgS. Me_2Hg is finally degraded to MeHg and methane (Baldi et al., 1993). Hence both reductive pathways are characterized to produce methane from MeHg.

The oxidative pathway is characterized by CO_2 and Hg^{2+} as an end-product of MeHg degradation (Oremland et al., 1991). The production of CO_2 defines the oxidative pathway where as methane and CO_2 might be formed in the reductive pathway (Oremland et al., 1991; Marvin-Dipasquale et al., 2000). The oxidative pathway with Hg^{2+} as end-product does not lead to a net elimination of Hg in contrast to the reductive pathway (Lambertsson & Nielsson, 2006).

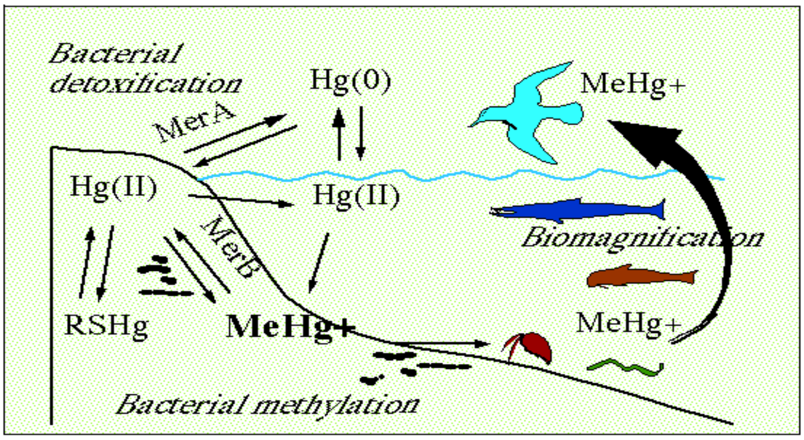

Figure 2: MeHg demethylation (detoxification) using the *mer*-operon reductive pathway and the following complex mercury cycle within the environment (source: http://rydberg.biology.colostate.edu/Phytoremediation/2003/Amy/chemicalpropertiesofmercury.html)

Abiotic MeHg degradation is occurring via DOC mediated photodegradation (photo reduction) (Ravichandran, 2004) and reaction with sulfide to Me_2Hg and HgS. Monperrus et al. (2007) used isotopically labeled mercury species $^{199}Hg(II)$ and $Me^{201}Hg$ to assess the demethylation and reduction of MeHg in coastal and marine surface waters of the Mediterranean Sea according to abiotic vs. biotic processes. MeHg in surface water was mainly photochemically degraded (6.4 – 24.5 % day^{-1}) and microbiological degradation accounted for 2.8 – 10.9 % day^{-1}. However, at the bottom of the euphotic zone biotic processes were the most significant ones.

2.3 Possible influence of forest activities on THg and MeHg mobilization and water quality

Sweden is one of the most forested countries in the world with about 60 % of its area forest covered (Skogstyrelsen, 2009). The northern part belongs to the boreal coniferous zone (*Pinus sylvestris L.)* where as the southern part belongs to the hemi-boreal forest zone (*Picea abies L*) (Ahti et al. 1968). 5/6 of the forest is classified as semi-natural (FAO, 2002) and 12 % of the Swedish export income are due to forest management (Skogstyrelsen, 2009). The forest sector is giving job to about 100,000 people and the forest is owned to 51 % by private people, to 25% by companies, and to 24 % by public forest owners and the state, respectively (Skogstyrelsen, 2009). From all owners, the companies tent to manage the forest more intensively.

Taking into account the importance of silviculture in Sweden and its wide spread anthropogenic influence on the catchment level the possible role of forest management in mercury mobilization from the terrestrial ecosystem needs to be carefully assessed. Forest composition, plant uptake rates, soil conditions and moisture, temperature regime, soil microbial activity and water fluxes might be changed as a result of forest management and hence altering the biogeochemical processes that control mercury mobilization and transport as well as nutrient leaching (Kreutzweiser et al., 2008).

Several studies revealed that logging activities may increase the DOC as well as the nitrogen (N) and phosphorus (P) availability and export to receiving water bodies, whereby P is affected to a lesser extent than N (Carmosinsi et al., 2003; Walley et al., 1996; Devito et al., 2000; Prepas et al., 2001; Kreutzweiser et al., 2008). Walley et al. (1996) documented a 2-fold increase of NO_3^- concentration in the upper soil layer after clear cutting in Saskatchewan. They suggested that the increase resulted from a reduced plant uptake due to clear cuting and from increased ammonium availability originating from the decay and mineralization of organic matter. Changes in forest properties (e. g. temperature, soil moisture) after logging activities may affect N uptake rates, microbial communities and mineralization, nitrification, denitrification and immobilization processes (Kreutzweiser et al., 2008). Increased P solubility, availability and mobility after logging resulting in increased P loads in boreal water bodies can lead to eutrophication problems (Prepas et al., 2001). However, Kreutzweiser et al. (2008) noted in their review that responses of the catchment after logging actives vary widely and are side specific depending on the soil types, stand and site conditions, hydrological connectivity, post-logging weather patterns and the type and timing of harvest activities.

Furthermore, several studies have documented increased THg and MeHg concentrations in streams after clear cutting (Porvari et al., 2003; Munthe & Hultberg, 2004; Skyllberg et al., 2009). Bishop et al. (2009) stated that forest activities (clear cuts, stump harvest, thinning) are associated to affect the DOC transport and therefore influences the Hg mobilization as Hg is associated with organic matter. The authors summarized the effects of forest management that might lead to an increased THg and MeHg transport: (i) raising of the ground water table (removal of trees), (ii) input of easily degradable organic matter, (iii) increasing of DOM in soils and runoff, (iv) increasing of inorganic sulfide concentrations due to changes in the redox potential (ground water raising, microbial activities) and (v) changing the input rate of THg and MeHg into surface waters.

Sörensen et al. (2009) found, in contrary to other studies, that forest harvest did not appear to change THg and MeHg concentration in that extent than in other studies. The lack of response was suggested to be related to little soil disturbances of the forest harvest achieved by best management practices. The soil was also protected by a thick snow pack and soil frost and the site seemed to be less sensitive to flow increases.

The above named differences in study results show that a closer and site specific look needs to be taken to assess the influence of forest activities on mercury mobilization and general water quality. Furthermore, a better understanding of the processes that control THg and MeHg concentrations at the catchment level is needed to develop proper guidelines for best management practices for forestry (Bishop et al., 2009).

Especially, stump harvest has become increasingly interesting due to higher prices on energy. Hofsten (2006) stated that an estimated 20 – 70 m³/ha of wood from conifer stumps (depending on the latitude) can be used for biofuel production in Sweden. However, before stump harvest techniques can be applied its potential contribution to the increase in THg and MeHg loads to surface water needs to be evaluated.

This study tries to contribute to reduce the large uncertainties in THg and MeHg output by assessing the influence of stump harvest and site preparation in a synoptic research.

II OBJECTIVES

The objectives of this study are to contribute to a better understanding of forest activities on the Hg and MeHg mobilization to the aquatic system. The objectives encountered in this study are: (i) to assess and compare the individual influence of site preparation and stump harvest on water quality (TOC, suspended solids, TSS) with special focus on Hg and MeHg levels, to evaluate the influence of treated areas irrespective their separation between stump harvested and preparation sites compared to reference areas and (ii) to determine the influencing parameter on THg and MeHg concentration.

III MATERIAL AND METHODS

1. Site description

Within a synoptic research a total of 55 sites where sampled across Sweden in autumn 2009 (***Figure 3***). In total 16 stump harvested sites, 21 preparation sites and 18 reference sites were sampled above and below the highest postglacial coastline (HCL). The sampling was done over a three weeks period during which the weather conditions were quite stable (e. g. no heavy rain occurred). The temperature was varying between 10 – 17 °C. The sample locations were dominated by birch (*Betula sp*.) and spruce (*Picea abies*) that formed mixed and coniferous forest within the catchments.

Figure 3: Sampling locations across Sweden

Information and location of stump harvested and site prepared areas was provided from forestry companies. The main treatment for site prepared areas was harrowing and scarification (light mechanical soil preparation). The stump harvested and site prepared sites were chosen according to following criteria: (i) the catchments should contain at least 20 % treated area, (ii) a stream should be passing through the treated area, (iii) the catchments should not be dominated by wetlands and (iv) the date of forest treatment was not longer than 2 years ago. However, the wetland area in certain catchments varied from 1.75 to 17.33 %. The stump harvest and preparation sites were averaged 27.98 ± 34.29 ha and 44.44 ± 56.36 ha, respectively. A majority of the sites were located above the HCL (14 of 16 for stump harvested sites and 13 of 21 for the site prepared sites).

The reference sites were selected a maximum of 50 km away from the stump harvested sites and contained mature forest stands (40 – 60 years old). A further criterion for the site selection was that the catchment should not be dominated by wetlands and that the range in stream discharge was approximately the same as that in the treated areas. The area of reference stands was in average 33.23 ± 25.35 ha. Four sites were situated below and fourteen sites above the HCL.

The HCL is situated between 230 and 260 m a.s.l (Granlund, 1943). Above the HCL glacial till is the predominant quaternary deposit. Up to a distance of 50 – 70 km from the present coastline the land was almost completely covered by sea water. Below the HCL fine material was reworked by wave action and valley bottoms as well as the coastal plains are covered with thick marine, fine grained sediments (clay and silt) (Jansson.& Ivarsson, 1994). The marine sediments below the HCL contain horizons of FeS and FeS_2 which are oxidized when e. g. the ground water table is lowered and hence iron and sulfate are released (Ivarsson and Karlsson, 1992).

2. Sampling and Chemical Analyses

Sampling took place during a three-week-period in autumn 2009. According to the clean-sampling protocols for THg 125 mL of stream water was collected in acid washed high density polyethylene (HDPE) bottles and kept in plastic bags. Water for MeHg was collected in disposable HDPE bottles (not acid washed) and water for general chemistry analyses was collected in disposable low density polyethylene (LDPE) bottles (not acid washed). To avoid contamination disposable gloves were used and each bottle was rinsed three times with the sample water before the bottle was filled to the top. After collecting the samples they were stored in a cooler until arriving at the laboratory mostly within 24 hours. THg was conserved with concentrated suprapur HNO_3.

Inorganic mercury (THg) was analyzed following the US EPA (Environmental Protection Agency) standards, method-EPA 1631 (U.S.E.P., 2002). The trace level concentrations of MeHg were detected by species-specific isotope dilution (SSID) followed by GC-ICP-MS analyses after a method of Lambertsson & Björn (2004).

The general chemistry analyses, including e. g. TOC, total phosphor (P_{tot}), total nitrogen (N_{tot}), electric conductivity (EC), total suspended solids (TSS), absorption (420 nm), Fe_{tot} and base cations (e. g. Mg^{2+}, Ca^{2+}), was carried out at the accredited (SWEDAC) laboratory of the Department of Aquatic Science and Assessment of the Swedish University of Agricultural Science (Department of Aquatic Science and Assessment, 2010).

3. GIS analyses

The identification of sampling sites was done in GIS, in co-operation with forest companies. However, this thesis did not involve the pre-work with finding the sample sites.

In ArcGIS 9.3 (ESRI) the catchments of the 55 sampled streams were delineated. Furthermore, the catchments sizes, the size of treated as well as reference areas within the catchment, and the percentage of wetland areas within the catchments were determined. GIS analysis was also used to determine the sites above and below the HCL.

4. Statistical analyses

The sampling scheme was divided into stump harvested sites (N = 16), preparation sites (N = 21) and reference sites (N = 18). Furthermore, the sites were differentiated according to their location above (stump harvest N = 14, site preparation N = 13 and reference N = 14) and below (stump harvest N = 2, site preparation N = 8, reference N = 4) the Highest Postglacial Coastline (HCL). Quality check of the analytical data was done by comparing the residues of THg and MeHg correlation with TOC. Values with residuals higher than three times (THg) and eight times (MeHg) the standard deviation were undergoing a manual verification.

Two values of MeHg for site R180 (stump harvest) and M 100 (site preparation) were excluded from the dataset as the values were exceptional high and were not fitting to the field observations (small stream in R 180 with turbulent water and for site M 100 the MeHg value (11.74 ng/L) was nearly double that of the THg (7 ng/L)).

Statistical analysis was carried out in JMP 8 (SAS). Regression analyses was done by a bivariant analyses using the coefficient of determination (R^2) and the significance of the regression (F-test, $p<0.05$).

Statistical analyses of the different sample groups (reference, site preparation and stump harvested sites) was done with one-way analyses of variance (ANOVA) and was based to test the null-hypothesis that subsets of the data were part of the same population (no significant differences). The null-hypothesis was rejected when ANOVA revealed a significant difference ($p<0.05$; right-tailed F-test). The significant differences between two sample groups (reference and treated sites) were also assessed with variance analysis and if revealed significant ($p<0.05$) a t-test (assumption: different variances) was done.

Partial Least Squares (PLS) regressions (Simca-P 11.5) was used to find fundamental relations between two data matrices (X (predictors) and Y (responses)) by a linear multivariate model ($Y = f(X)$). PLS is a generalization of multiple linear regression (MLR) but has the advantage to analyze correlated, noisy and numerous X-variables. In this study the influence of the multivariate dataset on THg (Y) and MeHg (Y) were assessed (Wold et al., 2001; Amaral & Ferreira, 2005).

To avoid the risk of “over-fitting” (good fit with little or no predictive power) cross-validation (CV) is used to test the predictive significance. The model strength is given by R^2 (goodness of fit) and Q^2 (cross-validated R^2; goodness of prediction) (Wold et al., 2001). Chin (1998) classified the goodness of fit (R^2) above 0.67 as substantial, above 0.33 as average, above 0.19 as week and below 0.19 as not relevant. Furthermore, the goodness of prediction (Q^2) should be as close as possible to R^2 and above 0.

The importance of individual variables is given by the variable importance in the projection (VIP). The VIP value is a summary of importance of the X matrix on the Y matrix (Wold et al., 2001). VIP values above 1 have a significant influence on the model and are most relevant for explaining the variation of Y (Amaral & Ferreira, 2005).

IV RESULTS AND DISCUSSION

1. Stream water chemistry above and below the highest postglacial coastline (HCL)

The objective of sampling sites above (N = 41) and below (N = 14) the HCL was to study the influence of the postglacial FeS (pyrite) deposits on the mobilization of THg and MeHg production. ***Table 1*** shows the results of the statistical analyses (mean, standard deviation (STADEV), ANOVA F-test p-value) irrespective their status as treated or reference areas.

Table 1: Stream water chemistry of reference and treated sites above and below the HCL with statistical results (mean, standard deviation (STADEV), ANOVA F-test p-value)

	Over HCL		**Under HCL**
Parameter	*Mean ± STADEV*	*p-value*	*Mean ± STADEV*
THg [ng/L]	8.23 ± 6.37	0.62	9.16 ± 5.12
MeHg [ng/L]	1.39 ± 1.82	0.44	0.99 ± 1.14
Alkalinity [meq/]	0.31 ± 0.11	0.28	0.007 ± 0.19
Ca [meq/L]	0.433 ± 0.85	0.27	0.18 ± 0.13
Mg [meq/L]	0.09 ± 0.06	0.068	0.065 ± 0.03
Na [meq/L]	0.13 ± 0.07	0.056	0.09 ± 0.05
EC [mS/m]	6.81 ± 7.84	0.102	3.29 ± 1.16
K [meq/L]	0.02± 0.02	0.078	0.01 ± 0.006
Fe [mg/L]	1.91 ± 2.59	0.56	1.48 ± 1.48
Mn [µg/L]	132.81 ± 264.29	0.79	68.69 ± 69.08
Al [µg/L]	497.07 ± 395.12	0.098	705.00 ± 407.77
Cl [meq/L]	*0.09 ± 0.07*	*0.013**	*0.03 ± 0.03*
F [mg/L]	0.12 ± 0.06	0.99	0.11 ± 0.04
SO_4 [meq/L]	0.07 ± 0.11	0.11	0.03 ± 0.01
∑anions [meq/L]	0.55 ± 0.97	0.19	0.18 ± 0.13
∑cations [meq/L]	0.71 ± 0.89	0.24	0.41 ± 0.20
NH_4-N [µg/L]	42.37 ± 71.62	0.79	49.71 ± 127.7
P_{tot} [µg/L]	31.27 ± 31.43	0.61	26.57 ± 25.03
N_{tot} [µg/L]	932.42 ± 750.62	0.52	793.71 ± 522.76
NO_2+NO_3 [µg/L]	182.96 ± 518.39	0.28	30.43 ± 55.86
TOC [mg/L]	29.26 ± 19.96	0.40	34.26 ± 16.42
Si [mg/L]	3.76 ± 1.09	0.057	4.37 ± 0.76
TSS [mg/L]	9.09 ± 16.97	0.50	5.93 ±6.34
Absorption (unfiltered)	0.67 ± 0.61	0.99	0.67 ± 0.40
Absorption (filtered)	0.57 ± 0.51	0.12	0.63 ± 0.38
THg/TOC	2.84e-7 ± 1.32e-7	0.99	2.84e-7 ± 1.23e-7
MeHg/TOC	3.9e-8 ±3.33e-8	0.15	2.52e-8 ± 1.74e-8
Fe/TOC	0.06 ± 0.07	0.31	0.04 ± 0.03
MeHg/THg	0.13 ± 0.10	0.37	0.10 ± 0.72

The only significant difference between the chemical parameters was given for Cl^- (F-test: p=0.0127; t-test: p=0.0006) (***Figure 4***), quite surprisingly, with higher concentrations above the HCL. According to Hultberg (1985) the concentration of Cl^- as well as Na^+ are ususally higher below the coastline as higher concentrations of sea salt were deposited. Gustafsson & Larsson (2000) studied the Cl^- deposition from the sea (Sea salt aerosols). They found a general decrease of chloride bulk deposition from the west to the east of southern Sweden. The deposition was highest in the period from January until March (1st quarter). However, the deposition was depending on the year and season, respectively.

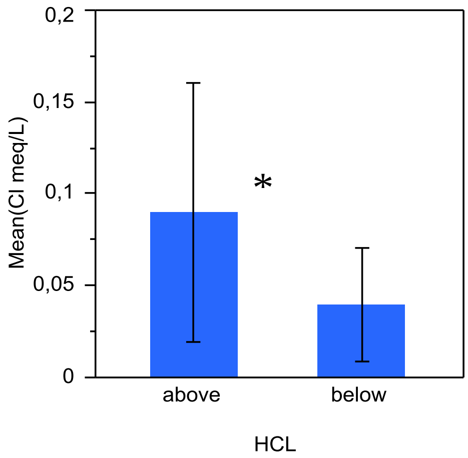

Figure 4: significant difference between mean Cl-concentration above and below the HCL (F-test: p=0.0127; t-test: p=0.0006)

The differences in nitrite and nitrate concentration above (182.96 ± 518.39 µg/L) and below (30.43 ± 55.86 µg/L) the coastline, although not significant due to a very high standard deviation, may be related to the properties of the till deposits above the HCL. Hendry et al. (1984) found an inverse relationship between the nitrate and the ammonium (NH_4^+-N) concentrations in till. The authors referred the increased nitrate concentration to the oxidation of exchangeable ammonium by nitrifying bacteria.

Generally speaking the concentrations of ions are higher above than below the coastline, which is confirmed by a higher electric conductivity (EC) as well as a higher sum of anions and cations (***Table 1***).

The p-values (F-test) for Mg^{2+} (0.068), Na^+ (0.056), K^+ (0.078), Al^{3+} (0.098), and Si (0.057) were nearly significant with Mg^{2+}, K^+ and Na^+ having higher concentration above the coastline and with higher levels of Al^{3+} and Si below the coastline. Silica (Si) is the most common element in the earth's crust (up to 90 % of the continental crust). Clay minerals (secondary clay) are mainly found below the HCL and are formed by weathering of other silicates (Ranka et al., 2004). The high Si content in the clay fraction could be a reason for the higher concentration below the HCL (***Table 1***).

This study found also higher Al-concentration under the HCL (***Table 1***). This could be explained with Al^{3+} being a major constitutive of clay. Especially, illite $(K,H_2O)_2Si_8(Al,Mg,Fe)_{4,6}O_{20}(OH)_4)$ is very common throughout Sweden and ion exchange is constantly happening (mainly Si^{4+} is exchanged with Al^{3+}) (Ranka et al., 2004). Acidification of the soil due to acid rain and subsequent release of Al-ions would be also plausible as coastal areas (below the HCL) receive higher amounts of precipitation (Munthe et al., 2007). However, contrary to this hypothesis the other base cations like Mg^{2+} and Ca^{2+} are higher above the coastline. Furthermore, Nilsson & Bergkvist (1983) stated that the Al^{3+}-concentrations depend very much on the vegetations as for the same type of podzol soil (Sweden) the concentrations were 260 µmole/L and 60 µmole/L for spruce and beach stands, respectively. They also found a very close relationship between Al- and C-dynamics ($Al_{organic}$). DOC in the form of fulvic acids affects the release of aluminum via complex formation. Higher TOC concentration under the HCL might explain therefore the elevated Al-concentrations. Another possibility to release aluminum is the so called sea salt effect, where Na^+ substitutes for hydrogen and aluminum on soil particles causing a subsequent release of these ions to surface waters (Hindar et al., 1995).

Ion exchange is one of the factors determining the Ca^{2+} and Mg^{2+} levels in the soil. Other factors are probably weathering and competition with other ions (e. g. Al^{3+}) (Nilsson & Bergkvist, 1983). Kerkes et al. (1986) stated that lakes with glacial till as bedrock on their catchment have higher Mg^{2+} and Ca^{2+} concentrations. This is also confirming the results of this study having higher Mg^{2+} and Ca^{2+}-concentrations above the HCL. Furthermore, a higher concentration of base cations (Mg^{2+}, Ca^{2+}, K^+) is likely to imply a higher alkalinity (***Figure 1)***. Low base cations concentrations might lead to an acidification of the soil with subsequent aluminum release, because of a depletion of the buffering capacity of the soil (Likens et al., 1996). This might be also a possible explanation for the higher Al^{3+} concentration below the HCL.

The alkalinity is the acid neutralizing capacity of a water body and is probably resulting from chemical weathering of substrates and ion exchange reactions in the terrestrial ecosystem. Central northern Sweden (particularly the coastal zone) is one of the most acidified regions showing low pH and alkalinity and comparatively high sulfate and aluminum concentrations (***Table 1***) (Monitor, 1991; Jansson & Ivarsson, 1994). The results of this study, however, are not in agreement with the assumed higher sulfate concentrations below the coastline due to the deposition of marine sediments (FeS and FeS_2) (not significant) noted in other studies (e. g. Skyllberg et al., 2009). The high standard deviation of the sulfate concentration above the HCL indicates that the catchment characteristics for the sulfate mobilization were very diverse.

Both sulfate and MeHg concentrations were higher above the HCL (***Table 1***). Westin (2008) and Skyllberg et al. (2009) found also higher MeHg concentrations above the HCL. The authors observed a significantly positive correlation between MeHg and Fe/DOC. Therefore it could be speculated that top soils changing from oxic to Fe^{3+} reducing conditions were of importance above the HCL (Skyllberg et al., 2009). This hypothesis was supported in this study by higher Fe concentration and a higher Fe/TOC ratio above the HCL. Furthermore, it might indicate that IRB play a more important role than previously estimated.

The very high standard deviation of MeHg might lead to the conclusion that the properties of the 55 catchments above and below the HCL were differing regarding e. g regarding soil properties, hydrological characteristics and wetland area.

One explanation for the unexpected results regarding e. g. MeHg, SO_4^{2-} and Cl^- is that the sampling scheme of this study was not preliminary designed to evaluate the differences below and above the HCL. Therefore, the streams sampled in this study showed a larger variability regarding e. g. stream sizes. Furthermore, many sampling points and their respective catchments were on the borderline either above or below the HCL and is it questionable if the resolution of the GIS layer was sufficient to assess these.

2. Treatment effects on water quality with respect to THg and MeHg concentrations

The different effects of forest treatment irrespective the differentiation of site preparation or stump harvest on the stream water quality can be seen in ***Table 2***.

Table 2: Mean value and standard deviation of all stream water chemistry variables in the treated and untreated areas, as well as the p-value for the F-test (ANOVA) between the treated and untreated areas.

	Reference Area		**Treated Area**
Parameter	*Mean ± STADEV*	*p-value*	*Mean ± STADEV*
pH	6.05 ± 0.97	0.25	5.71 ± 1.02
THg [ng/L]	6.43 ± 3.87	0.077	9.52 ± 6.69
MeHg [ng/L]	0.79 ± 0.86	0.14	1.51 ± 1.90
Alkalinity [meq/]	0.26 ± 0.44	0.92	0.24 ± 0.84
Ca [meq/L]	0.34 ± 0.45	0.85	0.38 ± 0.86
Mg [meq/L]	0.11 ± 0.09	0.15	0.08 ± 0.04
Na [meq/L]	0.12 ± 0.07	0.72	0.12 ± 0.07
EC [mS/m]	5.69 ± 4.39	0.87	6.02 ± 7.95
K [meq/L]	0.01± 0.02	0.15	0.02 ± 0.02
Fe [mg/L]	1.71 ± 2.16	0.85	1.84 ± 2.46
Mn [µg/L]	82.5 ± 106.2	0.45	133.02 ± 272.657
Al [µg/L]	497.39 ± 373.16	0.37	584.35 ± 420.2
Cl [meq/L]	0.08 ± 0.06	0.90	0.08± 0.07
F [mg/L]	0.10 ± 0.05	0.63	0.11 ± 0.05
SO_4 [meq/L]	0.07 ± 0.10	0.79	0.06 ± 0.10
∑anions [meq/L]	0.41 ± 0.49	0.77	0.49 ± 1.01
∑cations [meq/L]	0.64 ± 0.49	0.98	0.63 ± 0.90
NH_4-N [µg/L]	30.12 ± 71.88	0.41	51.08 ± 94.98
P_{tot} [µg/L]	*18.67 ± 17.40*	*0.0465**	*35.62 ± 33.02*
N_{tot} [µg/L]	*597.94± 364.33*	*0.0251**	*1042.65 ± 775.31*
NO_2+NO_3 [µg/L]	34.00± 42.42	0.21	197. 73± 544.609
TOC [mg/L]	*23.23 ± 13.72*	*0.0487**	*34.06 ± 20.47*
Si [mg/L]	4.12 ± 0.98	0.19	3.79 ± 3.79
TSS [mg/L]	6.45 ± 8.33	0.54	9.17 ± 17.39
Absorption (unfiltered)	0.51 ± 0.53	0.17	0.74 ± 0.57
Absorption (filtered)	0.45 ± 0.42	0.11	0.66 ± 0.49
THg/TOC	2.86e-7 ± 1.28e-7	0.94	2.83e-7 ± 1.31e-7
MeHg/TOC	2.89e-8 ± 2.37e-8	0.29	3.84e-8 ± 3.30e-8
Fe/TOC	0.07 ± 0.09	0.27	0.05 ± 0.04
MeHg/THg	0.11 ± 0.09	0.39	0.13 ± 0.09

Significant higher concentrations in the treated area were shown for total phosphor (P_{tot}; F-test: p = 0.0465, t-test: p = 0.0159), total nitrogen (N_{tot}, F-test: p = 0.0251, t-test: 0.0055), and TOC (F-test: p = 0.0487, t-test: p = 0.0254). THg revealed nearly significant higher values in the treated areas (F-test: p = 0.077). In the following sections the differences between treated and reference areas regarding water quality in general as well as the mobilization of THg and MeHg will be discussed.

2.1 Treatment effect on general water quality

2.1.1 TOC, suspended solids and absorption

As noted earlier the TOC concentrations showed significant differences (F-test: p = 0.0487, t-test: p = 0.0254) between treated and reference areas (***Table 2***). This result is in agreement with several other studies that showed an increase in organic matter mobilization after forest activities (Porvari et al., 2003; Pirainen et al., 2002). Forest treatment might lead to disruptions in C cycling and hence result in enhanced DOC export to receiving water. Logging activities lower the evapotranspiration resulting in raising water tables that saturate the upper organic rich soil layers. This, the leaching of DOC from logging slash and increased decomposition of organic material due to logging induced raises in soil temperature and soil moisture lead to higher DOC concentrations in soil water and export to surface water bodies (Kreutzweiser et al., 2008). The TOC concentrations for stump harvest (34.20 ± 19.55 mg/L) and site preparation (33.95 ± 21.63 mg/L) (***Table 3)*** were in the same magnitude than those reported by Povari et al. (2003).

Several studies reported increases of DOC 2 – 5 times shortly after logging which resulted in declining exports after 3 – 5 years (Startsev et al., 1998, Piirainen et al., 2002, Kreutzweiser et al., 2008). In this study significant effects of increased TOC can be seen about 2 years after site preparation and stump harvest, respectively. Only comparatively few studies have assessed the influence of other forest treatment than logging on changes in the TOC export to surface water streams.

TSS concentrations were 6.45 ± 8.33 mg/L for the reference area and 9.17 ± 17.39 mg/L for the treated area (***Table 2***), respectively. The results were not significant due to a very high standard deviation of the treated area showing different catchment characteristics regarding e. g. soil properties, erosion, and flow regimes. The larger variability of sampled stream sizes in this study might have an influence on high standard deviation of the TSS concentrations.

The absorption of the filtered and unfiltered water samples were 0.51 ± 0.53 and 0.45 ± 0.42 for reference sites and 0.74 ± 0.57 and 0.66 ± 0.49 for treated areas (***Table 2)***, respectively. The adsorption correlates with the amount of humic substances in the water sample. Therefore TOC and absorption showed a strong significant positive relationship towards all data points ($R^2 = 0.88$, $p < 0.0001$). TSS are also influencing the absorption and hence documented a positive correlation in the unfiltered samples ($R^2 = 0.43$, $p < 0.0001$; all data points).

2.1.2 Nutrients

P_{tot} (F-test: p = 0.0465, t-test: p = 0.0159) and N_{tot} (F-test: p = 0.0251, t-test: p = 0.0055) were significantly higher in the treated area compared to the reference site. The concentrations of nitrate and nitrite showed also a higher concentration in the treated sites, but remained insignificant due to a very high standard deviation (***Table 2***).

Logging increases the input of nutrients from logging residues and at the same time the nutrient uptake by trees and plants is reduced leading to an increase in nutrient leaching (Palvainen et al., 2004). The whole degradation process is favored by changes in forest properties, e. g. soil moisture, soil temperature, organic matter content, plant uptake, decomposition rates and reduced shading (Kreutzweiser et al., 2008).

Nitrogen is a major forest nutrient and tends to be limited in Boreal forests (Tamm, 1991). That is why Nitrogen removal by logging activities should be of great concern (Ballard, 2000). Nitrogen cycling involves N mineralization and decomposition, immobilization, nitrification and denitrification (Attiwill & Adams, 1993). Logging usually increases N availability by increasing e. g. mineralization and nitrification and hence the N export to streams (Carmosinsi et al., 2003; Walley et al., 1996). In this study the N_{tot} concentration in the stream water varied significantly between 5.97 ± 3.64 mg/L for the reference site and 10.43 ± 7.75 mg/L for the treated area, respectively.

Löfgren et al. (2009) reported that the combined effect of increased runoff and net nitrification enhanced the annual N_{tot} leaching from about 1.5 to 2.7 kg/ha/y for one of the study catchments. The authors noted that the N leaching and nitrification might persist for several more years. This is also in line with the results of this study as forest treatment occurred more than two years prior to sampling. What is more, Hazlett et al. (2007) reported that the logging effect on N cycling might be delayed for some years after post-harvest and hence the impact on surface waters quality could occur several years after clear cutting.

Kreutzweiser et al. (2008) stated in their review that the influence of logging on boreal forest N pools and cycling may be variable and that the magnitude and timing of the interaction between abiotic and biotic factors within a catchment lead to a highly site specific response. The large standard deviations of the N_{tot} concentrations in this study (***Table*** 2) confirm a rather site specific catchment response.

In this study the concentration of P_{tot} was significantly different between the reference (18.67 ± 17.40 µg/L) and the treated (35.62 ± 33.02 µg/L) area. The mobilization of P is also influenced by logging induced changes like e. g. moisture and temperature but also weathering, the adsorption onto particles and the co-leaching with organic matter from the forest soil play an important role (Kreutzweiser et al., 2008). Therefore, processes that increase the DOC fluxes after logging might likely increase the P_{tot} export. In this study, the significant positive relationship between TOC and P_{tot} for all sample points ($R^2 = 0.50$; $p < 0.0001$) supported this finding.

Palvianinen et al. (2004) found that substantial amounts of C and P were released from logging residues very soon after the clear cut. They noted that the N/P ratio was initially lower than the optimal suggested 10 (Vogt et al., 1986) but increased towards 15 – 20 during decomposition as P was released faster than N. However, in this study the N/P ratio in the stream water was much higher and about 32 for the reference site and 30 for the treated area. Also, a high P export to surface stream water might lead to eutrophication (Prepas et al., 2001).

2.1.3 Other parameters and ions

The physical impacts of logging as well as site preparation and stump harvest might affect the soil aeration. Porosity reduction due to compaction and other changes that lead to increased soil water retention hinder the gas exchange. Due to the limited gas transfer the metabolism of roots and soil microorganisms result in an increased carbon dioxide concentration which reacts with water to carbonic acid and largely dissociates into H^+-ions and HCO_3^- (bicarbonate). The formed H^+ might lead to the increased desorption of exchangeable cations, e. g. Ca^{2+}, Mg^{2+} and K^+ which might be leached along with mobile biocarbonate (charge balance) (McColl & Cole, 1968). In this study the lower pH at treated sites (5.71 ± 1.02) compared to reference sites (6.05 ± 0.97) as well as the generally higher leaching concentration of ions in stream water could commonly support this hypothesis.

Ca^{2+}, Mg^{2+} and K^+ are essential nutrients for forest productivity and are involved in the buffering capacity of the soil influencing the pH (Johnson et al., 2000, Likens et al., 1996). However, in this study no significant differences between base cations concentration in the reference and treated area were found. Kreutzweiser et al. (2008) found by comparing different studies that forest floor Ca^{2+} concentrations were most likely impacted by logging (compared to magnesium and potassium). This is also confirmed in this study as only Ca^{2+} showed elevated concentrations in the treated compared to the reference site (***Table 2***).

The concentration of Mn (not significant) was higher for the treated area (133.02 ± 272.657 µg/L) than for the reference site (82.5 ± 106.2 µg/L). Skyllberg et al. (2009) suggested that the elevation of Mn was mainly due to the release of Mn^{2+}-ions from newly added logging debris and degradation of soil organic matter.

The Al^{3+} and Fe_{tot} concentrations were also elevated (not significant) in the treatment site compared to the reference area (***Table 2***). The export of Al^{3+} and Fe_{tot} is also linked to the TOC output and the TOC-Al^{3+} and TOC-Fe_{tot} regression both revealed a significant positive correlation ($R^2 = 0.50$ and $p < 0.0001$, $R^2 = 0.49$ and $p < 0.000$).

2.2 Treatment effect on THg and MeHg

The comparison between treated areas and reference sites revealed no significant difference between THg and MeHg concentrations (***Figure 5***). However, the variation of THg concentration between reference (6.43 ± 3.87 ng/L) and treated areas (9.52 ± 6.69 ng/L) was nearly significant ($p = 0.077$). Also, MeHg concentrations were higher in the treated areas (1.51 ± 1.90 ng/L) compared to the reference site (0.79 ± 0.86 ng/L), although not significant ($p = 0.140$). The large variation of both THg and MeHg concentration between treated areas resulted in a large standard deviation. The high standard deviation might have been a reason for the non-significant difference between the references and the treated area.

The higher MeHg/THg ratio in the treated area (0.13 ± 0.09) than in the reference area (0.11 ± 0.09) might be an indication of higher methylation rate in the treated area. Based on empirical relations this ratio has been suggested to be a better predictor for the accumulation of mercury in fishes than the absolute MeHg concentration (Lee & Iverfeldt, 1991).

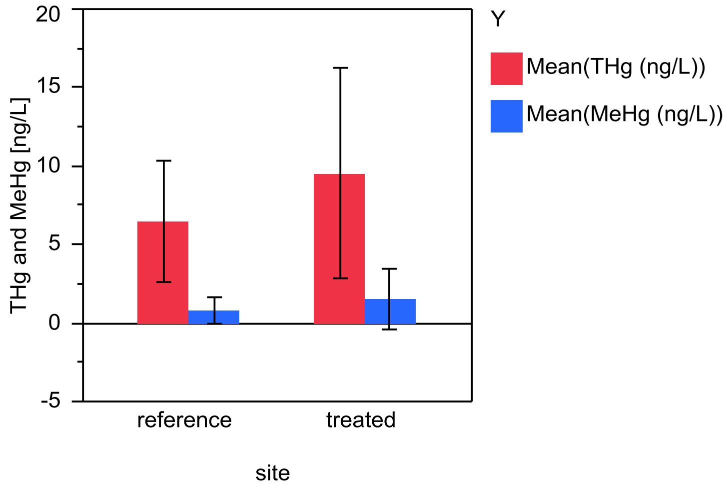

Figure 5: Mean values and standard deviations of THg and MeHg in reference and treated area

In a three years monitoring study of a catchment before and after clear cut (1997), soil preparation (1998) and replanting (1999) Porvari et al. (2003) documented increased MeHg concentrations during the first and second year after soil treatment indicating that not the clear cut but the soil treatment had major effect on Hg methylation and mobilization. On the other hand THg mobilization occurred earlier and was closely connected to TOC export which was more affected by clear- cutting. In this study even two years after forest treatment the TOC levels are significantly increased compared to the reference site (***Table 2***) and are most likely responsible for the increased THg concentrations found in the treated areas.

The high standard deviation of both the THg and the MeHg concentration indicated that the sampling sites possessed different properties depending on e. g. the respective catchment characteristics and hydrological conditions. Looking at the data set, the THg and MeHg concentrations for the treated areas varied between 0 and 29.5 ng/L and from 0.018 to 9.266 ng/L, respectively.

In order to get a better understanding about the processes within the different treatment sites and the different influences on THg and MeHg mobilization and transport a further separation into stump harvested and preparation sites is done in the following section. Furthermore, a more detailed discussion about the relationship between different parameter (e. g. absorption, TSS, TOC) and THg and MeHg, respectively, will be given in chapter 4.

3. Analyses of treatment effects regarding reference, stump harvest and site preparation

The results of the analyses of variance (ANOVA) revealed no significant difference between stump harvest and reference sites and also no difference compared to the reference area (***Table 3***). In the following sessions the results will be discussed in detail.

Table 3: Mean value and standard deviation of all stream water chemistry variables as well as the p-value for the F-test (ANOVA) in the reference, stump harvested and site prepared areas

	Reference Area		**Site preparation**	**Stump harvest**
Parameter	*Mean ± STADEV*	*p-value*	*Mean ± STADEV*	*Mean ± STADEV*
pH	6.05 ± 0.97	0.41	5.61 ± 0.98	5.84 ± 1.08
THg [ng/L]	6.43 ± 3.87	0.21	9.54 ± 7.45	9.49 ± 5.77
MeHg [ng/L]	0.79 ± 0.86	0.32	1.61 ± 2.29	1.39 ± 1.34
Alkalinity [meq/]	0.26 ± 0.44	0.87	0.18 ± 0.66	0.32 ± 1.04
Ca [meq/L]	0.34 ± 0.45	0.82	0.32 ± 0.58	0.47 ± 1.15
Mg [meq/L]	0.11 ± 0.09	0.25	0.07 ± 0.09	0.09 ± 0.04
Na [meq/L]	0.12 ± 0.07	0.94	0.12 ± 0.08	0.12 ± 0.06
EC [mS/m]	5.69 ± 4.39	0.85	5.48 ± 5.43	6.74 ± 10.54
K [meq/L]	0.01± 0.02	0.35	0.02 ± 0.02	0.02 ± 0.01
Fe [mg/L]	1.71 ± 2.16	0.92	1.96 ± 2.89	1.68 ± 1.83
Mn [µg/L]	82.50 ± 106.20	0.27	85.48 ± 87.63	195.4 2± 401.08
Al [µg/L]	497.39 ± 373.16	0.36	649.29 ± 435.63	499.13 ± 396.37
Cl [meq/L]	0.08 ± 0.06	0.99	0.08 ± 0.07	0.08 ± 0.07
F [mg/L]	0.10 ± 0.05	0.35	0.12 ± 0.05	0.10 ± 0.05
SO_4 [meq/L]	0.07 ± 0.10	0.73	0.05 ± 0.06	0.08 ± 0.13
∑anions [meq/L]	0.41 ± 0.49	0.84	0.42 ± 0.70	0.58 ± 1.32
∑cations [meq/L]	0.64 ± 0.49	0.85	0.57 ± 0.60	0.72 ± 1.20
NH_4-N [µg/L]	30.12 ± 71.88	0.70	54.05 ± 74.66	47.19 ± 119.12
P_{tot} [µg/L]	18.67 ± 17.40	0.12	38.57 ± 38.37	31.75 ± 25.00
N_{tot} [µg/L]	597.94± 364.33	0.059	962.48 ± 616.61	1147.88 ± 956.49
NO_2+NO_3 [µg/L]	34.00± 42.42	0.27	131.10 ± 218.64	285.19 ± 796.07
TOC [mg/L]	23.23 ± 13.72	0.15	33.95 ± 21.63	34.20 ± 19.55
Si [mg/L]	4.12 ± 0.98	0.43	3.81 ± 0.10	3.75 ± 1.19
TSS [mg/L]	6.45 ± 8.33	0.83	9.27 ± 21.03	9.04 ± 11.65
Absorption (unfiltered)	0.51 ± 0.53	0.39	0.74 ± 0.64	0.73 ± 0.46
Absorption (filtered)	0.45 ± 0.42	0.28	0.67 ± 0.53	0.66 ± 0.45
THg/TOC	2.86e-7 ± 1.28e-7	0.98	2.86e-7 ± 1.4e-7	2.79e-7 ± 1.20e-7
MeHg/TOC	2.89e-8 ± 2.37e-8	0.53	3.67e-8 ± 3.18e-8	4.07e-8 ± 3.53e-8
Fe/TOC	0.07 ± 0.09	0.54	0.05 ± 0.03	0.05 ± 0.04
MeHg/THg	0.11 ± 0.09	0.59	0.12 ± 0.09	0.14 ± 0.11

3.1 General water quality

3.1.1 TOC, suspended solids and absorption

In this study the values of TOC, absorption and TSS for stump harvest and preparation sites did not differ implying that the different treatment methods of site preparation (mainly harrowing and scarification) and stump harvest had the same influence on the overall mobilization of TOC and TSS. Furthermore, it might be also hypothesized that the logging activities prior to site preparation and stump harvest were already responsible for the increase in the concentration. In this study there was no sampling done after clear-cutting and before site preparation for this reason the influence of the initial clear cutting could not be evaluated.

3.1.2 Nutrients

N_{tot} as well as nitrate and nitrite concentration were elevated in the stump harvested sites whereas P_{tot} and NH_4-N concentrations were higher for the site preparation areas (***Table 3***). N_{tot} revealed nearly significant differences between site preparation, stump harvest and reference area ($p = 0.059$). However, when comparing only the statistical difference between the values of N_{tot} for stump harvest and site preparation, the analysis of variance revealed a p-value of 0.48.

3.1.3 Other parameters and ions

Ca^{2+} and Mn^{2+} concentrations were elevated (not significant) in the stump harvested site compared to site preparation and reference (***Table 3***). The generally higher ion concentration in the stream water for stump harvested sites was reflected in an increased electric conductivity (EC) which was 5.48 ± 5.43 mS/m for site prepared areas and 6.74 ± 10.54 mS/m for stump harvested sites (***Table 3***). To understand the reason for the differences between the leaching of ions and different forest treatment, further research is needed.

3.2 THg and MeHg

The little variation in the THg concentrations between stump harvest and site preparation (***Figure*** 6) might indicate that the different treatment methods of site preparation and stump harvest have no or little influence on the THg mobilization and export. MeHg production showed a slight difference between stump harvest (1.39 ± 1.34 ng/L) and site preparation (1.61 ± 2.29 ng/L), although not significant ($p = 0.32$).

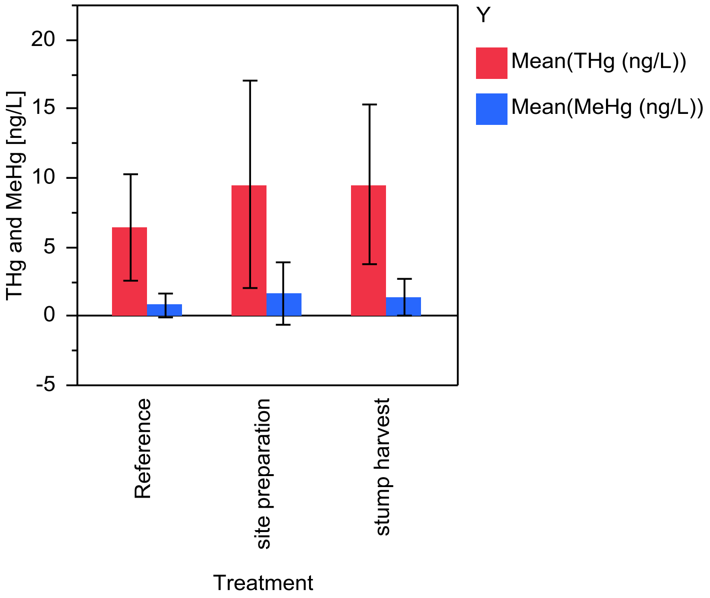

Figure 6: THg and MeHg concentration divided by reference area, site preparation and stump harvest

3.3 Analyses of the influence of catchment size on THg and MeHg export

Catchments characteristics, e. g. size and topography, the catchment to surface water ratio, the soil type, the land cover and the land use control the retention of Hg in the terrestrial ecosystem and the transport to surface water streams (Munthe et al., 2007).

In this study the relationship between MeHg and catchment size was not significant but correlated weakly negative for site preparation ($R^2 = 0.11$) and weakly positive for stump harvest ($R^2 = 0.13$). There was no correlation for reference areas ($R^2 = 0.03$) and the whole data set ($R^2 = 0.02$). Hence, the results were in line with the ones of Grigal (2002) as he also did not detect a clear trend between catchment size and MeHg concentrations.

The correlation between THg and catchment size was inverse and not significant for site preparation ($R^2 = 0.12$) and reference sites ($R^2 = 0.08$), and the values did not correlate for the whole data set ($R^2 = 0.009$). The weak inverse relationship was corresponding with the results of Grigal (2002). Grigal (2002) explained the weak negative correlation between THg flux and watershed size due to less effective transport processes to streams and rivers in larger catchments and due to increased loss processes (e. g. volatilization). Also, the decrease in flux with watershed size and hence with stream order might play a role.

Surprisingly the stump harvest sites revealed a significant positive correlation of THg and catchment size ($R^2 = 0.37$, $p = 0.0159$). One influencing factor might be the much smaller catchment size of the stump harvest sites (27.98 ± 34.29 ha) compared to the site preparation areas (44.44 ± 56.36 ha). The difference in catchment size is likely to display a difference in stream size that might influence the THg fate and transport.

Grigal (2002) mentioned in his analyses that the studies of THg and MeHg flux in relation to the watershed size are contradictory as each watershed is unique in its flow regime and land cover. For example, the wet MeHg deposition differed by the factor of three in two watersheds in Sweden as well as the volume of precipitation and stream flow (two fold difference), but the stream flow MeHg flux was comparable.

3.4 Analyses of the influence of the percent treated area within the catchment

The data of the average % treated area of the treated areas (irrespective the separation of stump harvest and site preparation), stump harvested and preparation sites together with the respective THg and MeHg concentrations are presented in ***Table 4.*** The % treated area in the reference site was zero. Especially for the stump harvested sites the variation of treated areas within the catchment was very high and ranged from 14.51 % to 97.88 %., what is also reflected in a rather high standard deviation (***Table 4).***

Table 4: Comparison of average % treated area and its influence on THg and MeHg concentration in different treatment sites

Site	% treated area	THg [ng/L]	MeHg [ng/L]
Stump harvest	47.68 ± 33.20	9.49 ± 5.77	1.39 ± 1.35
Site preparation	35.91 ± 15.83	9.55 ± 7.46	1.62 ± 2.28
Treated area	40.99 ± 25.17	9.52 ± 6.69	1.51 ± 1.90
Reference	0	6.43 ± 3.87	0.79 ± 0.86

The analysis of variance (ANOVA) for the % treated area of stump harvest and site preparation revealed p = 0.16. Stump harvested sites contained an 11.77 % higher fraction of treated areas in the catchment than site preparation areas, but revealed lower THg and MeHg values. The data set of all sites showed that a higher % of treated area in the catchment is not necessarily correlated with an increased THg and MeHg concentration.

This might be attributed to catchment specific responses. Also the location of the treated areas within the catchments is important as their influence on Hg mobilization will be higher next to a stream than further away. However, the GIS data sheet used for the analysis did not display the small forest streams. Hence, to further evaluate the findings in ***Table 4*** a closer assessment of the location of the treated areas in relation to the forest streams in the catchments is necessary.

4. Relationship of mercury and related variables

4.1 PLS regression with THg as dependent variable

The PLS regression with THg as dependent variable revealed a model with a goodness of fit (R^2) of 0.703 and goodness of prediction (Q^2) of 0.665 and was classified as substantial according to Chin (1998). The VIP values of the variables influencing the variation of the THg concentration (whole data set) are shown in ***Figure 7.***

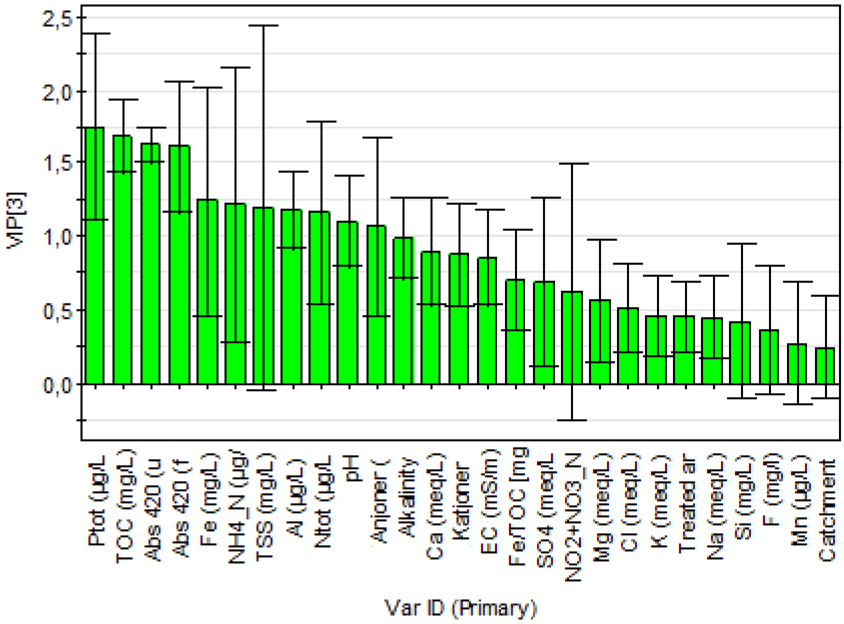

Figure 7: PLS analyses of variable importance in the projection (VIP) of the whole data set with Y: THg

The model showed that P_{tot}, TOC and absorption had a very high influence on the THg concentration. However, the amount of P_{tot}, absorption (unfiltered) and absorption (filtered) was closely linked to TOC mobilization which was represented in a positive correlation $R^2 = 0.50$ and $p < 0.0001$, $R^2 = 0.88$, $p < 0.0001$ and $R^2 = 0.92$, $p < 0.0001$, respectively. Hence, their influence on THg might be largely controlled by TOC. However, phosphorous like sulfur is a soft Lewis base that is commonly associated with soft Lewis acids (e. g. mercury), e. g. Girault et al. (1995) showed that inorganic Hg(II) was binding to membrane phospholipids.

The positive relationship of THg and MeHg with TOC and absorption (unfiltered) divided according to different treatment and reference sites is given in ***Figure 8***.

In ***Table 4*** the correlation characteristics of the relationship of MeHg and THg with TOC and absorption (unfiltered) are shown. The correlation of THg with TOC was very strong whereas the relationship of MeHg and TOC was weaker. The THg export is closely linked to the export of TOC and the data set showed a strong positive significant relation ($R^2 = 0.70$, $p < 0.0001$) which was in agreement with several other studies (Ravichandran, 2004; Skyllberg et al, 2009). Mercury is strongly binding to the reduced sulfur sites in DOM (dissolved organic matter) which are exceeding by far the natural mercury concentration in surface waters (Ravichandran, 2004). Skyllberg et al. (2009) noted also a very strong correlation between TOC and Hg^{2+} ($R^2 = 0.73$, $p < 0.001$).

In this study also a positive relation between MeHg and TOC across all sites was shown ($R^2 = 0.48$, $p < 0.0001$). Normally, the correlation between MeHg and organic matter is not so straight forward than the one of THg and organic matter.

The relationship of absorption with MeHg and THg revealed a strong positive correlation. Absorption is another method to measure the organic matter content and the particulate substances that disperse light in a water sample. Hence, this analytical method could be used as a first estimate of MeHg and THg concentration in water as it could be applied easily in the field. Furthermore, the absorption measurement is quite simple compared to the analytical laboratory methods used for MeHg and THg analyses. The possibility to use absorption measurement as an estimation for mercury concentration is also supported by the similarity of the slopes (graph forced through zero) of site preparation, stump harvest and reference site in the relationship of THg with TOC and absorption (***Table 5***). The mean values for the slopes in the correlation of THg with TOC and absorption (unfiltered) were about 0.27 and 10.74, respectively.

The THg/TOC value differed not much between all three sites (***Table 3***) which given the similarity of slopes of the relationship between THg and TOC might imply that TOC is the major mobilization mechanism of THg.

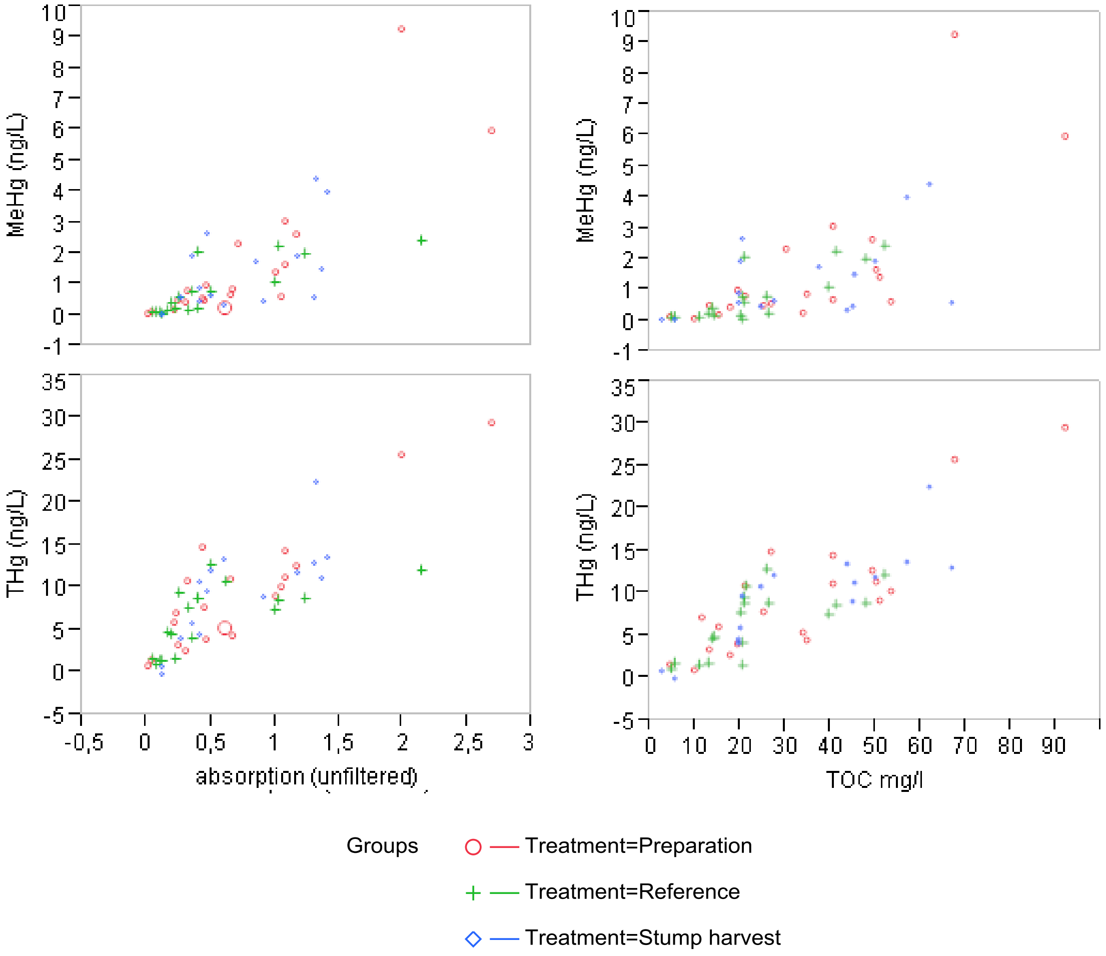

Figure 8: Relationship of mercury species with TOC and absorption (unfiltered), blue: stump harvest, red: site preparation, green: reference

Table 5: Correlation characteristics (R^2 and p-value) of the Relationship of THg and MeHg with TOC and absorption at 420 nm

Relationship	Site	R^2	p-value	slope
THg with TOC	Stump harvest	$R^2 = 0.71$	$p< 0.0001$	0.27
	Site preparation	$R^2 = 0.74$	$p < 0.0001$	0.28
	Reference	$R^2 = 0.48$)	$p = 0.0015$	0.26
MeHg with TOC	Stump harvest	$R^2 = 0.23$	$p = 0.0453$	0.04
	Site preparation	$R^2 = 0.56$	$p = 0.0002$	0.05
	Reference	$R^2 = 0.66$	$p < 0.0001$	0.04
THg with absorption (unfiltered)	Stump harvest	$R^2 = 0.59$	$p < 0.0009$	12.02
	Site preparation	$R^2 = 0.81$	$p= 0.004$	11.65
	Reference	$R^2 = 0.41$	$p= 0.004$	8.56
MeHg with absorption (unfiltered)	Stump harvest	$R^2 = 0.36$	$p = 0.0148$	1.86
	Site preparation	$R^2 = 0.72$	$p<0.0001$	2.45
	Reference	$R^2 = 0.68$	$p<0.0001$	1.42

The MeHg/TOC ratio differed not significantly between reference and treated areas but varied from 2.89e-8 ± 2.37e-8 ng/L for the reference, 3.67e-8 ± 3.18e-8 ng/L for site preparation to 4.07e-8 ± 3.53e-8 ng/L for stump harvest. The slopes of the relationship of MeHg with TOC (graph forced to zero) were 0.04 for stump harvest, 0.04 for reference and 0.05 for site preparation. Hence, given the similarity of slopes for the correlation of MeHg with TOC for the three sites and taking into account the differing MeHg/TOC ratios, additional processes than the mobilization via MeHg – TOC complexes might influence the MeHg concentration in the surface water.

Other VIP-values in ***Figure 7*** like Fe_{tot}, NH_4-N and aluminum were also linked closely to TOC and TSS export. MeHg and THg was further correlating with TSS and pH. The correlation of MeHg and THg with TSS (whole data set) was not as strong as with TOC but revealed significant and was $R^2 = 0.26$, $p = 0.0001$ and $R^2 = 0.35$, $p < 0.0001$, respectively. The negative relationship of MeHg and THg with pH for the whole data set can be seen in ***Figure 9.***

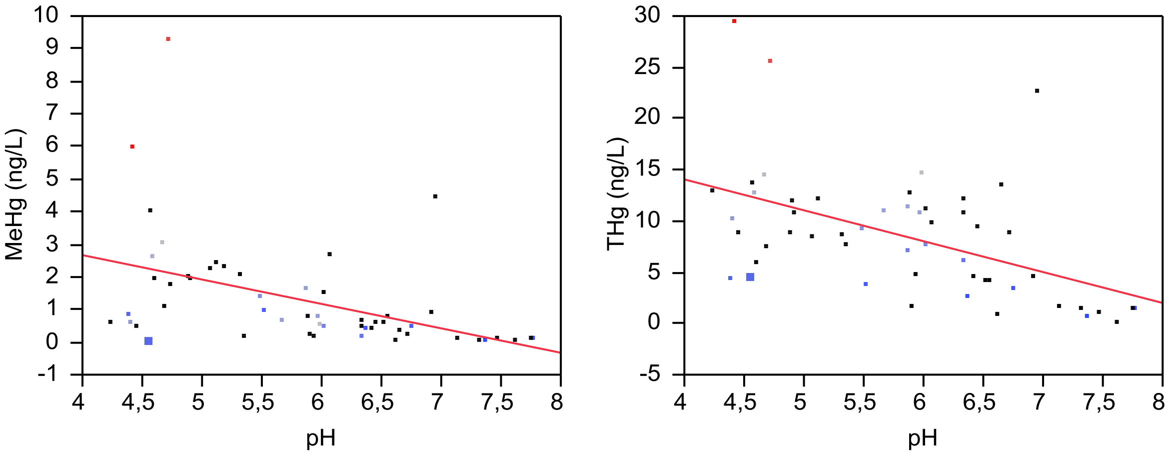

Figure 9: Relationship of MeHg and THg with pH, $R^2 = 0.20$, $p = 0.0007$ and $R^2 = 0.25$, $p = 0.0001$

Leng & Nies (1999) found in laboratory studies that the optimum pH for methylation is 4.5, as at higher pH (pH>8) the formation of Hg hydroxides was limiting the bioavailability of THg. The pH can be seen as a master variable for many different reactions and is strongly influenced by TOC. High organic C (TOC) is causing natural acidity which is responsible for the lower pH (Laudon et al., 2000). The relationship between TOC (mg/L) and pH can be seen in ***Figure 10*** and shows the expected negative correlation ($R^2 = 0.44$, $p < 0.0001$). As can be seen in ***Table 2***, forest activity is likely to increase the TOC in soils and runoff which is also reflected in lower pH values in treated areas compared to reference sites.

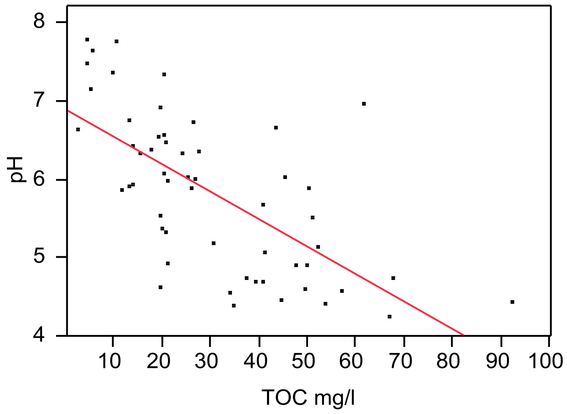

Figure 10: Correlation between TOC and pH of all sample sites ($R^2 = 0.44$, p<0.0001)

4.2 PLS regression with MeHg as dependent variable

The model revealed a goodness of fit (R^2) of 0.677 and goodness of prediction (Q^2) of 0.606 and was classified as substantial according to Chin (1998). The model results and the influencing variables on MeHg concentration (whole data set) is shown in ***Figure 11.***

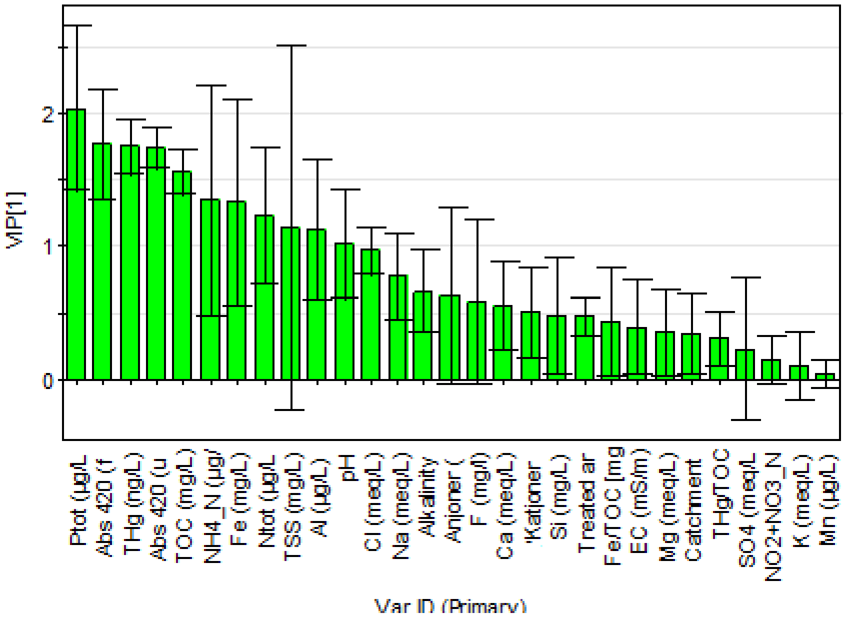

Figure 11: PLS analyses of variable importance in the projection (VIP) of the whole data set with Y: MeHg as dependent variable

The high VIP value of P_{tot}, might be attributed to the close relationship with TOC and TSS. However, P is also a major constituent of phospholipids which are on the other hand a major component of cell membranes (Madigan et al., 2008). As MeHg is very lipophil it is accumulated in the fat tissue of bacteria and higher organisms (Ullrich et al., 2001). Hence, the correlation of P_{tot} with MeHg showed a significant relationship with $R^2 = 0.82$ and $p < 0.0001$ that is much higher than the one of P_{tot} with TOC ($R^2 = 0.50$, $p < 0.0001$) suggesting that other mechanisms than the influence of TOC on P_{tot} are responsible for the high VIP value of phosphor. Therefore, more research on the mechanisms behind the high influence of phosphor on MeHg concentration is needed.

When looking at the parameter Fe and Fe/TOC (***Figure 11***) the influence of TOC on the VIP value becomes visible. Hence, the actual influence of Fe is more likely to be about 0.5 instead of around 1.3. Although having a lower value than 1 and therefore not significant for the Y variable, it is interesting that Fe/TOC has a higher influence on MeHg than sulfate. The parameter Fe signified the total Fe concentration in the stream and is the sum of Fe(II) (dominant under acidic conditions) and Fe(III) which is often complex by NOM ($Fe(OH)_{3-n}^{n+}$. When making the assumption that the Fe (III) is mainly complexed by NOM and hence associated with TOC an increase in the Fe/TOC ratio would be then reflecting the Fe(II) production in soils (Skyllberg et al., 2009). The Fe/TOC ratio was slightly higher in the reference sites than in the treated areas (***Table 2 and Table 3)*** which might imply a higher Fe(II) concentration at the reference site. Further research about the role of IRB in the whole methylation process is therefore required.

The relationship of MeHg with Fe/TOC was only significant in the site preparation ($p = 0.0453$, $R^2 = 0.31$, ***Figure 12***).

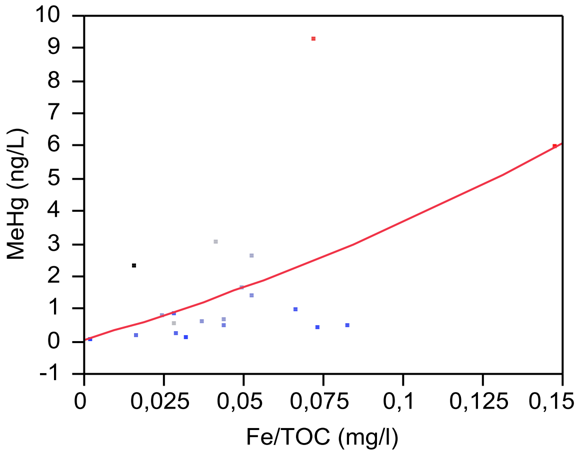

Figure 12: Correlation of MeHg with Fe/TOC, p = 0.0453, R² = 0.31)

Also, THg revealed an expected high VIP value (***Figure 11)***. The significant positive correlation of THg and MeHg can be seen in ***Figure 13*** ($R^2 = 0.62$, $p < 0.0001$). However, the relationship between MeHg and THg is highly complex and MeHg is not a simple function of THg but more the interaction of several environmental factors (Ravichandran, 2004; Ullrich et al., 2001). However, sufficient bioavailable THg is one of the basic components that are required for methylation.

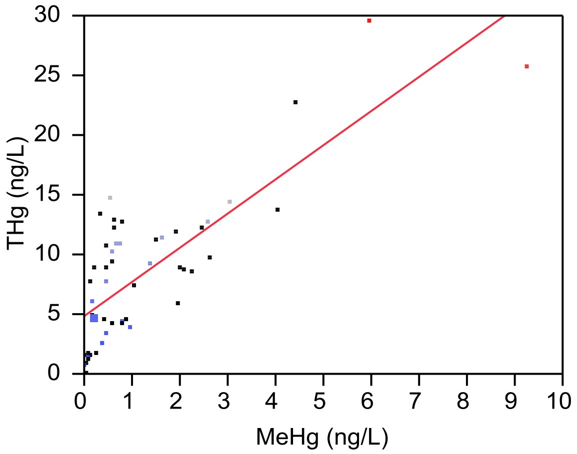

Figure 13: Correlation between THg and MeHg, $R^2 = 0.62$, $p < 0.0001$

V CONCLUSIONS AND OUTLOOK

Within this synoptic research it was found that forest treatment (site preparation and stump harvest) might lead to higher nutrient, organic carbon and mercury leaching compared to reference sites. It was shown that treated areas exhibited statistical significant higher TOC, P_{tot} and N_{tot} concentrations than reference sites. Furthermore, the THg concentration in the treated areas was nearly significant higher ($p = 0.077$) compared to reference sites indicating that forest treatment might increase the THg mobilization to surface water streams. The THg concentration between stump harvest and site preparation revealed no difference. It could be hypothesed that the individual treatment method of stump harvest compared to site preparation did not reveal any different impact on THg mobilization.

The MeHg concentrations did not differ significantly between treated and non-treated areas as well as between reference, site preparation and stump harvesting areas. However, the very large standard deviations for MeHg but also for THg showed that catchment specific processes play an important role in the overall fate and transport of MeHg and THg and that catchments exhibit different responses regarding forest treatments.

To conclude, this study could not confirm the indications in literature that forestry operations is severalfold increasing the THg and MeHg load to aquatic systems (Povari et al., 2003, Bishop et al., 2009, Munthe and Hultberg, 2004). This study was the first one with such a large spatial sampling distribution in Sweden and indicated that the effects of forest treatments were highly site specific. This might be the reason why several studies reported 2 – 3 times increase of mercury load to surface streams and others did not.

The influence of phosphorous (e. g. phospholipids) on the THg and MeHg concentration in aquatic ecosystems need to be further assessed.

In order to give advice in the form of good management practices to forest companies a closer assessment of the different catchment specific factors influencing the Hg cycling and mobilization needs to be done. Furthermore, this study indicated that stump harvest has more or less the same influence on Hg mobilization, nutrient and ion leaching than site preparation. However, to assess the benefit of stump harvest regarding biofuel production also the implications concerning biodiversity need to be seriously taken into account.

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