Swedish University of Agricultural Sciences
Faculty of Natural Resources and Agricultural Sciences

University of Natural Resources
and Applied Life Sciences, Vienna

Factors Controlling the Temporal Variability of Mercury in Runoff from Seven Catchments in Northern and Southern Sweden

Andrea Kraus

Uppsala, 2011

SLU, Swedish University of Agricultural Sciences
Department of Aquatic Science and Assessment

Factors Controlling the Temporal Variability of Mercury from Runoff in Seven Catchments in Northern and Southern Sweden

Andrea Kraus

Supervisor:	Karin Eklöf Swedish University of Agricultural Sciences, Uppsala Department of Aquatic Science and Assessment
Co-Supervisor:	Prof. Dr. Walter Wenzel University of Natural Resources and Life Science, Vienna Department of Forest and Soil Sciences
Examiner:	Prof. Dr. Kevin Bishop Swedish University of Agricultural Sciences, Uppsala Department of Aquatic Science and Assessment Uppsala University, Uppsala Department of Earth Sciences
Credits:	30 ECTS
Level:	E
Course Title	Independent project/Degree project in Environmental Sciences
Course Code:	EX0431
Programme/education:	Environmental Science in Europe
Place of publication:	Uppsala
Year of publication:	2011
Picture Cover:	**Catchments in Balsjö and Örebro (Photo: Andrea Kraus, Karin Eklöf)**
Online publication:	http://stud.epsilon.slu.se
Key Words:	Mercury, Methylmercury, TOC, flow, temperature

ACKNOWLEDGEMENT

This thesis was done at the Department of Aquatic Science and Assessment of the Swedish University of Agricultural Sciences and would not have been possible without the contribution of a lot of people. Some of them I would like to mention:

First and most off all I want to thank my supervisor Karin for her engagement, enthusiasm, comments, support, knowledge, patience, help, advice, open ear and many things more. While working under her supervision I learnt an unbelievable amount of new, interesting things about the mercury issue, computer programs, but also other useful things, e. g. how to find the “red thread” and how to tell a scientific story. Every time I had questions or problems she always took time to solve them with me and finally put me back on track. Without her - one of the most competent supervisors I have ever met - this challenging project would not have been finished the way it is laying now in front of you. I wish her all the best for the “finish” of her PhD and for all the possibilities that are waiting for her afterwards!

I also very much want to thank Kevin, for his enthusiasm in this project and for the great support he gave. He always took time for a meeting to discuss and to comment on the work and the RIM modelling. I am very grateful for this support! Thanks a lot as well for the calculation of the flow-concentration plots for the RIM section!

Furthermore, a big “thank you” to Martyn for running the countless RIM models and the RIM model efficiency calculations presented in this study! Thanks also for helping me to understand the RIM! He always welcomed me to his office, if there was any problem. I know that he was extremely busy and hence value his engagement even more.

I also want to thank Prof. Wenzel for agreeing on being my Co-supervisor and for giving valuable comments on this work!

Thank you to Jakob for the data he sent, for the support he gave regarding field work und for giving me a roof when the hostel did not ☺.

Thanks a lot to Lenka for sharing her data with me!

Thank you to everybody at the department in Uppsala and Umea for assistance and help with data, field work or other things.

THANK you also to all my friends that supported me, distracted me and invited me for dinner. Special thanks to: Martina, Berna, Laima, Anatoli and the rest of the Enveuro community in Racka, as well to my korridor kompisar: Jan, Elin, Jesper and Claess for an unforgettable year!

Last but not least I want to thank my parents, Kristina and Malte for their invaluable support during all my study time and during this thesis. Special thanks for sorting out the bibliography! You cheered me up when things looked not so bright and always had an open ear for me, no matter what it was, no matter where I was and no matter what I did.

TABLE OF CONTENT

INDEX AND ABBREVIATIONS

Index of Figures

Index of Tables

Abbreviations

Abs	**Abs**orption
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
HPOA	**H**ydro**p**hobic **o**rganic **a**cid
IRB	**I**ron **r**educing **b**acteria
MeHg	**M**ethylmercury (**Hg**)
N_{tot}	**Tot**al **n**itrogen
N_{org}	**Org**anic **n**itrogen
OC	**O**rganic **c**arbon
OM	**O**rganic **m**atter
PLS	**P**artial **L**east **S**quares
POC	**P**articulate **o**rganic **c**abon
P_{tot}	**Tot**al **p**hosphor
RIM	**R**iparian Profile Flow-Concentration **I**ntegration **M**odel
RZ	**R**iparian **z**one
SOM	**S**oil **o**rganic **m**atter
SRB	**S**ulfate **r**educing **b**acteria
TC	**T**otal **C**arbon
THg	**T**otal mercury (**Hg**)
TN	**T**otal **n**itrogen
TOC	**T**otal **o**rganic **c**arbon
TSS	**T**otal **s**uspended **s**olids
VIP	**V**ariable **i**mportance in the **p**rojection
VWC	**V**olume **w**eighted **c**oncentrations

ABSTRACT

The increased input of anthropogenic mercury in the environment has led to the accumulation of mercury (Hg) in the aquatic food chain and poses serious problems to the ecosystem and human health. Time series data from May 2004 – May 2010 in three catchments in northern (Balsjö) and from October 2006 – 2009 in four catchments in southern (Örebro) Sweden associated with different forest treatments (e. g. clear cut, site preparation) were assessed to determine the influence of different factors on the temporal pattern of total organic carbon (TOC), total mercury (THg) and methylmercury (MeHg).

Mean THg and MeHg concentrations varied in Balsjö between 4.92 – 5.48 and 0.39 – 0.47 ng/L and between 5.60 – 10.36 and 0.90 – 1.71 ng/L in Örebro. MeHg mean concentrations peaked in all catchments during summer period coinciding with maximum biological activity and were associated with low flow conditions. Analyzing THg concentrations over all seasons it was found that they also peaked in summer, however, the concentrations were more attributed to high flow in Balsjö and to low flow in Örebro. Site SP in Örebro had the highest export of MeHg, THg and TOC in this study (19.49 µg/d*ha, 137.89 µg/d*ha and 405.50 g/d*ha).

In Balsjö, THg concentrations showed a good correlation with flow, whereas the THg-flow relationship had no significant importance in Örebro. The Riparian Profile Flow-Concentration Integration Model (RIM) was used to show controls over TOC, MeHg and THg stream concentration in the different catchments. The RIM achieved highest Nash-Sutcliff (NS) coefficients at all sites after adding a seasonal component to the simulations. The RIM simulated soil solution profiles for the sites in Örebro and Balsjö supported the results gained from time series and soil dry fraction analysis.

This study highlighted the importance of different drivers for the seasonal variation in THg and MeHg concentrations. The results indicated that the Balsjö sites were more flow driven, whereas the catchments in Örebro were characterized by a strong seasonal pattern. Furthermore, the high importance of antecedent flow and temperature on THg and MeHg concentrations (Past Least Square (PLS) analysis) highlighted the influence of the watershed conditions prior to an event. Across all sites, it was shown that organic matter was the number one factor explaining total mercury dynamics. In Örebro 54 – 85 % and in Balsjö 62 – 72 % of the variation in THg concentrations could be explained by TOC.

I INTRODUCTION

1. Mercury (Hg) in the environment

Mercury, named quicksilver by Aristotle, is mainly 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, is relatively inert and has 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 during the industrial revolution (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, in particular coal, has significantly elevated the atmospheric mercury concentration since the start of industrialization. It is estimated that geologic sources of Hg did not contribute significantly to this increase during the period over the last 100 – 150 years as geological processes e. g. associated with plate tectonics can be regarded as constant over this short time interval (Fitzgerald et al., 1998).

The atmospheric transport depends on the chemical and physical form of mercury. Reduced mercury (Hg^0) has a residence time in the atmosphere of about one year and can be transported for several 10.000 km, which makes it a global pollutant (Schroeder & Munthe, 1998; Fitzgerald et al., 1998). Hence, long range atmospheric transport caused increased Hg deposition (compared to the pre-industrial time) even in remote areas of Europe and North America, which are exceeding natural concentrations (Fitzgerald et al., 1998). It should be mentioned that mercury deposition (precipitation, throughfall, dry deposition, litterfall) is much higher in forested areas due to the high amount of Hg attached on forest canopy entering the soil by litterfall or throughfall (Munthe et al., 2007). Grigal (2002) noted that atmospheric deposition on forests exceeds open precipitation by a factor of four. According to Munthe et al. (2007) concentrations of Hg in wet precipitation (open deposition) are varying between 10 – 11 $\mu g/m^3$ in southern Scandinavia and only 5 – 6 $\mu g/m^3$ in the inland of northern Sweden (data from 1999 – 2002). This north-south gradient is strongly dependent on local precipitation amounts and emissions of mercury from central Europe.

The mercury chemistry in the environment is highly complex as compounds can be interconverted and hence released from sediments or soil to the water phase, can be taken up by aquatic biota (bioaccumulation), can be lost to the atmosphere (volatilization) or transported with sediment particles depending on the predominant chemical, physical and biological conditions within the system (Ullrich et al., 2001). Furthermore, the ecological and toxicological effects of Hg in the environment are strongly related to its speciation (Clarkson, 1997, Ullrich, et al., 2001). Consequently due to the complicated interlinkage of biotic and abiotic factors many of the processes that control the export of Hg from the terrestrial storage pool to the aquatic system, the methylation and the bioaccumulation in the food chain are still poorly understood (Grigal, 2002).

In order to reduce the large uncertainties and to determine the factors that influence the spatial and temporal behavior of mercury, a closer assessment of the climatic impact is needed. Facing the increased interest to understand and hence manage the mercury pollution this study will contribute by analyzing the seasonal influence of two catchments with different climatic conditions in Sweden on mercury mobilization and transformation. This study gains importance when taking into account that climate change is expected to change the distribution of the seasonal pattern during the year which might shift the temporal and spatial scale of Hg export. Furthermore, silviculture is an important income source in Sweden accounting for 12 % of the export income (Skogstyrelsen, 2009). The influence of forest activities on Hg mobilization needs to be assessed as forest management is linked to soil disturbances and changes in the hydrological flow regime. Recent research showed that there is a high spatial variability in mercury output between harvested sites (Povari et al., 2003a; Skyllberg et al., 2009; Sörensen et al., 2009a). The underlying mechanisms why some sites show increased Hg export after harvest and others do not are still unclear and this study offers a closer assessment to reduce the uncertainties by analyzing the seasonal influence on treated and untreated forest areas.

2. Relationship between Hg and organic matter (OM)

The understanding of the strong relationship between Hg and organic matter (OM) is crucial to determine the fate and transport of Hg in the different environmental compartments (Grigal, 2003). Nevertheless, it should be noted that differences in the biogeochemical cycling of MeHg and THg show, that THg dynamics are more dependent on the mobilization of DOC whereas the mobilization of MeHg is to a higher extent related to net MeHg production rates and its concentration indicates a greater variation regarding temperature and runoff pattern than the one of THg (Bishop & Lee, 1997).

Organic matter (OM) is omnipresent in the aquatic and terrestrial environment and is known to bind metals and affect their solubility and speciation (Reuter & Perude, 1976). It can be therefore seen as a vehicle influencing the fate, transport, transformation (e. g. reduction) and bioavailability of mercury (Ravichandran, 2004; Haitzer et al., 2003). Hg most likely binds covalently to thiol (R-SH) and other sulfur containing groups within OM as the Hg-S complexation revealed the highest stability constant among other ligands (Ravichandran, 2004).

In Scandinavia much of the atmospheric Hg deposition is retained in the soils mor layer, which can be regarded as a filter for mercury deposition on forest soils (Johansson et al., 1991; Aastrup et al., 1991). Data from a survey assessing the Hg concentration in the O-horizon (organic layer) over Sweden showed elevated concentrations in southern Sweden that decreased irregularly towards the north with a high local variability. Furthermore, the concentrations decreased with increasing soil depth, which coincided with the decrease of organic carbon (Alriksson, 2001). Aastrup et al. (1991) showed that in an area in southern Sweden 75 – 80 % of the yearly deposition was retained in the humus layer. Furthermore, the authors noted that the amount of Hg present in the B horizon was probably only to a little extent influenced by anthropogenic emissions due to the short time scale of increased Hg emissions compared to the time scale of geological sources.

Temnerud (2002) stated that forest soils and mires can be regarded as a nearly infinite source of dissolved organic matter (DOM) for runoff, but the amount and behavior of water is often the limiting factor. Kalbitz et al. (2000) found in their review comparing influencing factors on DOM dynamics in soil from laboratory and field studies that in theory dissolved organic carbon (DOC) concentrations should be mainly biotically controlled with a strong dependence on temperature and other seasonal disturbances, but that in practice water fluxes through the organic soil layer can mask biotic control.

Soil organic matter (SOM) and Hg show often a similar spatial distribution (Alriksson, 2001), that might, however, vary due to historical loadings, the degree of mineralization or the amount of reduced S groups (Grigal, 2003). Nevertheless, the link between Hg and SOM mostly implies that landscape conditions, which lead to a different accumulation in SOM are also probably leading to differences in Hg accumulation. The SOM distribution is strongly influenced by soil properties like redox status, cations, and particle size distribution (texture) (Grigal, 2003). For example, SOM is stabilized and protected from oxidation by high concentrations of cations, in particularly Ca^{2+} (Oades, 1988). In the soil, the highest concentrations of SOM are mainly related to the fine silt and clay fraction (Anderson et al., 1981). Furthermore, soils that are poorly drained with low soil oxygen content have higher SOM than well drained soils due to reduced microbiological activity (Grigal, 2003). These soil properties - SOM relationships also affect Hg distribution, e. g. the Hg content in surface soil increased from the summit to base of a forest slope from 3.4 to 5.5 mg/m² along with SOM (Grigal et al., 1994).

The role of vegetation in SOM is determined by the interplay of production and decomposition (Grigal, 2003). The decomposition rate *k* increased with temperature, but revealed lower values for lignin rich conifer than deciduous forests (Johnson, 1995). Consequently, forests with greater production of biomass and nutrient cycling are therefore likely to have lower SOM and soil Hg concentrations as the occurring climate and litter favor rapid decomposition (Grigal, 2003). Furthermore, a longer growing season leads to an increased foliar uptake of Hg, but at the same time leads to an increased mineralization and Hg flux from the soil (Grigal, 2003; Fleck et al., 1999). The short mineralization season at higher latitudes might lead therefore to a greater retention of SOM and Hg in the watershed and hence to a higher potential for hydrologic export of Hg to the aquatic system (Grigal, 2003).

Compared to the Hg soil storage the annual output of mercury is relatively small (Johansson et al., 1991). Johansson et al. (1991) estimated that only about 0.1 % of the mercury content in the mor layer is released annually by run-off water. It should be noted that even this small fraction of the total Hg storage in runoff contributes to the high levels of mercury within the food chain (Bishop & Lee, 1997).

3. Methylmercury (MeHg) production

The increased input of anthropogenic mercury in the environment has led to the accumulation of Hg in the aquatic food chain. In Fennoscandia and elsewhere the concentrations of Hg and especially its organometallic form, methylmercury (MeHg), in fresh water fishes are often above the WHO recommendations (0.5 mg/kg) posing risks to the aquatic community as well as to humans (Hakanson 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 as it is the most bioavailable species and can be concentrated more than a million-fold in living organisms compared to surface water concentrations (Schuster et al., 2008; Grigal, 2002). MeHg is a neurotoxin that is able to cross the blood-brain and the placenta barrier (Clarkson, 1997). The ingestion of methylmercury via fishes is able to cause damages to the central nervous system as well as the adult and developing brain (Clarkson, 1997), which was shown during the Minamata disease in Japan (Clarkson, 1987). That is why in Sweden the given European standards are often supplemented with dietary recommendations, e. g. reduced fish consumption of Hg contaminated species for pregnant woman (Johansson et al., 1991).

As most mercury is present as inorganic mercury in freshwater systems and >95 % of the mercury in fishes in the form of MeHg, it is essential to define the processes and influencing factors that determine the transformation of inorganic Hg to organic mercury and the bioaccumulation of MeHg in the food chain in order to regulate 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 number of abiotic and biotic factors (Ullrich et al., 2001).

Methylation is dominantly a biotic process and obligate anaerobic sulfate reducing bacteria (SRB) are the primary methylators. However, recently the significant contribution of Iron reducing bacteria (IRB) has been identified (Devereux et al., 1996; Kerin et al., 2006; Ullrich, 2001). 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). The methylation is therefore not a simple factor of THg and might depend on other factors than those affecting total Hg (Grigal, 2003).

The transformation of THg to MeHg occurs normally in semi-anoxic systems (e .g. riparian zones, sediments, water column). In terrestrial ecosystems wetland and peatland are the most important sources of MeHg (Skyllbert et al., 2003). It can be assumed that terrestrial ecosystems with C accumulation and anoxic systems are sites of MeHg production (Grigal, 2003). As the methylation rate is *inter alia* a temperature dependent process, the mayor source of MeHg is most likely related to surficial or near-surface processes (Branfireun et al., 1996; Bishop et al., 1998). Furthermore, the concentration of MeHg in pore water and streams are highly dependent on seasonal changes with often highest concentrations in summer that are often associated with low flows (Branfiruen et al., 1996; Bishop et al., 1995; Grigal, 2003).

On average 4 % of the available Hg flux is estimated to be present as MeHg (Grigal, 2002). If considering, that only a small portion of Hg is released annually from the soil storage and that only a small percentage of this released Hg is in the form of MeHg, any changes in the export of mercury from the soils and/or the methylation rate due to changes in land use, atmospheric deposition, catchment biogeochemistry and climate would have a severe impact on the aquatic ecosystem and subsequently severe impacts on the human health (Bishop & Lee, 1997).

4. Export of Hg from the terrestrial to the aquatic ecosystem

The export of Hg via stream water is the dominant pathway in a lot of watersheds, whereby 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 dissolved organic carbon (DOC) or particulate organic carbon (POC) are affecting the Hg mobility.

Wetlands with organic rich soil located next to streams (riparian zones) 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 highlights the importance of the riparian zone (RZ) that has been shaped by uphill flows over millennia and is often characterized by distinctive soil properties due the interplay of hydrological and biological factors (Seibert et al., 2009, Agren et al., 2010). As the ground water flow paths change with time, different fractions the RZ are connected with the stream water. The stream water chemistry could be therefore regarded as a fingerprint of the RZ at a given flow rate (Seibert et al., 2009).

As the water table rises during episodic events the flow paths are shifted to the upper organic soil horizons and are mobilizing reactive phases of DOC which are known to bind Hg (Shanley et al., 2008). It is estimated that hydrological factors determine short-term organic carbon (OC) dynamics while long term changes in OC concentrations are more related to climate (precipitation, warmer temperatures, droughts), land use change and acidic deposition (Dittman et al., 2010; Evans et al., 2006). Although hydrology is often the first order control of DOC and hence Hg export at events, Laudon et al. (2004) noted that the relationship between DOC and flow is varying depending on the landscape cover, e. g. the authors mentioned an inverse relationship between flow and DOC in wetland dominated watersheds and a positive one in forested catchments. For the DOC and Hg export the water flow, the residence time and the season of residence are important characteristics (Grigal, 2002). Hydrology is also influencing the methylation process by supplying solutes, influencing the redox condition and finally transporting MeHg (Shanley & Bishop, in press).

To illustrate the highly complex interaction between environmental factors, DOC and Hg, Raymond & Saiers (2010) mentioned the importance of interacting processes that operate at different time scales. The authors noted that temperature and antecedent discharge influence short term processes on DOC export (e. g. dissolution, microbial activity) as well as long term processes (e. g. primary production, soil OM pools). Furthermore, the authors highlighted the importance of temperatures and watershed wetness on the DOC export at event time scales (hours).

Faced with the above mentioned interaction of multiple factors at different spatial and temporal scales there is a need to simplify the influencing processes on DOC and Hg mobilization. In order to assess the impacts of the RZ on the seasonal variability of DOC, Hg and MeHg concentration in stream water, Bishop et al. (2004) proposed a perceptual model that is built upon the interaction of soil solution chemistry in the RZ and lateral water flux in different soil depths. The idea of the Riparian Profile Flow-Concentration Integration Model (RIM) is simply that the incorporation of flow and concentrations and their changes with depth in the soil determine the variation in stream water chemistry with varying runoff

(Bishop et al, 2004, Seibert et al., 2009). For example DOC soil water concentrations increase upwards with the soil profile so that in the case of a hydrological event the lateral transport of DOC to the stream is likely to be increased resulting in higher DOC concentrations (Agren et al., 2010, Seibert et al., 2009). The RIM model will be used in this study to assess the capacity of flow and/or temperature to model and hence explain the seasonal variation of total organic carbon (TOC), Hg and MeHg concentration in the two different study catchments.

5. Highlighting the importance and objective of the work

In boreal regions forestry is one of the dominant land uses and elevated Hg concentrations in fishes in these regions are quite common (Shanley & Bishop, in press). Taking into account the importance of silviculture in Sweden and its widespread 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 have revealed that forest disturbances (logging, site preparation, etc.) might result in an increased THg and MeHg mobilization (Porvari et al., 2003; Munthe & Hultberg, 2004; Skyllberg et al., 2009). However, recent studies e. g. Sörensen et al. (2009), did not find the expected severalfold increase of Hg output to surface water streams after forest harvesting. The differences in sensitivity of the study sites indicate the highly complex situation of mercury dynamics not only in relation to forest management but also to other catchment specific factors. Further, the huge variation in the above named study results show that there is a shortage of knowledge of the processes that control the export of THg and MeHg at the catchment level. So far, only limited research has been done in the field about how and to what extent seasonal factors (temperature, precipitation, flow, etc.) influence the mobilization of mercury from the terrestrial ecosystem. Together with catchment characteristics that control the retention of Hg like size, topography, the catchment to surface water ratio, the soil type, the land cover and the land use (Munthe et al., 2007) the understanding of the interaction between mercury dynamics and seasonal factors is likely to contribute significantly towards the question why the export of THg and MeHg shows such a high spatial and temporal variation.

Also, in the light of climate change it is more than necessary to assess the influence of the seasonal variability on mercury mobilization to aquatic systems. The climate change impacts in Sweden are estimated to increase precipitation by 10 – 20 % and to rise annual mean temperature by about 4 degrees within 100 years. The temperature increase is estimated to affect mostly the winter season and therefore the spring snowmelt period especially in northern Sweden (SWECLIM, 2001). This will change the timing, extent and duration of snow cover in boreal forests during winter and as a result lead to changes in the annual runoff pattern and hence influence the overall export of dissolved organic carbon (DOC) and Hg (Venäläinen et al., 2001).

Seasonal parameters, e. g. temperature, precipitation, soil water fluxes, soil moisture, and snowmelt that are influencing and controlling dissolved organic matter (DOM) dynamics in the soil and hence influence the DOC concentration in aquatic systems (Kalbitz et al., 2000) are also likely to affect the mercury concentration, specification, mobilization and distribution between the solid and liquid phase. A thorough understanding of the processes that control mercury mobilization in the terrestrial ecosystem would lead to effective and efficient tools to manage its output and to a better understanding of the terrestrial component in the global mercury cycle (Babiarz et al., 1998).

As the concern about the magnitude of the Hg problem is rising, this study will contribute to a better understanding about the processes and factors that determine the huge spatial and temporal variation in Hg export from terrestrial catchments.

The objectives of this study are (i) to assess and compare the different climatic and seasonal patterns between seven catchments in northern and southern Sweden and their influence on Hg mobilization and methylation, and (ii) to determine the influence on THg and MeHg concentration from various chemical variables and catchment specific factors. Furthermore, the results will be linked to the impacts of forestry and climate change on Hg mobilization providing knowledge that might potentially be helpful to find useful management strategies to regulate the Hg export.

II EXPERIMENTAL SECTION

1. Site description

The northern catchments (commonly referred to as ‘Balsjö’) are located in the boreal forest zone (64°02’N, 18°57’E) and are situated approximately 60 km west of the city of Umeå (**Figure 1**). The three study sites were the 20 ha small reference catchment (Ref-S), the 37 ha clear cut catchment (CC) and the 31 ha north clear cut catchment (NorthCC). The monitoring started in 2004 and is still ongoing. The North and CC catchments were harvested in 2006 on frozen ground. About 36 % of the NorthCC catchment and 73 % of the CC catchment was harvested (Sörensen et al., 2009b).

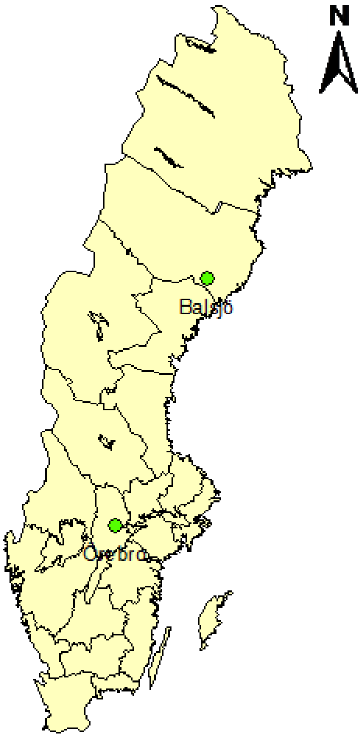


Figure 1: Location of the two major study areas in Sweden

In the northern catchments the bedrock underlying the till consists out of pegmatite. The main soil type is podsol with histosols in wetter areas (Löfgren et al., 2009). The forest vegetation consists mainly out of Scots pine (*Pinus sylvestris*) in well drained upland areas and Norway spruce (*Picea abies*) in wetter, lower areas. Along the stream channels some birch (*Betula sp.)* can be found (Sörensen et al., 2009a). There are mires and fens distributed in each catchment and the portion of wetland varies from 19 %, 14 %, and 8 % in the Ref-S, NorthCC, and CC catchment, respectively. The mean annual temperature and precipitation of the data used in this study (approximately May 2004 – November 2009) were 2.93°C and 634 mm (1.74 mm/d).

The southern catchments (commonly referred to as ‘Örebro’) are located 40 km south-west outside the city of Örebro (59°10’16,385’’N, 14°34’3.011’’E) (**Figure 1**). The studied sites in the area are the large reference catchment (R1, 209.2 ha), the site prepared area (SP, 5.2 ha) and the stump harvested area (SH, 28.3 ha). Another small reference catchment (R2, 17.4 ha) is situated in the inlet to the stump harvested area. The monitoring of the sites started in 2006 and the subsequent forest treatment was carried out in November 2007 (stump harvest) and January 2008 (site preparation). The monitoring of the Örebro catchments continued until December 2009 (Eklöf et al., in prep.).

The proportion of treatment (stump harvest or site preparation) in the SP and SH catchments was 65 % and 29 %, respectively (Eklöf et al., in prep.). There was no treatment in the R1 and R2 catchments. The portion of wetlands within the catchments in Örebro was estimated with the help of GIS, however, it should be noted that the presented figures are just a rough estimate as the quality of the layer was very limited. According to the map no data was available for wetlands in R2 and SP. The amount of wetlands in SH and R1 was about 4 % and 6 %, respectively.

The soil type in the area is mainly cambisol with podsols (Troedsson & Wiberg, 1986) and about 10 – 20 % of the area it dominated by broadleaved forest (Swedish National Forest inventory, 2010).

In this study (October 2006 – December 2009) the mean annual values for temperature and precipitation were 6.28°C and 758 mm (2.07 mm/d).

2. External Data

Data of precipitation and temperature from the Swedish Metrological and Hydrological Institute (SMHI) at nearby metrological stations to Balsjö (Umeå, Fredrika, Hamling, Basljö village) between the years 2003 and 2009 were used by Kuglerová (2010) to calculate interpolated temperature values for the coordinates of the sampling sites used in this thesis.

3. Sampling and Chemical Analyses

3.1 Flow measurements

In Örebro (R1, SP and SH) and in Balsjö (CC, NorthCC and Ref-S) the runoff was measured using 90°, thin plate, V-notch weirs. The measurements started in summer 2004 in Balsjö and autumn 2006 in Örebro (Eklöf et al., in prep.; Sörensen et al., 2009a). Details about the flow measurements, calibrations and calculations in both catchments are presented elsewhere (Eklöf et al., in prep.; Sörensen et al., 2009a).

In Örebro the automatic water level measurement was not operating from November 2006 until June 2007. The values for this period were modeled according to the hydrological discharge model HBV (see Eklöf et al., in prep. for further information). Furthermore, the sampling site in the R1 catchment was moved in summer 2007 due to difficulties in hydrological measurements and remained questionable as disturbances by beaver and forest activities occurred. As there were no flow measurements at R2, the specific discharge of the SH catchment was used.

In Balsjö approximately six months (depending on the site) of flow data of the whole data series (June 2004 – January 2010) are missing.

The uncertainties in flow determination caused due to uncertainties in the rating curve were reported for Balsjö by Sörensen et al. (2009b) and were higher for high flow events (e. g. the prediction uncertainty at a flow rate of 30 L/s with a 95 % prediction uncertainty was ± 5 L/s) than for low and intermediate flows.

3.2 Water samples

The analyzed streams were sampled on average biweekly in Balsjö (May 2004 – October 2010) and Örebro (October 2006 – December 2009) with greater frequency during high flow events. Since the beginning of March 2005 in Balsjö and the beginning of November 2006 in Örebro stream water THg and MeHg analysis was carried out and the samples were collected according to the clean sampling protocol. Sörensen et al. (2009a) and Eklöf et al., (2011) are stating the sampling and analyzing procedures for the catchments in Balsjö and Örebro.

The sampling scheme especially in Balsjö was biased towards high flow events, as the sampling frequency increased during events. Hence, 12.5 % (CC, n = 168), 12 % (NorthCC, n = 167) and 16 % (Ref-S, n = 157,) of all samples were taken during high flow. Comparatively, in the R1 (n = 91), SP (n = 102) and SH (n = 110) catchments in Örebro only 5, 5 and 8 % of the samples were collected during high flow events.

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). THg, MeHg and general chemistry analysis were carried out at the laboratory of the Chemistry Department, Swedish University of Agricultural Science, Umeå.

Previous measurements showed that the DOC fraction presented more than 90 % of TOC under all flow conditions (Sörensen et al., 2009a). Therefore the notation TOC will be used throughout the thesis.

3.3 Soil samples

Soil samples were taken with a soil coring tube (2.3 cm in diameter, 50 cm long) or by manual digging of profiles in Örebro and Balsjö in order to assess the THg, TC and TN soil storage. Manual digging was carried out if the handling of the soil coring tube was not efficient due to stones or roots in the soil. Most of transects were manually dug in Örebro, while drilling was mainly carried out in Balsjö. Two transects in Örebro (SH, R2) and three in Balsjö (Ref-S, CC, North) were established perpendicular to the direction of stream flow. Four sites were sampled on one river side approximately 0.5, 3, 7, and 21 m from the stream. In Örebro (SH) samples were taken at a distance of 14 m and in Balsjö samples for catchment Ref-S and CC were taken at a distance of 1 m and 9 m as frozen soil and stones made it impossible to dig at the previous mentioned distances. At every site five soil samples were taken in a depth of 0-10, 10-20, 20-30, 30-40 and 40-50 cm.

From each site (Balsjö and Örebro) about 40 -150 g (wet weight) of sample at the respective depths was directly transferred to a zip back and stored in a cooler until reaching the laboratory.

The samples where dried at 35-40°C and then sieved (2mm). The samples were further divided for mercury and TC/TN analysis. Mercury samples were kept frozen until analysis and TC/TN samples were stored in the dark at room temperatures.

Total mercury analysis was carried out at the chemistry department at the University of Umeå using US EPA method 7473 (US EPA, 2007). The method consists of a thermal decomposition of the solid sample, followed by trapping the containing mercury (amalgamation) and atomic absorption spectrophotometric detection (working range 0.05 – 600 ng). The analysis cycle was programmed as followed: 60 s drying, 300 s decomposition and 45 s waiting time. Prior to each analysis the sample boats were cleaned in an ethylene flame to remove Hg residuals. Reproducibility and accuracy of the measurements were checked by including sample replicates and reference standards about every 10th sample. Furthermore, to assess if milling of the samples had an influence on the amount of Hg detection four samples out of the Örebro sample set were milled and the analysis revealed no major differences compared to the ungrounded samples.

TC and TN were determined at the Soil Department, Swedish University of Agricultural Sciene, Uppsala.

4. GIS analyses

In ArcGIS 9.3 (ESRI) the catchments of the sampled streams in Örebro were assessed and the percentage of wetland areas within the catchments was determined.

5. Statistical and multivariate analyses

With respect to the quality verification of the THg and MeHg concentrations in Örebro more detailed information can be found in Eklöf et al. (in prep). Furthermore, the THg and MeHg values obtained in the Balsjö catchments were already published in several articles (Sörensen et al., 2009a; Sörensen et al., 2009b) and therefore not further verified.

Statistical analysis was carried out in JMP 8 (SAS). Regression analyses was done by Pearson bivariant analyses using the coefficient of determination (r^2) and the significance of the regression (F-test, $p<0.05$). In order to assess differences between the sampling catchments in Örebro and Balsjö a non-parametric Wilcoxon/Kruskal-Wallis test was carried out and sample groups were significantly different when $p<0.05$.

Differently modified data sets were used in this study depending on the research question. The unmodified data set of both sites was used to analyze and compare the time series data as well as to assess the correlation among data. As the sampling frequency was much higher in Balsjö during spring flood that would have biased a comparison with the southern catchments, the episode samples were removed. The data sets of Örebro and Balsjö were analyzed with randomized intervention analysis (RIA) (Sörensen et al., 2009a; Sörensen et al., 2009b; Eklöf et al., in prep.). These data sets were used when chemistry concentrations were compared and also for the calculation of the volume weighted concentrations (VWC). A linear interpolated data set (interpolated values of THg, MeHg and TOC) was used for the calculation of the seasonal export

Multivariate analysis was carried out in Simca-P$^+$ 12.0.1 (Umetrics). Partial Least Squares (PLS) regressions 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 (Wold et al., 2001; Amaral & Ferreira, 2005). In its basic principle PLS creates orthogonal score vectors (latent vectors) by maximizing the covariance between different X and Y variables (Rosipal & Krämer, 2006).

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 the most significant influence on the model and are most relevant for explaining the variation of Y where as values higher than 0.7 are considered important (Eriksson et al., 1999; Lepori et al., 2005).

In this study the influence of the multivariate dataset of each catchment on THg (Y), and MeHg (Y) was assessed as well as the influence of the division Balsjö (northern catchments) and Örebro (southern catchments) differentiated according to treatment or reference catchments on THg (Y) and MeHg (Y). The PLS models were made in two steps; from the first model with all variables included the variables with a VIP higher than 1 were chosen to make up the final model. Weekly flow and temperature values were calculated of the 7 days before the sampling date in order to assess if previous events influenced THg and MeHg concentrations. Soil temperature was not included in the PLS analysis in Balsjö.

In order to visualize the effect of flow on THg and MeHg concentration, the flow rates (specific discharge) were divided into low flow (< 1 mm/d), intermediate flow (1 – 5 mm/d) and high flow (> 5 mm/d) (Sörensen et al., 2009b). Also the change in flow varying with temperature as well as the influence of temperature on THg and MeHg concentrations was assessed according to the different seasons: spring (March, April, May), summer (June, July, August), autumn (September, October, November) and winter (December, January, February).

6. Riparian Profile Flow-Concentration Integration Model (RIM)

RIM is a conceptualization how the riparian soil solution profile concentration is exported to the stream depending on the lateral water flow (Bishop et al., 2004; Seibert et al., 2009; Winterdahl et al., 2011). The Stream flow Q can be linked to the ground water table level in the RZ with an exponential function from which the lateral groundwater flow q(z) that is needed in the RIM approach, can be derived (Grabs, 2010) (**Figure 2** (left panel)).

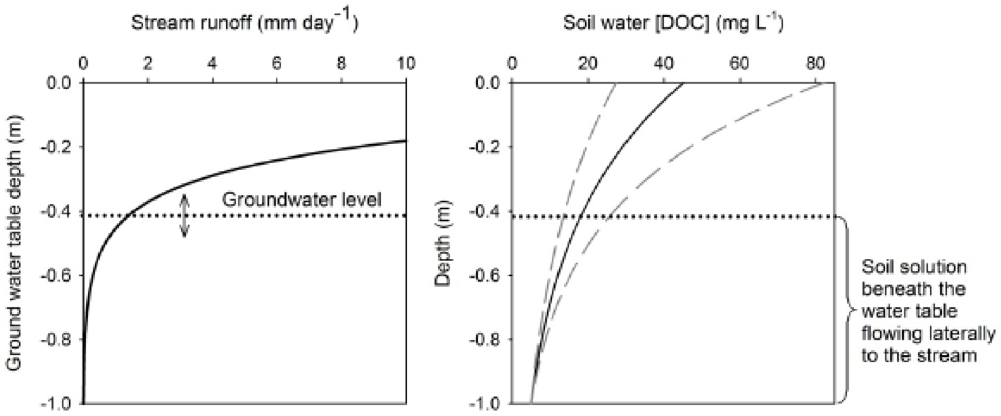


Figure 2: Schematic principle of RIM. The left panel shows the relationship between flow and groundwater level and the right panel shows the concentration variation of DOC with soil depth, whereby the dashed lines indicate the differences in the *f*-factor (Agren et al., 2010)

The stream water load (L) can be modeled (exponential relationship) by multiplying the lateral water flux at a certain depth *z* $q(z) = ae^{bz}$ (**Figure 2**, left panel) with the concentration of the soil water at that depth $c(z)=c_0e^{fz}$ (**Figure 2**, right panel) followed by the integration over these lateral mass fluxes over depth from a certain base level z_0 to the groundwater table, z_1 (**Equation 1**), whereby *a* and *b* are parameters estimated from the functional relationship between groundwater level and stream flow, *f* is a shape factor that describes the changes of concentration with depth in the soil water profile, and c_0 is the base concentration at depth 0 (Seibert et al., 2009; Bishop et al., 2004).

$$\mathrm{L}=\int_{z_0}^{z_1} ae^{bz}c_0e^{fz}dz \qquad \textbf{(1)}$$

The analytical solution of this equation is presented in **Equation 3**, whereby a new parameter η is introduced (**Equation 2**) (Seibert et al., 2009).

$$\eta=\frac{b+f}{b} \qquad \textbf{(2)}$$

$$L=c_0\frac{(a/b)^{1-\eta}}{\eta}Q^{\eta} \qquad \textbf{(3)}$$

In this study we suggested that the mobilization of THg and MeHg follows the same assumption as for TOC in the RIM model calculations (Agren et al., 2010; Winterdahl et al., 2011). Even though hydrology may be a key factor in controlling DOC and other solute concentrations, it is not the only factor explaining the chemistry variations in stream water (Agren et al., 2010). Consequently, RIM was applied on TOC, THg and MeHg in order to (i) remove the hydrological effect (static RIM) and (ii) to determine to what extent other factors such as seasonality influenced TOC, THg and MeHg concentration at each site (dynamic RIM).

As mentioned above two different RIM model approaches were applied in this study: static and dynamic. In the static RIM ($\mathrm{RIM}_{\mathrm{static}}$) the f-factor (shape of the profile) and c_0 (base concentration) are constant over time and hence the model can be simplified to a rating curve (discharge vs. ground water level). In the dynamic RIM ($\mathrm{RIM}_{\mathrm{dyn}}$) the soil solution concentration profile changes with time which is given by a varying f-factor and changes in $c_{0.}$ $\mathrm{RIM}_{\mathrm{dyn}}$ is able to better simulate the seasonal variation in stream water concentrations by establishing e.g. a seasonal depending function for f and c_0 (Winterdahl et al., 2011).

In total 4 different models were produced for each catchment site in Balsjö and Örebro: (i) $\mathrm{RIM}_{\mathrm{static}}$ only taking into account variations in stream flow, (ii) $\mathrm{RIM}_{\mathrm{dyn}}$c0 with varying base concentration (c_0) linked to a sine function, (iii) $\mathrm{RIM}_{\mathrm{dyn}}$f incorporating variations in the f-factor (sine function) and (v) $\mathrm{RIM}_{\mathrm{dyn}}$c0+f with variations in both f-factor and base concentration (c_0) (sine function). For all models ($\mathrm{RIM}_{\mathrm{static}}$ and $\mathrm{RIM}_{\mathrm{dyn}}$) and all catchments the same hydrological parameters a (0.1) and b (0.5) were used. The models for NorthCC were calculated with a slightly different specific discharge. Furthermore, the model efficiency was assessed with the Nash-Sutcliffe coefficient (NSC, Nash & Sutcliffe, 1970), whereby the NSC ranges from -∞ (poor fit) to 1 (perfect fit) (Carruba, 2000). The models were classified as behavioral when NS was above 0.2 (Winterdahl et al., 2011).

III RESULTS

1. General characteristics of seasonal factors, Hg and general chemistry in the study catchments

1.1. Hydrology

The measured mean specific discharge at the Balsjö sites (2004-2010) were 1.31±1.86, 1.07±1.79 and 0.76±1.83 mm/d for the CC, NorthCC and Ref-S catchments. In Örebro (2006-2009) the flow was 1.39±1.56, 1.49±1.45 and 1.27±1.56 mm/d for the sites R1, SP and SH, respectively.

The yearly specific discharge between Balsjö (383±667 mm/yr, 2004-2010) and Örebro (503±554 mm/yr, 2006-2009) was significantly different (Wilcoxon test, $p < 0.0001$) and showed a significantly higher variation in Balsjö (Welch test, $p<0.0001$). The highest annual discharge in Balsjö (638±649 mm/yr in CC, 481±959 mm/yr in NorthCC and 441±1062 mm/yr in Ref-S) occurred in 2006 (CC) and 2009 (NorthCC and Ref-S). At the Örebro sites the highest stream discharge was recorded in 2008 (649±573 mm/yr in R1, 609±551 mm/yr in SP and 532±613 mm/yr in SH).

In Örebro 60 – 68 % of the total flux[1] was in the intermediate (1 – 5 mm/d) flow range at all three sites and the high and low flow events accounted for approximately 15 – 20 % each. At CC and NorthCC, respectively, 52 and 46 % of the total flow were accounted to intermediate flow events and about 23 – 29 % accounted for low (< 1 mm/d) or high (> 5 mm/d) flow. At Ref-S, however, 37 % of the total flow was attributed to intermediate flow, whereas high and low flow accounted for 34 and 29 % respectively.

Low flow events occurred in Balsjö during winter periods (CC: 0.77±0.73, NorthCC: 0.46±0.67 and Ref-S: 0.23±0.42 mm/d), whereby the streams in Örebro were characterized by summer low flow (R1: 0.55±0.75, SP: 1.10±1.26 and SH: 0.65±1.12 mm/d) (**Figure 3**). At the Balsjö catchments about 20 % of the annual discharge was released in May, which is attributed to the snowmelt. In Örebro the months November and December contributed with a proportion of 15 and 16 %, respectively, to the annual flow. The large standard deviation of the flow at Balsjö in Spring/Summer was attributed to the large difference between event flows, lower flow periods and differences in the annual flows.

---

[1] Based on the share of the grouped parameter “low”, “intermediate” and “high” flow of the total sum of all groups together

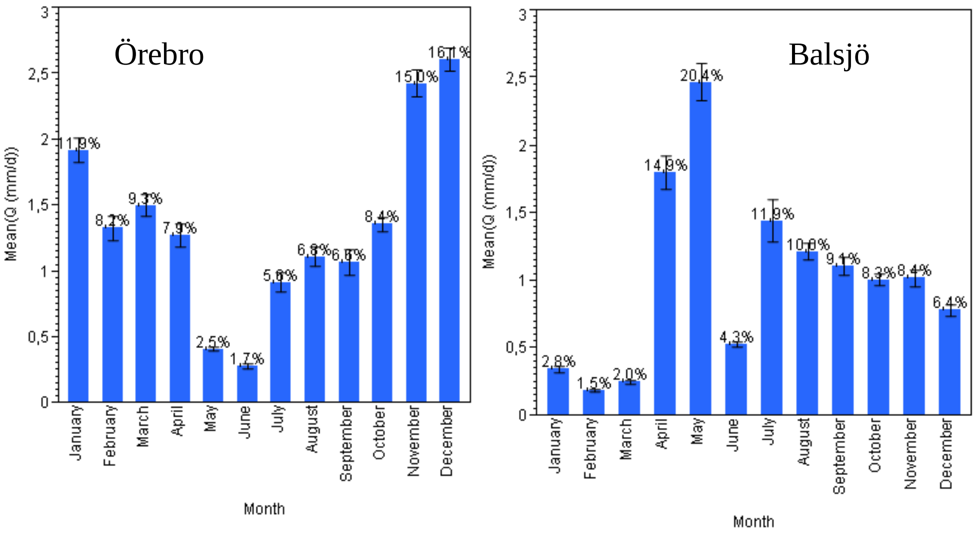


Figure 3: Mean specific discharge with % of total mean flow during the monitoring period in Balsjö (left) and Örebro (right)

Flow duration curves were calculated to compare the hydrologic response of the streams (**Figure 4**). The curves for the sites in Balsjö were very steep within the first 10 % of exceedance whereby extreme values occured around 30 – 35 mm/d. The curves for the sites in Örebro are less steep especially in the first 10 % of the curve with maximum values occurring around 10 – 13 mm/d. A higher sensitivity to rainflow events was indicated in the Balsjö area by the steep high flow region of the duration curve within the first 10%. Summer/Winter low flow with the possibility of intermittent stream flow was displayed by a flat low flow region. The stream response in Balsjö was somewhat flashier with higher maximum flow in the upper 1% of the flow distribution and a comparatively low base flow.

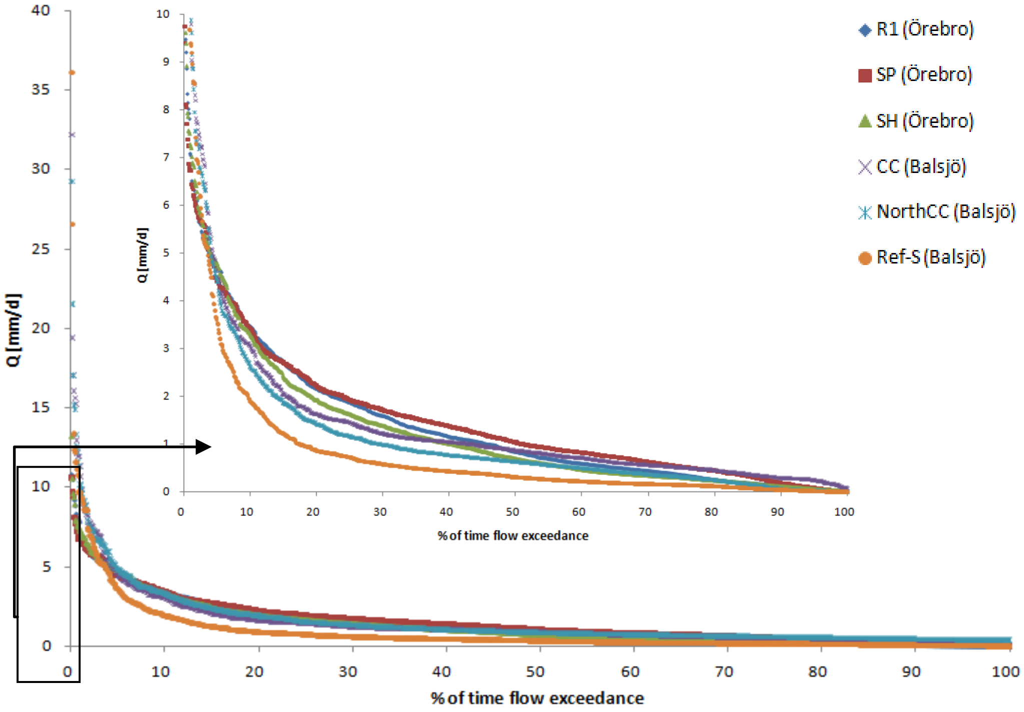


Figure 4: Flow duration curves for the streams in Örebro (SP, SH, R1 all n=1165) and Balsjö (CC n=1165, NorthCC n=1165, Ref-S n=1063) from October 2008 until December 2009

1.2 Temperature and precipitation

The air temperatures and precipitation data were the same for all sub-catchments in Örebro and Balsjö, respectively (**Table 1**). The mean temperature and precipitation values (see chapter II) were significantly higher at Örebro (Wilcoxon test, precipitation: p<0.001; air temperature: p=0.013).

In January and July the mean temperatures (May 2004 – November 2009) were -6.39°C and 13.71°C in Balsjö and the highest and lowest recorded daily temperatures over the study period were 20.53°C and -24.03°. In Örebro (October 2006 – December 2009), the average temperatures in January and July were -1.17°C and 15.56°C with 23.5°C and -14.66° as the maximum and minimum recorded temperatures.

Table 1: Seasonal precipitation and air temperature values of Balsjö and Örebro

	Balsjö	**Örebro**
Air Temperature [°C]		
Spring	0.93±6.08	5.76±5.13
Summer	12.53±3.02	14.76±3.16
Autumn	2.63±5.78	5.70±4.57
Winter	-6.37±5.49	-0.91±4.30
Precipitation [mm/d]		
Spring	0.95±1.97	1.23±3.50
Summer	2.75±6.10	2.62±5.07
Autumn	1.80±3.50	2.42±4.11
Winter	1.33±2.28	1.96±3.38

Soil temperature data were available for each site in Balsjö at a depth of 15, 30 and 50 cm and for the Örebro area (no site specific data available) at depths of 5, 20 and 50 cm (**Figure 5**). As the data between the sites in Balsjö did not vary significantly the data were combined across sites.

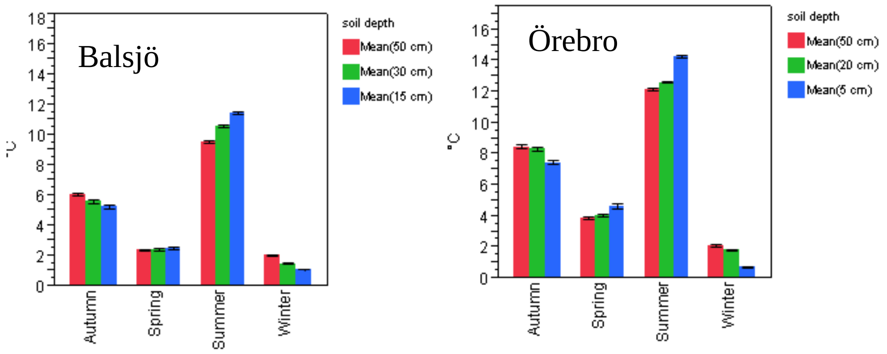


Figure 5: Soil temperature data at different depths for Örebro (left, n= 820 for each depth) and Balsjö (right, n = 700 for each depth). Temperature data were available for 29 months between July 2007 and December 2009 in Örebro and for 25 months between August 2007 and March 2010 in Balsjö.

1.3 Hg and general chemistry concentration in stream water

TOC concentrations were elevated in the Örebro catchments (**Table 2**). THg concentrations showed the same trend and were especially in SP and SH nearly double the concentrations recorded in the Balsjö areas. MeHg concentrations were 3 – 4 times higher in Örebro than in Balsjö. This was further confirmend when looking at the MeHg/THg ratio, which was elevated in Örebro and suggested a higher MeHg production. The THg/TOC ratio was rather similar for the two study catchments besides for SP and SH.

The total suspended solids (TSS) concentrations were higher at the sites in Balsjö than in Örebro. Moreover, the reference site Ref-S showed a very high TSS concentration. The absorption (420 nm) was higher in Örebro, indicating a higher fraction of humic (colored) substances in the stream water. However, when looking at specific absorption coefficient (Abs filt/TOC) the colored fraction of TOC was the same at all sites. In general all nutrients (N_{tot} and P_{tot}) as well as sulfate concentrations were higher at the Örebro sites. The nutrient leaching was higher in the treated areas than in the reference sites in Örebro. The same observation could not be clearly made for the sites in Baljö.

The C/N_{org} ratio was lower in the southern catchments suggesting a better carbon quality and implying a better microbiological available carbon and nitrogen source.

Table 2: Average concentration of selected chemical variables between October 2007 to December 2009 in Örebro and May 2004 to May 2010 in Balsjö

	Balsjö			**Örebro**			
	CC	*NorthCC*	*Ref-S*	*R1*	*SP*	*SH*	*R2*
TOC [mg/L]	20.47±11.20	20.11±8.60	19.53±9.41	24.42±9.56	28.63±12.93	26.33±9.99	23.25±10.52
THg [ng/L].	5.12±2.49	5.48±2.20	4.92±1.89	6.88±4.67	10.36±4.32	8.35±3.69	5.60±2.52
MeHg [ng/L]	0.46±0.64	0.47±0.49	0.39±0.34	0.90±0.57	1.71±1.03	0.98±0.59	0.99±0.52
THg/TOC	0.27±0.09	0.28±0.09	0.28±0.10	0.27±0.06	0.38±0.12	0.31±0.06	0.25±0.06
MeHg/THg	0.09±0.10	0.09±0.09	0.09±0.07	0.14±0.06	0.17±0.07	0.11±0.03	0.18±0.05
THg/Abs filt	12.47±4.38	12.84±3.85	13.80±5.51	12.07±2.77	16.23±4.32	15.39±2.72	12.77±3.12
*							
TSS [mg/L]	15.34±7.15	15.32±7.73	25.98±36.80	0.99±0.71	8.00±10.49	3.80±9.27	10.29±20.06
Absorbtion unfilt.	0.54±0.25	0.53±0.17	0.52±0.18	0.59±0.28	0.71±0.30	0.60±0.31	0.53±0.32
Absorbtion filt.	0.43±0.22	0.43±0.17	0.40±0.19	0.56±0.26	0.67±0.29	0.56±0.28	0.47±0.26
pH	5.19±0.74	5.05±0.69	5.23±0.89	5.23±0.47	5.21±0.37	4.76±0.21	4.77±0.16
$SO4^{2-}$ [mg/L]	1.39±0.26	1.32±0.30	1.35±0.34	2.87±1.00	3.55±0.88	3.19±1.36	2.81±1.62
N_{tot} [mg/L]	0.61±0.30	0.37±0.14	0.36±0.13	0.63±0.30	1.68±0.57	0.98±0.33	0.62±1.01
NO_3+NO_2 [µg/L]	188.33±201.3	16.57±22.13	24.56±21.37	35.43±33.14	729.8±470.4	273.6±269.3	9.73±1.41
NH_4 [µg/L]	35.91±56.53	13.21±7.68	12.30±6.44	39.50±38.99	149.9±129.5	50.79±31.15	23.41±66.99
P_{tot} [µg/L]	23.28±15.05	21.70±15.37	20.69±46.94	19.69±17.66	108.9±45.83	41.13±21.14	26.34±33.20
Fe [mg/L]	0.86±0.37	0.81±0.28	1.2±0.57	0.79±0.43	0.46±0.24	0.61±0.36	0.93±0.80
C/N_{org}	53.01±20.13	60.99±18.81	61.13±17.99	45.35±5.38	37.12±8.31	41.00±4.85	48.94±7.34
Abs fil/TOC	0.022±0.003	0.022±0.003	0.02±0.003	0.022±0.003	0.02±0.003	0.023±0.003	0.019±0.003

2. Seasonal dynamics of MeHg, THg and TOC

2.1 Seasonal distribution of THg, MeHg and TOC

2.1.1 Concentration and volume weighted concentrations (VWC)

The volume weighted concentrations (VWC) are especially important for downstream biota as the concentration is given in relation to the flow. VWC were calculated as followed, whereby c_i is the concentration Q_i is the flow for an observed period:

$$VWC = \frac{\sum (c_i * Q_i)}{\sum Q_i} \qquad \textbf{(4)}$$

In Balsjö the distribution of THg during the year was rather homogenous with lower concentrations and VWC in Winter (**Figure 6**). The distribution of THg showed a clear seasonality in Örebro.

In Balsjö, the highest mean concentration (VWC) of THg occurred during Summer and were 6.02 ng/L (8.12 ng/L) and 6.46 ng/L (8.33 ng/L) for CC and NorthCC, respectively. At Ref-S the highest mean concentrations were equally distributed between Summer (5.42 ng/L) and Autumn (5.44 ng/L), however the VWC was highest during Summer (7.68 ng/L). In Örebro, there was a clear peak of concentrations and VWC during the Summer period which were 11.79 ng/L (12.36 ng/L, VWC), 15.27 ng/L (16.75 ng/L, VWC) and 13.38 ng/L (12.01 ng/L, VWC) for R1, SP and SH, respectively. Hence, nearly half of the annual THg concentrations were found during the Summer months (R1=42.8%, R2=39.9%, SH=40.2% and SP=36.8% of the total mean THg concentration for each site). The lowest THg concentrations occurred at both Balsjö and Örebro in Winter and the share of the annual total concentrations ranged from 16.8 – 18.9 % in Balsjö and from 14.6 – 18.6 % in Örebro. In the Winter months in Balsjö concentrations and VWC varied between 3 – 4 ng/L, whereby VWC were elevated. In Örebro during the same period of the year THg concentrations and VWC ranged from 5 – 7 ng/L and for all sites besides R1, VWC were lower than mean concentrations.

TOC followed in general the same trend as THg concentrations and VWC with also highest concentration in Summer and lowest in Winter at both major study sites. However, in Örebro also quite low TOC concentrations and VWC occurred during Spring, whereas in Balsjö VWC were elevated during Spring compared to mean concentrations.

The seasonal distribution of MeHg concentrations and VWC showed a clear peak during Summer for both major study sites (**Figure 7)** and MeHg mean concentrations were mostly higher than VWC (not SP). For CC, NorthCC and Ref-S the mean concentrations (VWC) were 0.77 ng/L (0.53 ng/L), 0.74 ng/L (0.57 ng/L) and 0.65 ng/L (0.36 ng/L) and contributed with 44.8%, 42.2% and 43.0% to the annual share of total mean concentrations. MeHg oncentrations (VWC) were higher in Örebro compared to Balsjö and showed values of 1.59 ng/L (1.19 ng/L), 1.62 ng/L (2.44 ng/L) and 1.67 ng/L (1.35) ng/L for R1, SP and SH. Furthermore, summer MeHg concentrations accounted for 44.9 (R1), 42.4 (SH) and 36.57 % (SP) of the total mean concentrations.

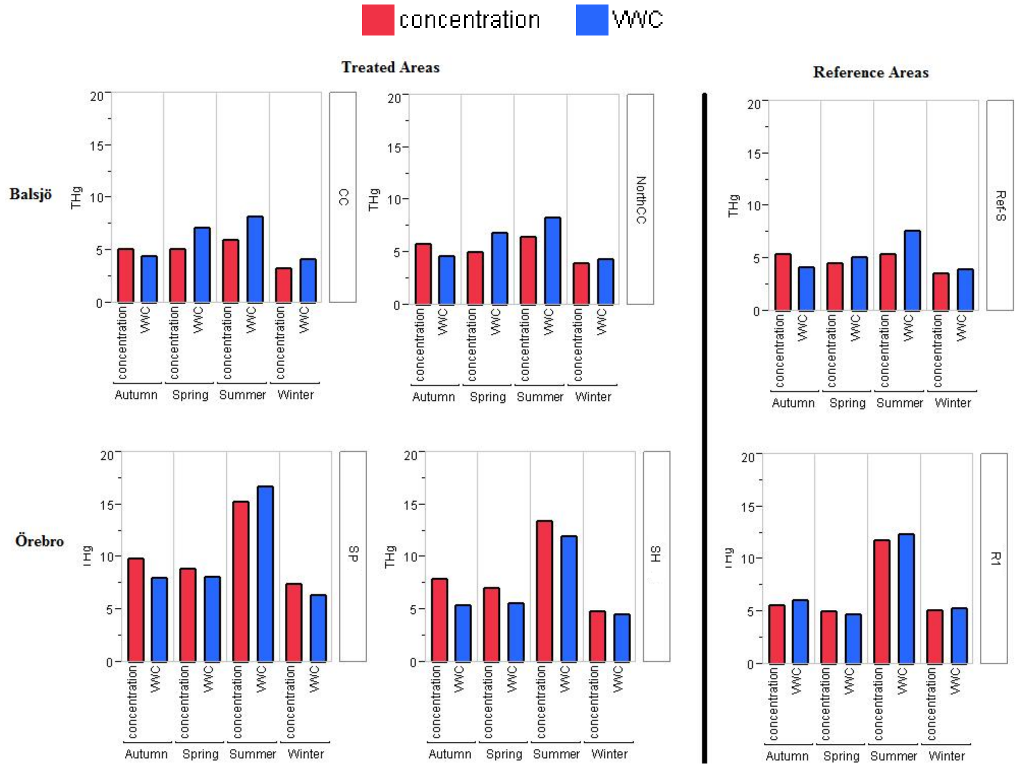


Figure 6: Seasonal disbribution of THg concentration and VWC (Balsjö: autumn: n=87, spring: n=110, summer: n=94, winter: n=47; Örebro: autumn: n=67, spring: n=58, summer: n=49, winter: n=44)of the two study sites grouped according to treated and untreated areas.; Site R2 (Örebro) not present as no flow data were available

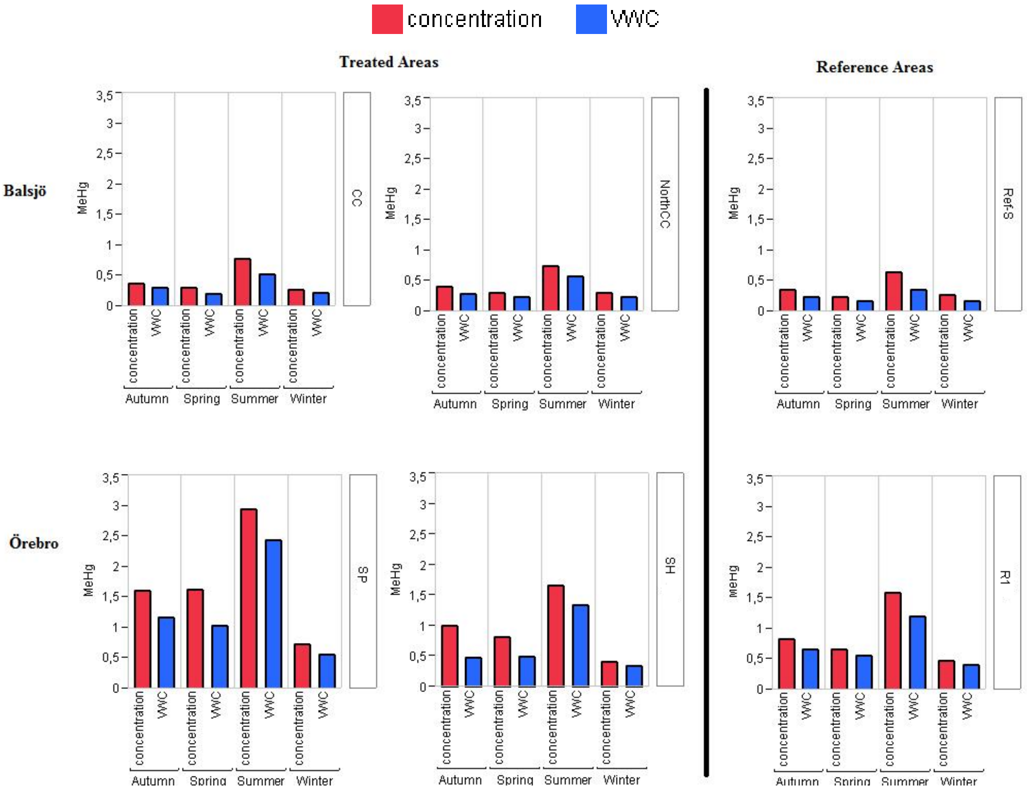


Figure 7: Seasonal disbribution of MeHg concentration and VWC (Balsjö: autumn: n=87, spring: n=110, summer: n=94, winter: n=47; Örebro: autumn: n=67, spring: n=58, summer: n=49, winter: n=44)of the two study sites grouped according to treated and untreated areas.; Site R2 (Örebro) not present as no flow data were available

2.1.2 Mercury fluxes over the vegetation periods

The export of THg, MeHg and TOC was in general higher in Örebro than in Balsjö, although the exports of THg and MeHg from CC (Balsjö) were in the same magnitude as the export from the Örebro catchments (**Table 3**). Especially, the MeHg export was distinctively elevated in Örebro with site SP exhibiting the maximum stream export (19.49±20.00 µg/d*ha). The standard deviation for the sites in Balsjö was significantly higher to the ones in Örebro (Welch test, $p<0.0001$).

Table 3: Mean daily export of THg, MeHg and TOC for Örebro (Oct. 2007 – Dec. 2009) and Balsjö (Apr. 2005 – Jan. 2010).

	Balsjö			**Örebro**		
	CC	*NorthCC*	*Ref-S*	*R1*	*SP*	*SH*
THg [µg/d*ha]	91.97±207.07	71.91±167.81	51.53±166.21	83.25±103.37	137.89±147.39	82.28±122.43
MeHg [µg/d*ha]	6.60±18.85	4.46±9.75	2.22±5.58	8.65±8.77	19.49±20.00	7.68±8.62
TOC [g/d*ha]	335.39±624.02	248.53±481.36	182.94±506.06	304.87±360.42	405.50±418.55	281.16±369.8

In Balsjö the export of THg (**Figure 8,** lower figure) was highest during Spring (142.99±276.80 µg/d*ha in CC, 102.18±223.27 µg/d*ha in NorthCC and 87.86±212.16 µg/d*ha in Ref-S). In Örebro the stream export of THg was more equally distributed between the vegetation periods, whereby highest fluxes occurred in R1 in Winter (119.86±91.06 µg/d*ha), in SH in Autumn (100.99±153.39 µg/d*ha) and in SP in Summer (165.33±192.25 µg/d*ha).

The distribution of MeHg between the seasons followed a more distinctive pattern in Balsjö (**Figure 8,** upper figure) with highest export in Summer. At Balsjö the highest flux of MeHg varied between 4 – 12 µg/d*ha in Summer depending on the site, whereby CC had the highest export (11.97±33.43 µg/d*ha). At site CC (NorthCC and Ref-S) about 45 % (43 and 41 %) of the total recorded MeHg export occurred during July and August. In Balsjö the highest export occurred in August 2005 at site CC with 386.84 µg/d*ha (yearly daily mean export 2005: 16.25±46.74 µg/d*ha). Hence, the export during one day was about 2000 % higher than the yearly daily mean export. It should be noted that only a few days of high flux in summer contributed to the total annual stream export in Balsjö.

From all sites in Örebro the MeHg export was highest at SP in Summer (28.95±27.04 µg/d*ha). It should be noted that at R1 the highest MeHg flux occurred in Winter (10.43±7.07 µg/d*ha).

At the catchments in Örebro the percentage of annual MeHg fluxes were quite evenly distributed over the year and only 19, 31 and 25 % of the total MeHg stream export for site R1, SP and SH were located in July and August. The highest mean daily flux occurred in Örebro at site SP in August 2008 and was 163.64 µg/d*ha (yearly daily mean export 2008: 19.04±16.90 µg/d*ha).

The pattern of TOC flowed more or less the one of THg with highest seasonal export in Spring at site CC (474.31±718.88 g/d*ha) and in Autumn at site SP (551.92±403.54 g/d*ha)

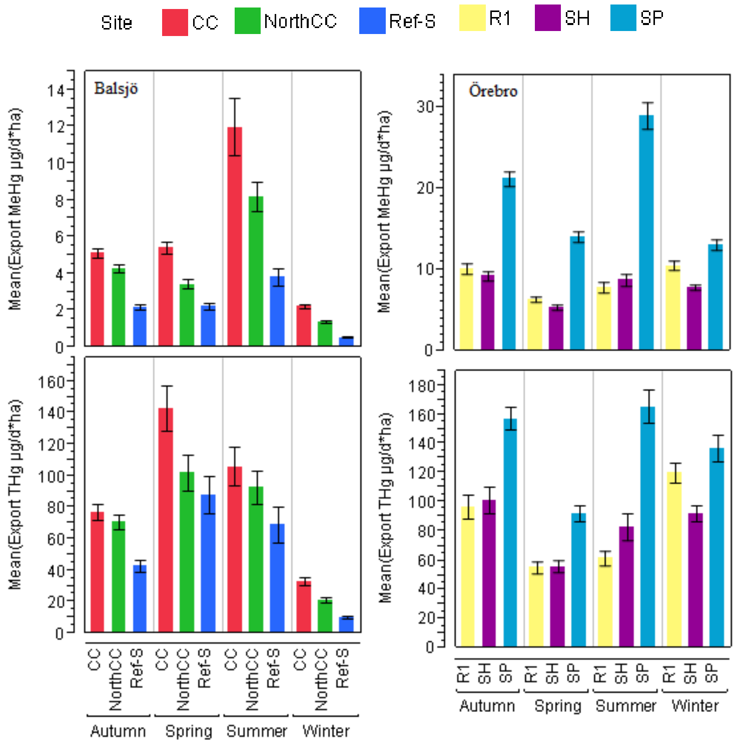


Figure 8: Mean THg and MeHg flux divided according to season. Örebro: Autumn (R1,SH, SP n=334) Spring (R1,SH, SP n=276), Summer (R1,SH, SP n=276)), Winter (R1,SH, SP n=279); Balsjö: Autumn (CC, NorthCC, Ref-S, n=598), Spring (CC, NorthCC, Ref-S, n=568), Summer (CC, NorthCC, Ref-S, n=644), Winter (CC, NorthCC, Ref-S, n=541)

2.2 Time series analysis

2.2.1 THg and TOC dynamics

The THg concentrations in Balsjö varied generally between 2 ng/L and 9 ng/L before April 2008 (**Figure 9**). The THg peaks were relatively sharp and followed the general flow pattern with highest concentrations at peak flows. After April 2008 the concentrations increased and were between 3 and 20 ng/L. TOC concentrations varied between 4 and 48 mg/L across all sites and treatments.

The Balsjö sites were harvested in March 2006 and site prepared in 2008, details about the treatments effects on THg, MeHg and TOC concentrations can be found in Sörensen et al. (2009a) and Eklöf et al (in prep.). Further details about post harvest flow increase can be found in Sörensen et al. (2009b).

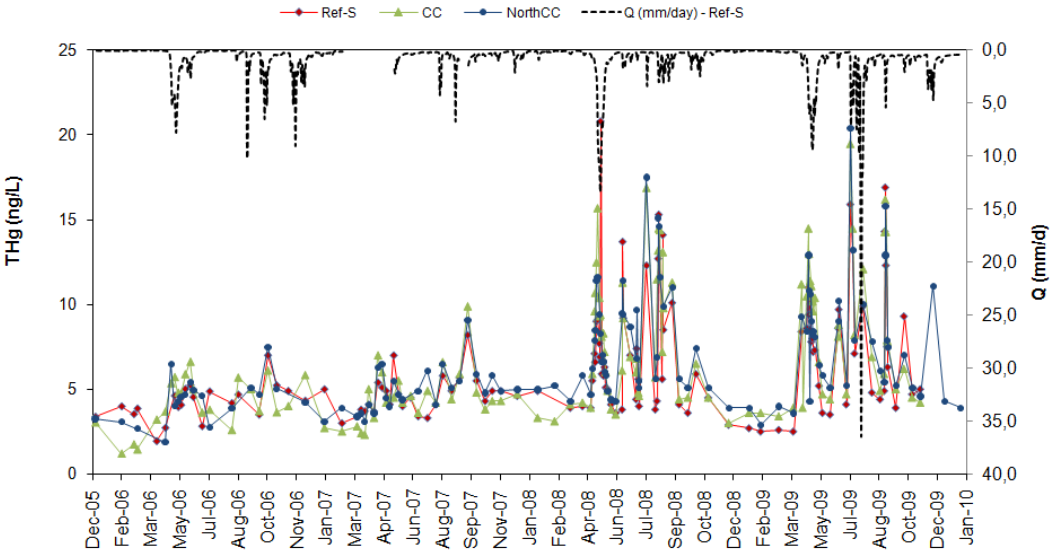


Figure 9: Time series data (Dec. 2005 – Jan. 2010) of THg concentrations across all sites in Balsjö

In Örebro, the THg (TOC) concentrations varied in general between 3 and 27 ng/L (10 – 78 mg/L) and showed a strong seasonality (**Figure 10; Figure14**). The THg peaks in Örebro were wider and not well correlating to high flow periods compared to the ones in Balsjö. Low flow events and high THg concentrations were a characteristic pattern in Summer as well as high flow and lower THg concentrations in Winter. Hence, the Örebro sites seemed to be less sensitive to flow, although elevated values occurred together with high flows in Nov/Dec 07/08 and Jul/Aug 09. It seemed that THg and TOC concentrations in the south were on a smaller scale influenced by high flow peaks.

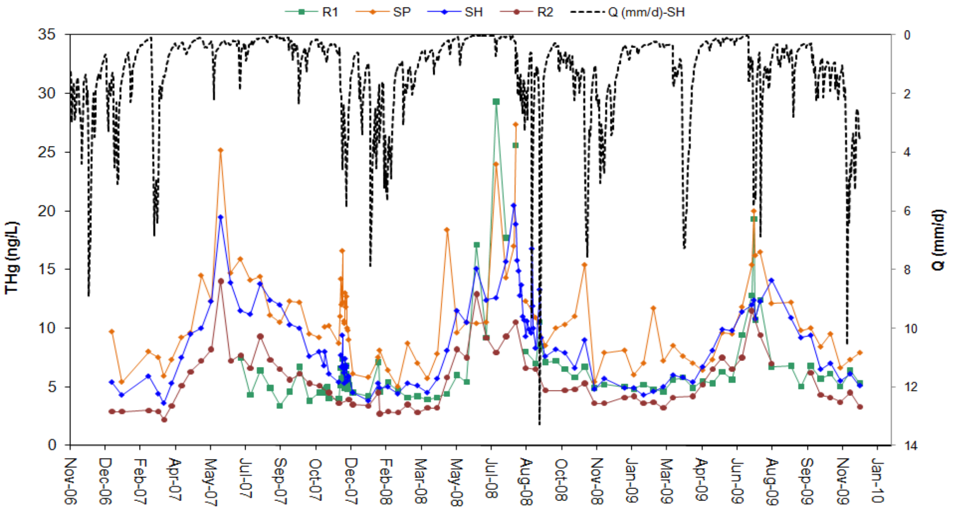


Figure 10: THg and flow dynamics (December 2006 – December 2009) of the Örebro catchments

Especially in 2007, THg declined after peaking earlier than TOC in Örebro. Otherwise THg and TOC concentrations matched very well. In Balsjö, THg and especially TOC kept on increasing after the maximum flow peak occurred. THg and TOC concentrations followed also the same pattern in Balsjö, however, THg peaked sometimes before or after TOC concentrations peaked.

The TOC and THg pattern was strongly relating at both Balsjö and Örebro (**Figure 11**). The influence of temperature on THg concentration is very well documented at Örebro as THg concentrations peaked during the highest summer temperature peak. At Balsjö THg and TOC concentrations were lower during Winter and higher in Summer, however, a clear correlation of high THg concentration and high temperatures could not be found.

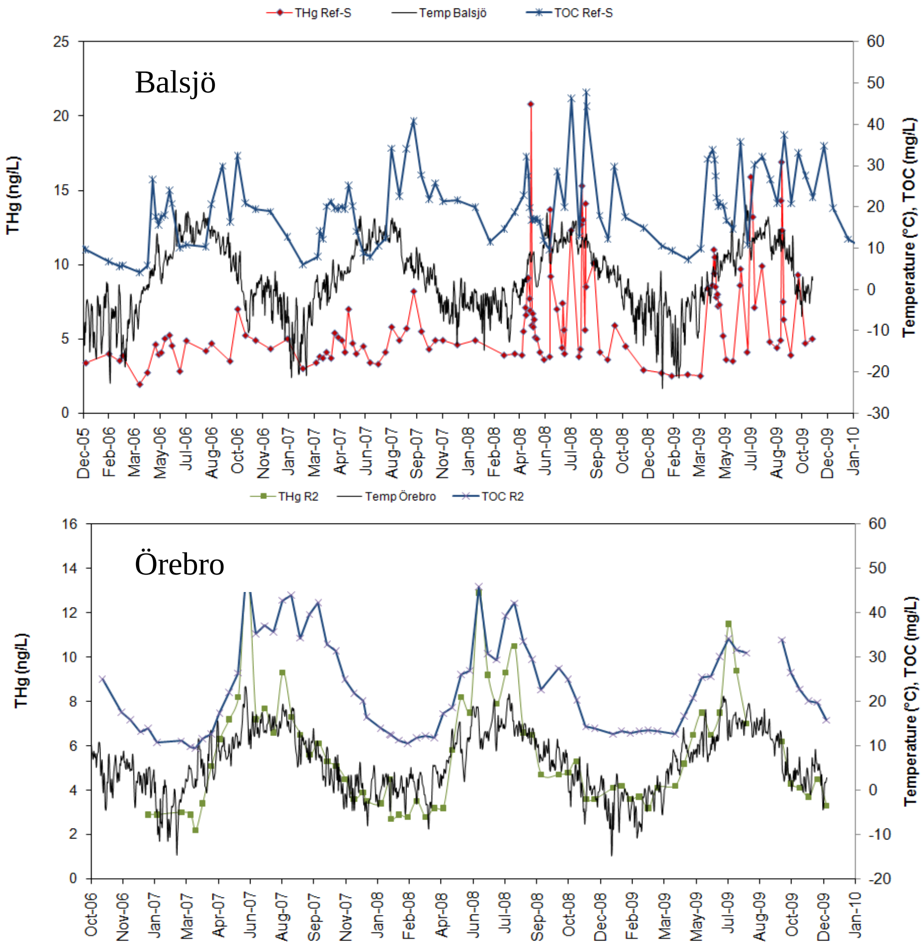


Figure 11: TOC and THg pattern for Balsjö (Ref-S) and Örebro (R2) in relation to air temperature, black line: temperature; blue: TOC, green: THg-R2, red: THg-Ref-S

2.2.2 MeHg dynamics

MeHg concentrations varied at the Balsjö sites between 0.10 and 5.5 ng/L (**Figure 12**). The peaks occurred always in the end of July, beginning of August and the highest overall recorded peak was 5.5 ng/L (CC, August 2005) compared to a relatively low mean MeHg concentration over the study period (0.46±0.64 ng/L (CC), **Table 2**). Hence, only during one day about 12 times the annual concentration was released to the stream water. As the peaks were very narrow there is a high risk that in the following years the maximum MeHg concentrations were not captured.

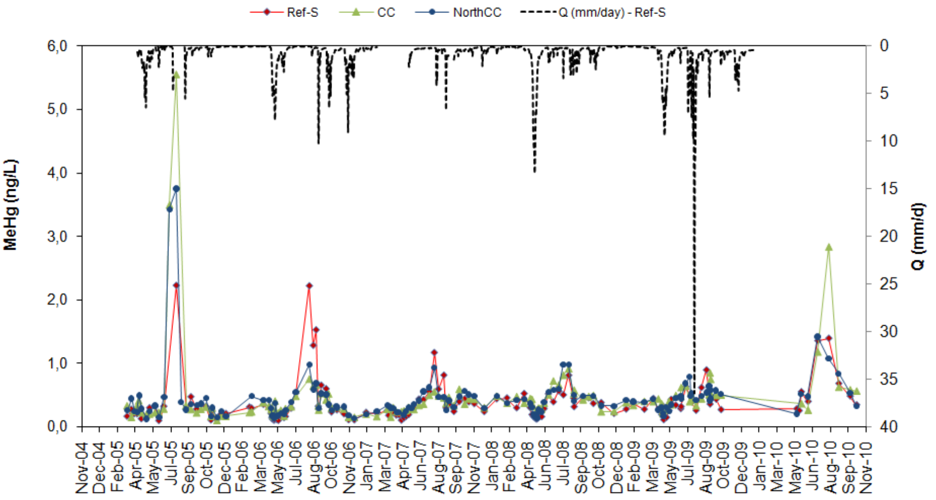


Figure 12: MeHg concentration and flow for the Balsjö sites (Mars 05 – Oct 10)

In Örebro the concentrations varied between 0.30 – 5 ng/L depending on the season and site (**Figure 13**). Mean MeHg concentrations were highest at SP (1.71±1.03 ng/L) and lowest at R2 (0.10±0.52 ng/L). The peaks were much wider than the once in Balsjö and were rising throughout Spring/Summer/Autumn and declined generally in late Autumn/Winter. The highest recorded concentrations peaked in June (R1 3.83 ng/L; SP 5.01 ng/L; R2 3.45 ng/L) and August (SH 3.00 ng/L) High MeHg concentrations at Örebro were assosicated with Summer low flow.

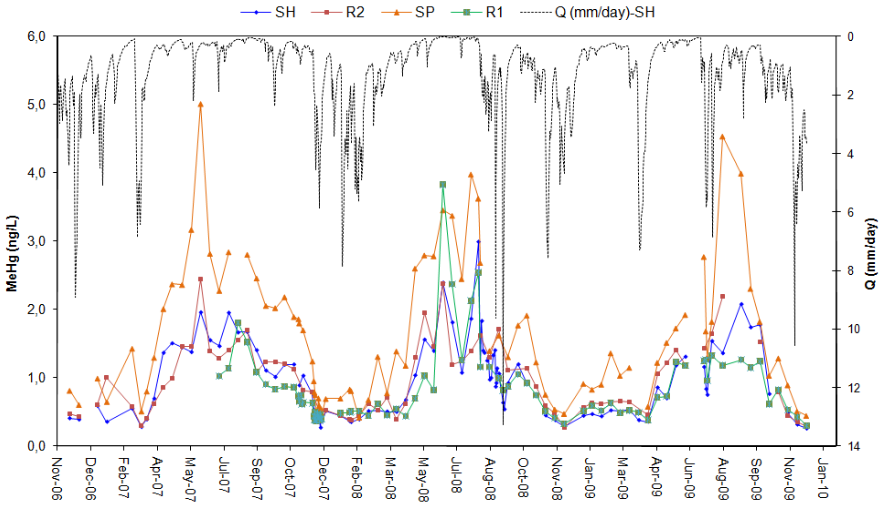


Figure 13: MeHg and flow pattern in the Örebro catchments (Nov. 06 – Dec. 09)

2.2.3 THg, MeHg and TOC episode data

Episode data were available for the sites in Örebro (**Figure 14**, 21st November – 19th December 07). TOC and THg showed a positive response to flow, whereby site SP showed the highest sensitivity towards flow. MeHg concentrations were negatively correlated to flow and hence exhibited the same pattern when analyzing the episode data as well as the whole data series.

When comparing the THg and TOC episode data with the whole time series (**Figure 14** and **10**) local THg peaks occur during high flow periods that were, however, still lower than the maximum THg concentrations during summer low flow (Eklöf et al, in prep).

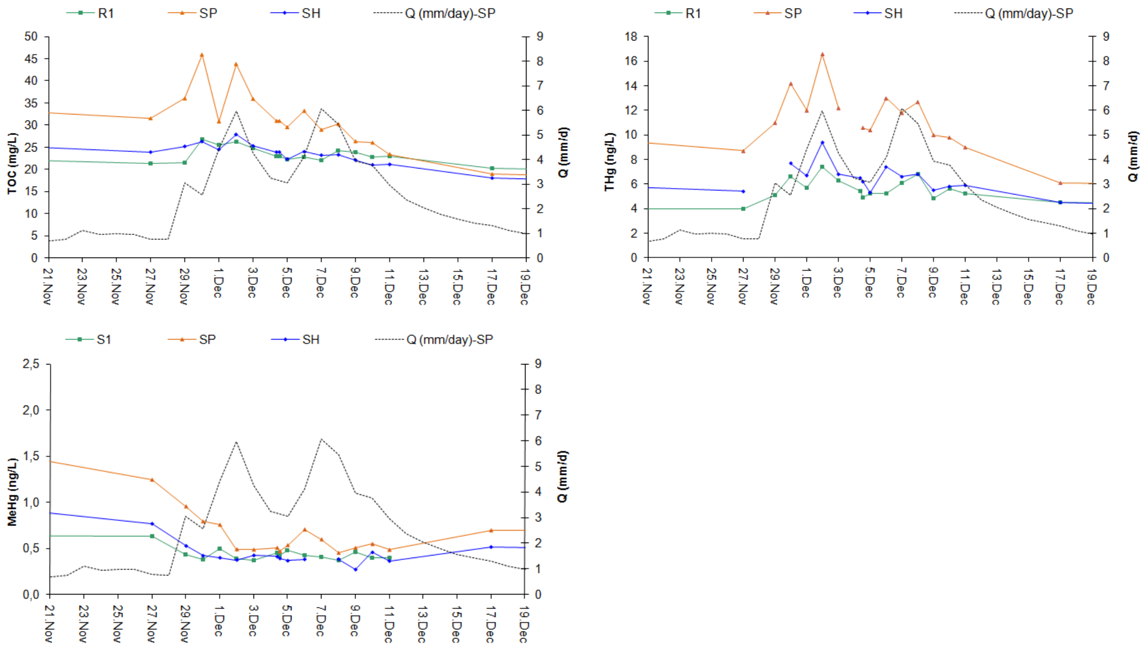


Figure 14: Episode data of THg, MeHg and TOC from 21st November – 19th December 2007

2.3 Flow and temperature effects on Hg dynamics

2.3.1 Influence of discharge rate on mercury concentrations

In Balsjö high flow was the most important transport mechanism for THg and accounted for 9.21±2.49 ng/L. Low flow seemed to be more important in Örebro (8.60±4.44 ng/L, **Figure 15**). High MeHg concentrations are in general associated with high temperatures during summer and lower flow periods. This was confirmed by the calculations in this study. TOC followed the pattern of THg, but high flow seemed to be less important for the TOC concentration in stream water at the Balsjö sites.

Single catchment analysis prior to pooling the sites together to Balsjö and Örebro (number per subgroup (high, intermediate and low flow) were not enough to justify a site specific analysis) showed that R2 and SP had a different behavior. These two catchments showed no link between high flow events and MeHg and THg concentrations.

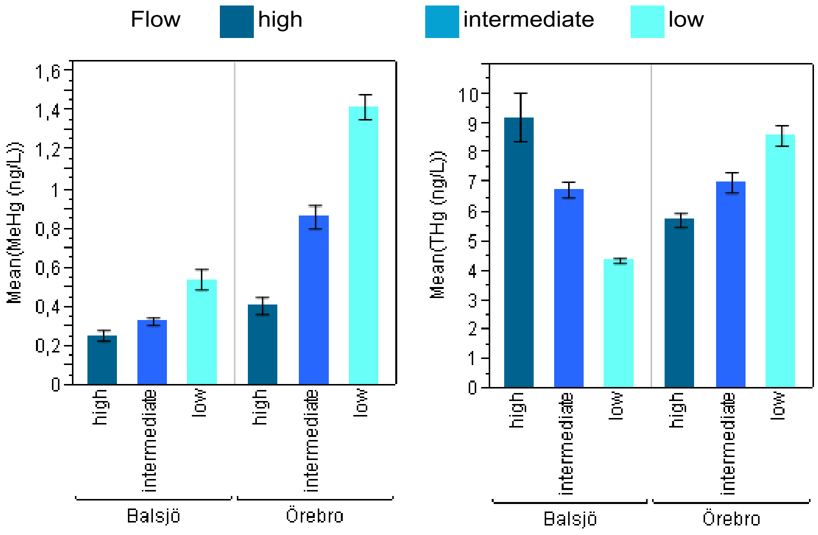


Figure 15: Analysis of THg and MeHg in relation to flow (Balsjö: high: n=13, intermediate: n=95, low: n=179, missing values: n=51; Örebro: high: n= 4, intermediate: n= 129, low=159)

2.3.2 Analysis of the RIM models and the effects of seasonality and flow

The Nash-Sutcliffe coefficient (NSC) was in general rather poor for the static RIM models (**Table 5**, appendix). However, $\text{RIM}_{\text{static}}$ was able to model the THg concentrations for the Balsjö sites as well as the MeHg concentrations for the Örebro sites (not SP) rather well. The model efficiency of $\text{RIM}_{\text{static}}$ was lower for the TOC concentrations compared to the THg concentrations in Balsjö. When plotting the model residuals of NorthCC, CC and Ref-S against flow and soil temperature the regression model showed no correlation for the residual-flow relationship, but THg TOC and MeHg residuals correlated significantly with soil temperature (15 cm). Furthermore, TOC residual at CC was also correlating significantly with air temperature (r^2=0.12, p=0.0002). In Örebro, THg, TOC and MeHg model residuals showed rather high r^2-values and significant relationships with air and soil temperature. No correlation of the model TOC, THg and MeHg residuals with flow was detected.

The dynamic RIM models gave better simulations of the concentrations in the stream water for all sites. Interestingly, the step from $\text{RIM}_{\text{static}}$ to RIM_{dyn}f or RIM_{dyn}c0 revealed a higher model improvement than from the one-parameter dynamic models to the two-parameter dynamic model (both variable f and c_0, **Table 5,** appendix). From both one-parameter dynamic models RIM_{dyn}c0 was able to better model THg, MeHg and TOC stream concentrations than RIMd$_{\text{yn}}$f.

RIM_{dyn}c0 showed for each respective major study area similar offset and amplitude values when modeling THg concentrations, whereby the highest amplitude occurred in SP (**Table 6,** appendix). The f-factor of the modeled THg concentrations was negative for R2 and SH and positive for all the other sites and the c_0-base concentrations varied more in Örebro but were in the same range in Balsjö. The model parameter for RIM_{dyn}c0 modeling MeHg concentrations showed similar results, however, all sites showed negative f-values (higher values in Balsjö than Örebro, **Table 7,** appendix). Also, the c_0-base concentrations of MeHg were grouped accordingly to Balsjö and Örebro (**Figure 16**). For TOC the offset was also in general specific regarding the two major study catchments. The f-factor showed negative values for SH and R2 (Örebro) and was positive for all the other catchments with higher values in Balsjö compared to Örebro (**Table 8**, appendix).

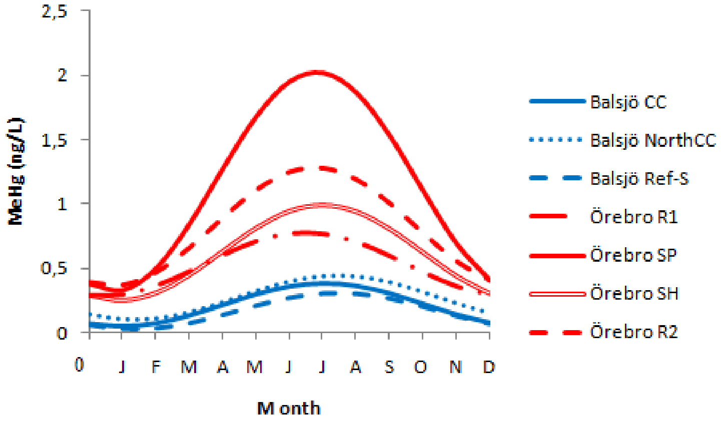


Figure 16: Modeled c0-base concentrations of MeHg over time with RIM$_{dync}$0 for the sites in Balsjö and Örebro

Modeled soil solution concentrations (RIMd$_{yn}$c0) of THg and MeHg for site CC (Balsjö) and SH (Örebro, **Figure 77**) showed similar behavior to the THg-Q and MeHg-Q relationships plotted in **Figure 24**.

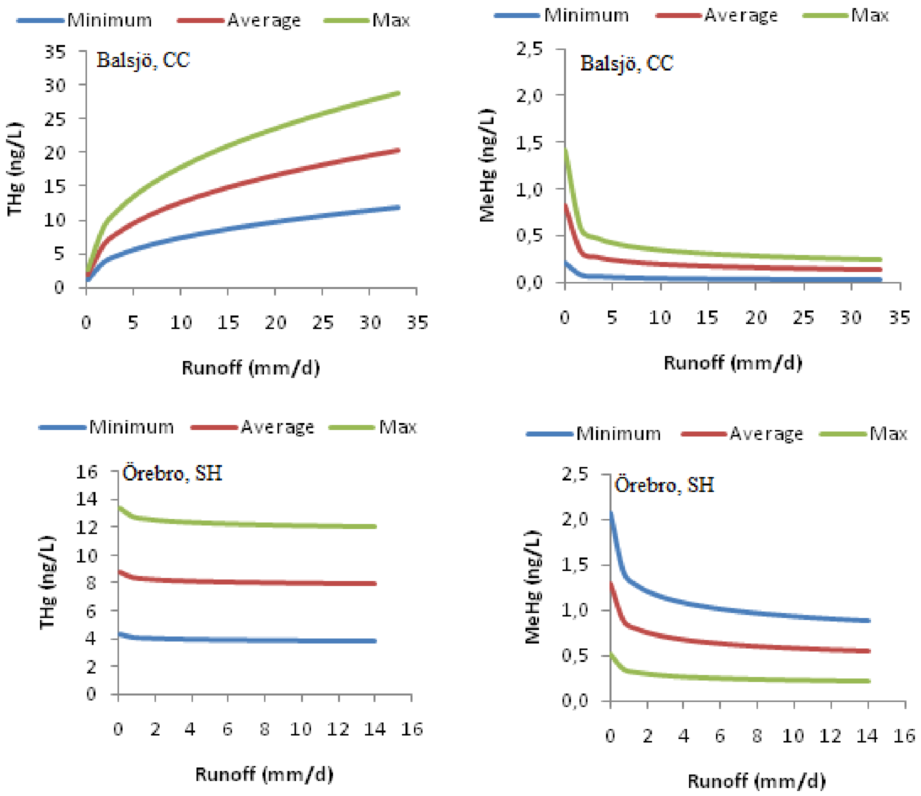


Figure 17: Modeled maximum, minimum and average THg and MeHg concentrations with RIM$_{dyn}$c0 in relation to flow. **Note: different y-axes for the THg concentrations in Örebro and Balsjö.**

3. THg soil storage in Balsjö and Örebro

The TC, TN and THg soil analysis results of Balsjö (**Table 5**) and Örebro (**Table 6**) as well as their profiles (**Figure 19**) can be seen in the appendix**.** In general, for all sites the THg concentration decreased with depth. This was not true for NorthCC (3 m) and Ref-S (21 m), where the concentration increased again at 40 – 50 cm. In Örebro distinctively higher concentrations of Hg were associated with the top organic layer that was located close to the river (**Figure 18**). The TC (%) decreased with increasing depth and Hg followed this trend. THg concentrations decreased also with increasing distance from the stream in Örebro, e. g. from 195 ng/g Hg (0-10 cm, 0.5 m, R2) to 50 ng/g (0-10 cm, 21 m, R2).

In Balsjö the % TC was rather constant for site NorthCC and Ref-S (~ 50%) but varied for site CC (**Figure 18**). The highest THg concentrations were also found in the top layer, but the variation across the soil profile seemed to be smaller compared to Örebro. Furthermore, THg concentrations seemed to be more independent of % TC in the peat soil. When THg declined with depth in NorthCC and Ref-S, % TC decreased only slightly, or increased even at some sampling distances (**Table 5**). Overall the THg soil storage was higher in Balsjö and was attributed to the high organic soil content. However, the THg/TC ratio in the soil in Balsjö was mainly varying between 0.75 and 5.78 (lower values occurred normally at deeper soil depth). In Örebro, the ratio varied between 2.0 and 24.5, whereby higher values appeared more in the lower soil depth.

The correlation of TC and TN showed for both sites in Örebro a significant positive linear trend (R2: $r^2=0.98$, n=18; SH: 0.68, n=20). For Balsjö the correlation was only significantly positive for site CC ($r^2=0.84$, n=20). At Örebro the C/N ratio was rather showing a decreasing trend with depth associated with higher THg/TC ratios. At Balsjö the trend was not so straight forward and showed decreasing as well as increasing tendencies for C/N with depth, whereby the THg/TC ratio exhibited high values in association with low C/N ratios.

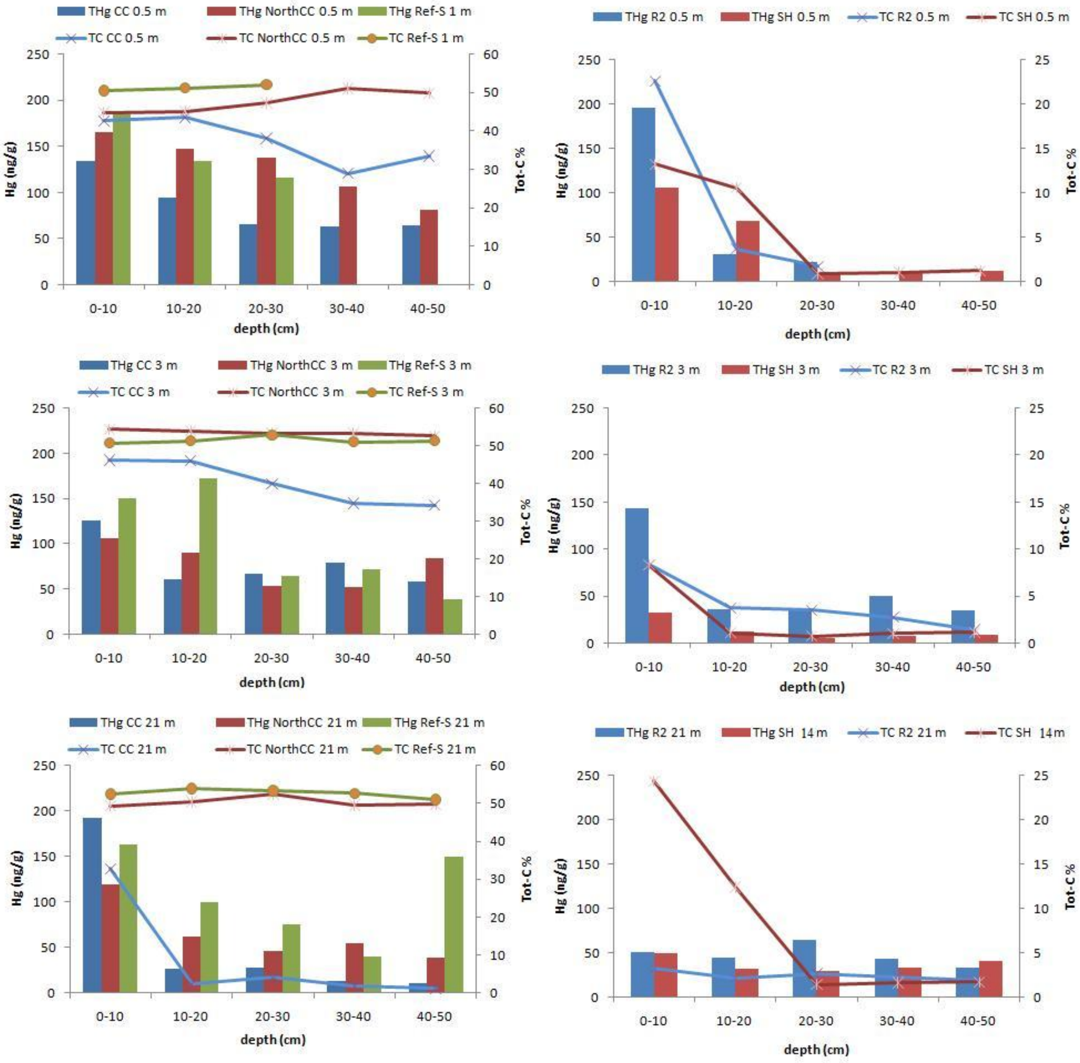


Figure 18: Total carbon (%) and Hg concentration in the soil at Balsjö (left) and Örebro (right) for the sampling points at 0.5, 3 and 21 or 14 m, Bars represent Hg levels and lines TC %, note that the scale on the TC axis is different for Balsjö and Örebro

As expected the correlation of THg and TC (%) revealed significant positive relationship for site R2 (r^2=0.85), SH (r^2=0.46) and CC (r^2=0.36) (**Figure 19**). However, for site NorthCC and Ref-S (only peat soil) THg correlated negatively with TC (%), whereby only the relationship at NorthCC was significant (NorthCC: r^2=0.45, p=0.0012).

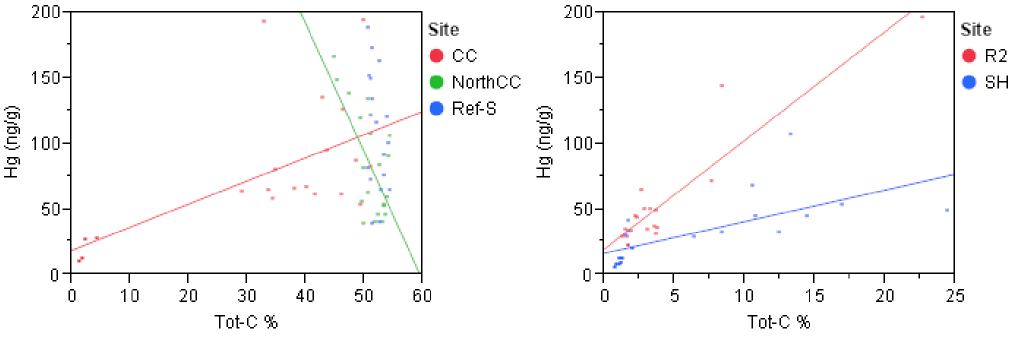


Figure 19: Correlation of THg with TC (%) for Balsjö (left) and Örebro (right)

4. Relationship of THg, MeHg and TOC and related variables

4.1 Multivariate analysis of factors influencing Hg concentrations

4.1.1 PLS analysis with THg as dependent variable

The PLS analysis with THg as dependent variable showed good Q^2 and R^2 values of around 0.8 – 0.9 for the first PLS run with the original data set in Örebro, only SP showed lower model strength of about 0.6. The 2nd cycle of the PLS analysis was also characterized by very good model strength (lower model strength for SP) and indicated that absorption (filtered and unfiltered), soil temperature, TOC, air temperature, iron, aluminum, calcium, sulfate and total phosphorous (P_{tot}) were the most important variables influencing the THg concentrations (**Figure 20**). At all sites in Örebro temperature had a very high influence, but R1 showed a rather different pattern.

The 1st cycle of the PLS analysis for Balsjö showed also a good model strength with Q^2 and R^2 varying between 0.7 and 0.9. The 2nd PLS run showed the same variation, whereby, CC had the best and Ref-S the lowest model strength. The PLS analysis showed that the weekly calculated flow, TOC, absorption (filtered and unfiltered), flow, electric conductivity (EC), mangan (Mn), total nitrogen (N_{tot}), alkalinity, aluminum, and pH were the most important variables explaining THg concentrations (**Figure 21**).

When comparing the PLS results from Balsjö and Örebro (**Figure 20** and **21)**, flow had a much higher influence at the Balsjö catchments on THg concentrations, whereby temperature was more important in Örebro.

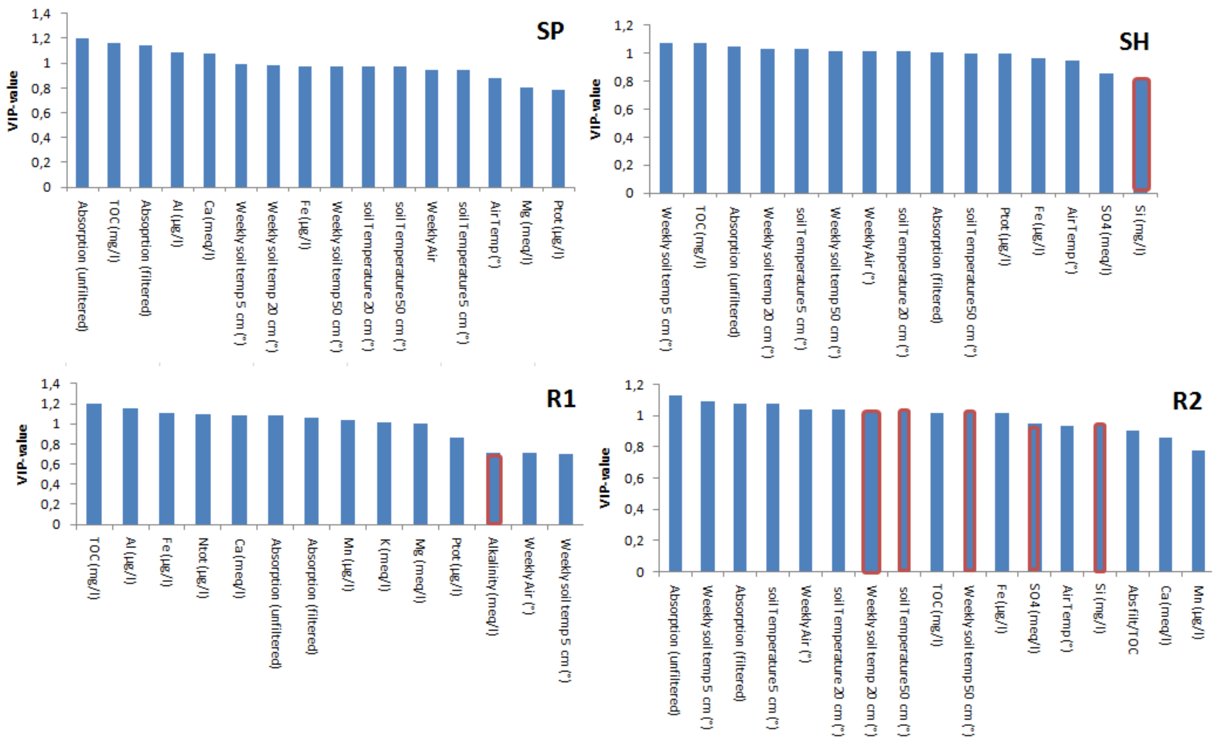


Figure 20: VIP values of the variables that highly significantly (VIP>1) influenced the response variable (Y), THg in Örebro. Entirely blue bars represent positive, red bars negative correlation

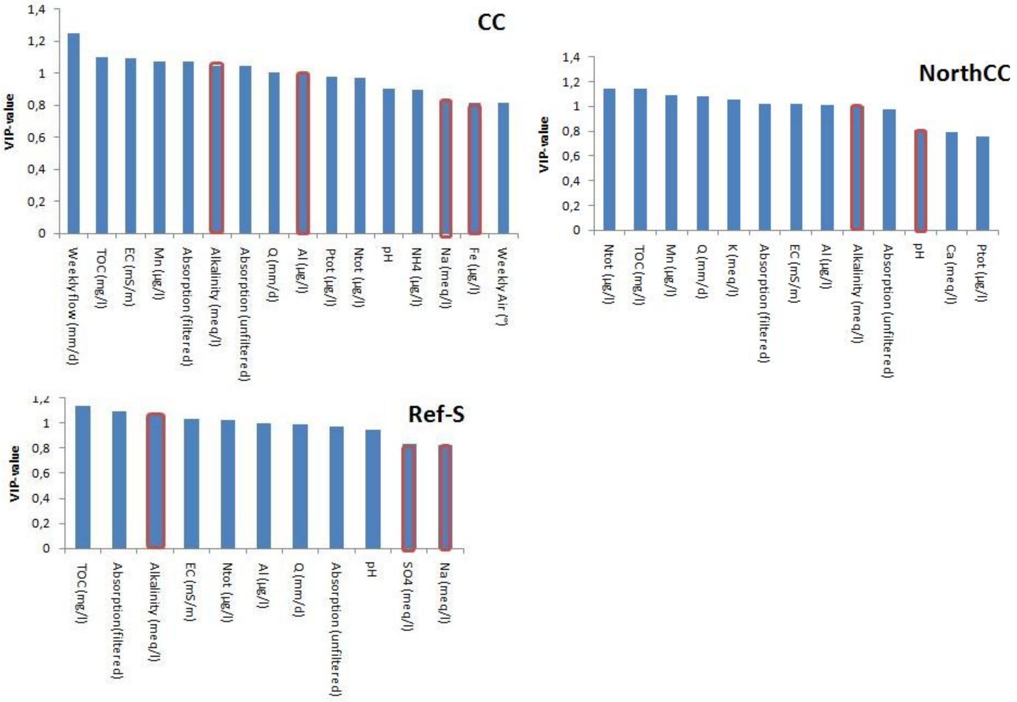


Figure 21: VIP values of the variables that highly significantly (VIP>1) influenced the response variable (Y), THg in Balsjö. Entirely blue bars represent positive, red bars negative correlation

4.1.2 PLS analysis with MeHg as dependent variable

The 1st PLS analysis of the original data set with MeHg as dependent variable was very strong in Örebro (Q^2 and R^2 ranged between 0.7 and 0.9). The 2nd cycle of the PLS analysis was also characterized by a very good model strength and soil temperature, absorption, Fe, Abs filt/TOC (specific absorption), sulfate, air temperature, Fe/TOC, P_{tot} and THg were the variables most influential for MeHg concentrations (**Figure 22**). At SP and SH also flow played a major role in explaining the variability of MeHg concentrations compared to the reference areas. Furthermore, at SH and R2 silicon (Si) also seemed to have a high importance. Weekly mean temperatures (air and soil temperature from 5 cm depth) were in general more important than the daily measured temperatures at the respective sampling date (**Figure 20, 22**). Especially at site SP (highest MeHg mean concentration, **Table 2**) soil and air temperatures had an exceptional high influence.

The PLS model strength for the 1st and 2nd PLS run was weak for CC and North and additionally Q^2 and R^2 values differed much, however, the model strength was good for Ref-S. The most important variables influencing the MeHg concentrations were air temperature, sodium (Na), flow, sulfate, iron, total suspended solids (TSS) and P_{tot} (**Figure 23**). At NorthCC and Ref-S also chloride had a strong influence on the MeHg concentrations.

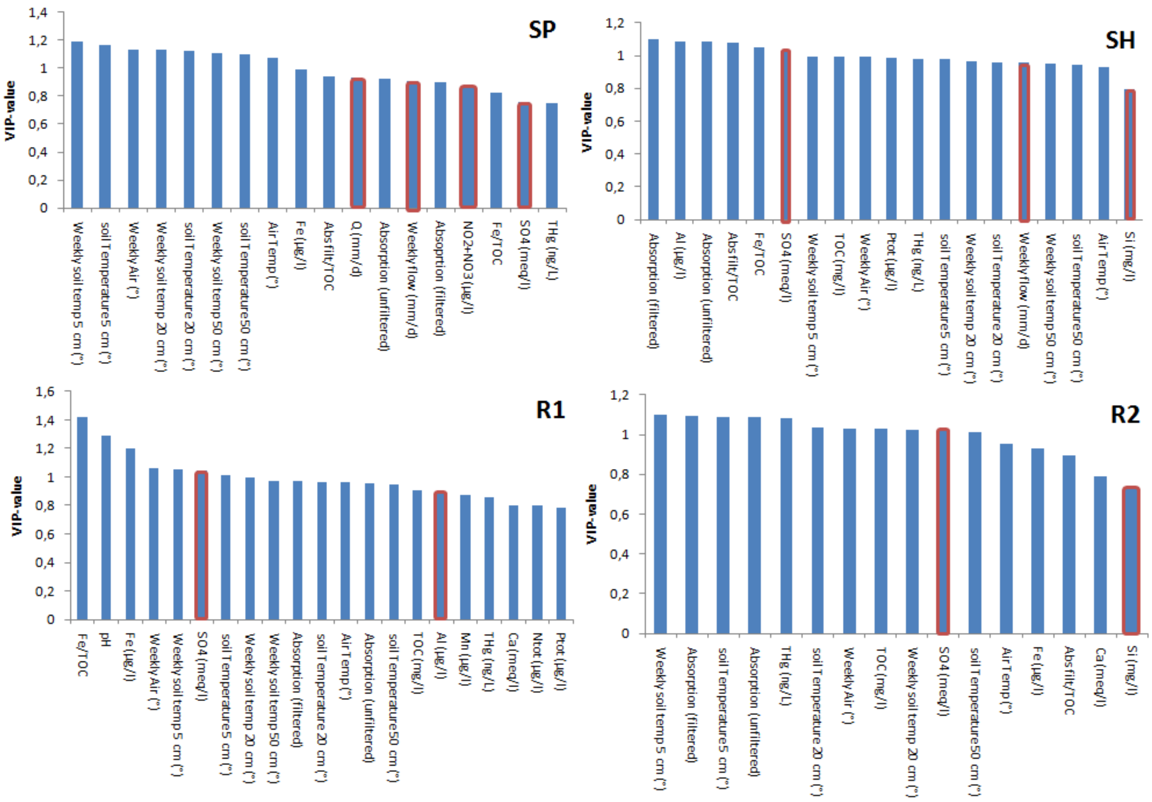


Figure 22: VIP values of the variables that highly significantly (VIP>1) influenced the response variable (Y), MeHg in Örebro. Entirely blue bars represent positive, red bars negative correlation

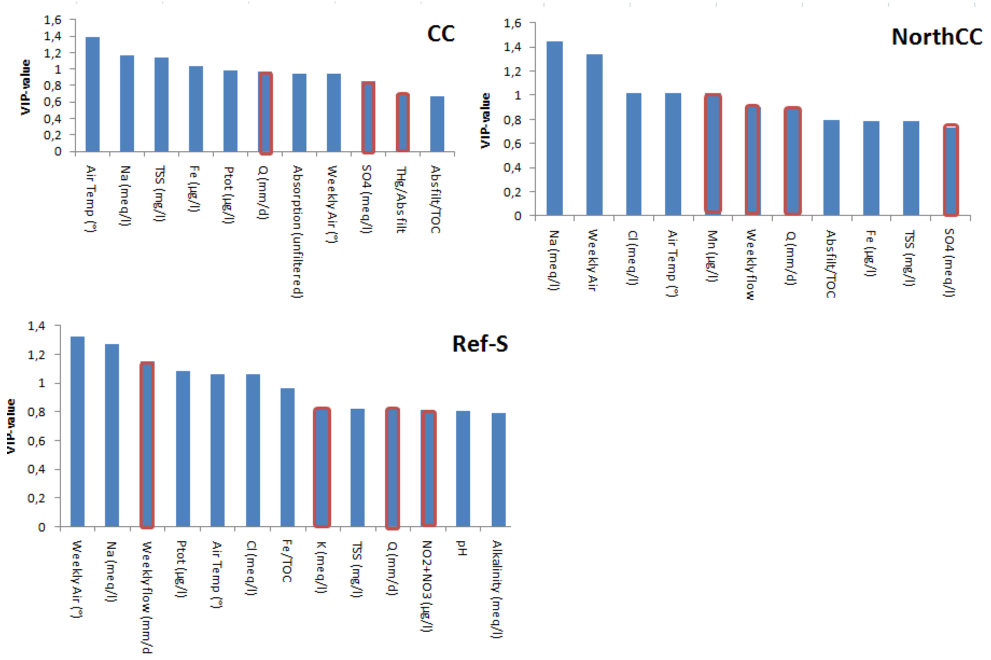


Figure 23: VIP values of the variables that highly significantly (VIP>1) influenced the response variable (Y), MeHg in Balsjö. Entirely blue bars represent positive, red bars negative correlation

4.2 Factors influencing THg and MeHg concentrations

4.2.1 Influence of pH and THg

All sites in Balsjö showed a strong relationship between logTHg and logpH. Also, the logTOC-logpH regression revealed a strong significant relationship towards CC (r^2=0.84), NorthCC (r^2=0.75) and Ref-S (r^2=0.77).

In Örebro the logTHg-logpH showed no correlation and the relationship between logpH and logTOC was only significant for R1 (r^2=-0.12) and SP (r^2=0.10).

MeHg-THg regressions were only significant at Örebro (**Figure 24**) and not in Basljö. The correlation of MeHg-THg/Abs revealed a week negative significant relationship for R2 and SH.

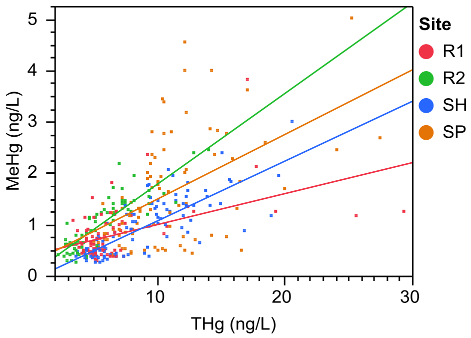


Figure 24: Correlation of MeHg with THg for the sites in Örebro. R1: r^2=0.26, $p<0.0001$; R2: r^2=0.75, $p<0.0001$; SH: 0.62, $p<0.0001$; SP: r^2=0.27, $p<0.0001$

4.2.2 Relationship between mercury, sulfate, iron and Fe/TOC

Al and Fe correlated at all sites in Örebro and Balsjö significantly positive with THg, besides the THg-Fe regression line for Ref-S which was characterized by a very low r^2-value. It is very likely that the significant relationship of TOC with Fe and Al was masking the “real” influence of these variables on THg. The r^2-value of the TOC-Fe and TOC-Al correlations varied between 0.19 – 0.73 and 0.84 – 0.88 at the Balsjö sites and between 0.47 – 0.79 and 0.69 – 0.89 at Örebro. THg-sulfate correlations were significantly negative for all sites in Balsjö and Örebro, besides R1 and SP.

The MeHg-sulfate regression was significantly negative for SP (r^2=-0.29), R1 (r^2=-0.29) SH (r^2=-0.67), and R2 (r^2=-0.67). Furthermore, although SP had the lowest r^2-value it showed the steepest slope and hence highest sensitivity towards sulfate concentrations. Interestingly, by grouping the MeHg-$SO4^{2-}$ relationship in Örebro into seasons (**data not shown**), R1 showed a negative significant correlation for Autumn (r^2=-0.57; n=26), Spring (r^2=-0.56, n=14) and a positive significant one for Winter (r^2=0.32, n=22). For SP only Spring (r^2=0.27, n=21) and Autumn (r^2=0.35, n=24) showed a significant negative correlation. Site SH showed a highly significant negative correlation for Autumn (r^2=-0.76, n=24), Spring (r^2=-0.67, n=22) and Summer (r^2=-0.46, n=30). The MeHg-Sulfate relationship for R2 were significantly negative correlating for Autumn (r^2=-0.62, n=18), Spring (r^2=-0.84, n=21) and positive for Winter (r^2=0.24, n=16, not significant).

Sulfate mean concentrations divided over all seasons in Balsjö varied significantly with the seasons at all sites (Wilcoxon/Kruskal-Wallis test, $p<0.0001$). The concentrations were lowest in Summer and highest in Winter (according to microbiological activity), whereby the biggest difference occured at site SP.

There was no correlation of MeHg with SO_4^{2-} and Fe in Balsjö. However, when excluding the extreme values from the data set, the Fe-MeHg relationship was significantly positive for CC (r^2=0.15, p<0.0001), NorthCC (r^2=0.17, p<0.0001) and Ref-S (r^2=0.09, p<0.0011). For the MeHg-Sulfate correlation CC (r^2=-0.09, p<0.0015) and NorthCC (r^2=-0.12, p<0.0002) revealed a significant weakly negative relationship.

The MeHg-Fe/TOC regression was significantly positive for R1 (r^2=0.63), SH (r^2=0.60), SP (r^2=0.28) and R2 (r^2=0.20) in Örebro (**Figure 25**). The mean Fe/TOC ratio was higher at the Balsjö sites (CC: 0.046±0.017, NorthCC: 0.042 ±0.015, Ref-S: 0.072±0.076) compared to the Örebro sites (R1: 0.030±0.007, R2: 0.036±0.020, SH: 0.021±0.005, SP: 0.016±0.008).

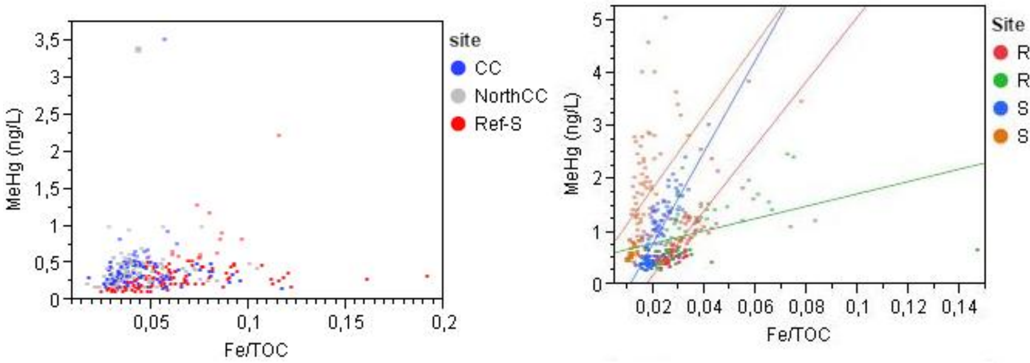


Figure 25: Relationship of MeHg with Fe/TOC for the sites in Örebro and Balsjö. Balsjö sites, no significant relationship, MeHg vs. Fe/TOC: R1: r^2=0.63, p<0.0001; R2: r^2=0.20, p<0.0001; SH: r^2=0.60, p<0.0001; SP: r^2=0.28, p<0.0001

4.2.3 Regression analysis between mercury, TOC, absorption and TSS

The THg-TOC and THg-absorption relationship showed for all sites in Balsjö and Örebro a strong significant positive correlation (**Table 4; Figure 26**). The slopes for the THg-TOC and THg-absorption regression lines in Örebro were significantly different from each other (t-test, p<0.0001). The analysis of the THg-absorption regression lines of the treated sites (SH, SP) revealed that the slopes (t-test, p=0.2925) and intercepts (t-test, p=0.1562) were not significantly different.

In Balsjö, the slopes of the THg-TOC relationships were significantly different (t-test, p=0.0099), however, when only analyzing the regression lines of CC and NorthCC, the slopes were not significantly different from each other (t-test, p=0.915). The intercepts of the THg-TOC regression lines from site CC and NorthCC were significantly different (t-test, p=0.042). The slopes (t-test, p= 0.0504) and intercepts (t-test, p=0.2856) of the THg-absorption regressions showed no statistical difference for the comparison of CC-Ref-S and NorthCC-Ref-S. Also, the slope and intercept of the CC and NorthCC regression were not significantly different (t-test, p= 0.146 and p= 0.669).

The correlation of THg and TSS was significant in Örebro for site SP (r^2=0.41, p<0.0001), R1 (r^2=0.72, p<0.0001) and R2 (r^2=0.39, p<0.0001)

MeHg-TOC and MeHg-absorption relationships were only significant for the sites in Örebro (**Table 4**). TSS correlated weakly positive with MeHg at R2 (r^2=0.14; p=0.0014) and SP (r^2=0.18, p<0.0001) in Örebro.

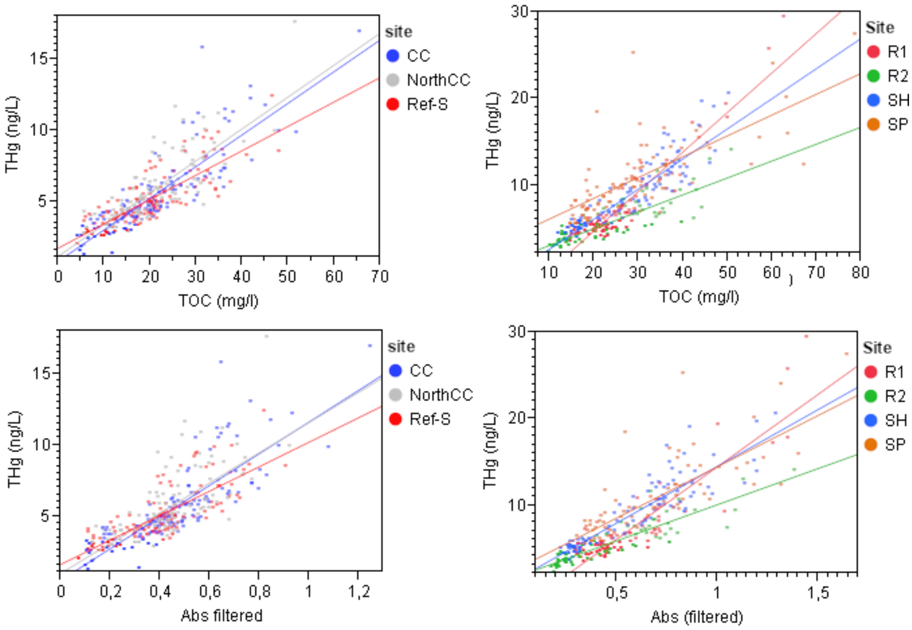


Figure 26: Relationship of THg and MeHg with TOC and Abs (filtered) for the sites in Örebro and Balsjö

Table 4: Regression analyzes of the THg and MeHg with TOC and absorption (filtered) relationships for Balsjö and Örebro

Relationship	Site	r^2	p-value	slope
THg-TOC	CC	0.72	< 0.0001	0.22
Balsjö	NorthCC	0.62	< 0.0001	0.22
	Re-S	0.65	0.0001	0.17
Örebro	R1	0.85	<0.0001	0.46
	R2	0.69	<0.0001	0.20
	SP	0.54	<0.0001	0.24
	SH	0.80	<0.0001	0.35
MeHg-TOC	CC	No correlation		
Balsjö	NorthCC	No correlation		
	Ref-S	No correlation		
Örebro	R1	0.32	<0.0001	0.03
	R2	0.68	<0.001	0.04
	SP	0.12	0.0006	0.03
	SH	0.61	<0.0001	0.05
THg –Abs filt	CC	0.68	<0.0001	11.09
Balsjö	NorthCC	0.48	<0.0001	10.59
	Ref-S	0.59	<0.0001	8.55
Örebro	R1	0.80	<0.0001	16.75
	R2	0.79	<0.0001	8.41
	SP	0.61	<0.0001	11.86
	SH	0.80	<0.0001	13.20
MeHg –Abs filt	CC	No correlation		
Balsjö	NorthCC	No correlation		
	Ref-S	No correlation		
Örebro	R1	0.54	<0.0001	1.59
	R2	0.72	<0.0001	1.71
	SP	0.39	<0.0001	2.21
	SH	0.82	<0.0001	1.90

The Örebro sites exhibited rather strong significant relationships between MeHg and Abs filt/TOC, whereas the sites in Balsjö showed no correlation (**Figure 27**).

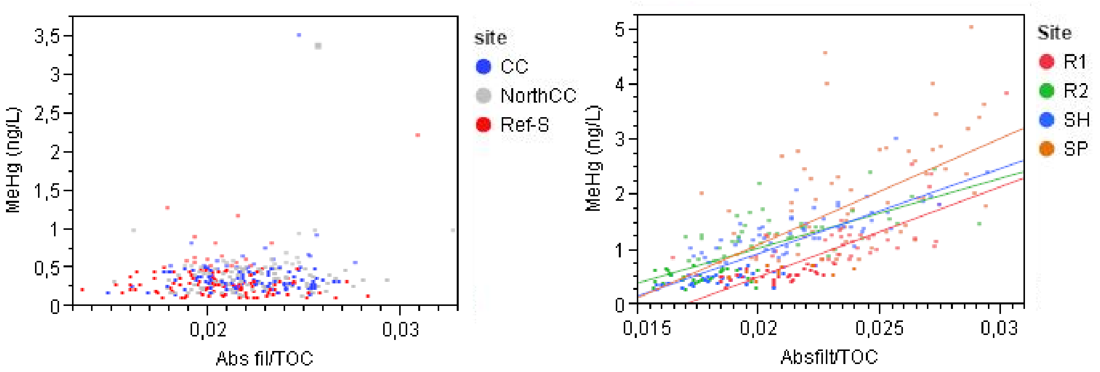


Figure 27: Relationship of MeHg with Abs filt/TOC for the sites in Örebro and Balsjö. Balsjö sites, no significant relationship, MeHg vs. Abs filt/TOC: R1: $r^2=0.57$, $p<0.0001$, R2: $r^2=0.52$, $p<0.0001$, SH: $r^2=0.65$, $p<0.0001$, SP: $r^2=0.36$, $p<0.0001$.

4.2.4 Stream water chemistry correlation with flow and temperature

In Örebro, absorption (filtered and unfiltered) correlated positive with air temperature (unfiltered: $r^2=0.44$, $p<0.0001$; filtered: $r^2=0.44$, $p<0.0001$). Furthermore, sulfate showed a significant negative correlation towards air temperature ($r^2=0.41$, $p<0.0001$) and iron indicated a significant positive relationship with temperature ($r^2=0.28$, $p<0.0001$) The correlations with flow were in general week at Örebro, besides for a negative relationship with pH ($r^2=0.20$, $p<0.0001$), Fe ($r^2=0.11$, $p<0.0001$) and a positive correlation with sulfate ($r^2=0.13$, $p<0.0001$)

In Balsjö, the relationship between air temperature and absorption was significant (unfiltered: $r^2=0.25$, $p<0.0001$, filtered: $r^2=0.27$, $p<0.0001$) as well as the Abs-flow regression (unfiltered: $r^2=0.17$, $p<0.0001$, filtered: $r^2=0.23$, $p<0.0001$). Also, total nitrogen (N_{tot}) showed a positive correlation with flow ($r^2=0.17$, $p<0.001$).

Base cation, Al^{3+} and Si^{4+} concentration (data not shown) correlated in Örebro with air temperature: Al^{3+} ($r^2=0.13$, $p<0.001$), Si^{4+} ($r^2=-0.34$ $p<0.001$). Na^+ indicated a significant negative correlation with flow ($r^2=-0.11$, $p<0.0001$). In Balsjö, the correlation with aluminum exhibited a positive relationship with air temperature (Al^{3+}: $r^2=0.23$, $p<0.001$) and Mn^{2+} and Al^{3+} a positive one with flow (Mn^{2+}: $r^2=0.26$, $p<0.0001$; Al^{3+}: $r^2=0.20$, $p<0.001$). Furthermore, Na^+ showed a significant negative correlation to flow ($r^2=-0.49$)

At the Örebro sites THg and MeHg correlated very well with air temperature (**Figure 28**). For the correlation of MeHg-air temperature, the coefficient of determination varied between 0.43 (R1, $p<0.0001$), 0.56 (R2, $p<0.0001$), 0.52 (SH, $p<0.0001$) and 0.54 (SP, $p<0.0001$). The highest slope and hence sensitivity towards air temperature was given by site SP. However, SP showed also the highest intercept at the THg-air temperature relationship, indicating that other mechanism than air temperature were important for the THg mobilization. The correlation between MeHg, THg and the weekly soil temperature mean at a depth of 5 cm exhibited very strong significant relationships (MeHg-soil temp 5 cm: R1:

r^2=0.53; R2: r^2=0.72, SH: r^2=0.61, SP: r^2=0.62). It should be noted that SP showed the highest slope in the MeHg-soil temp 5 cm regression that was about double compared to the other sites.

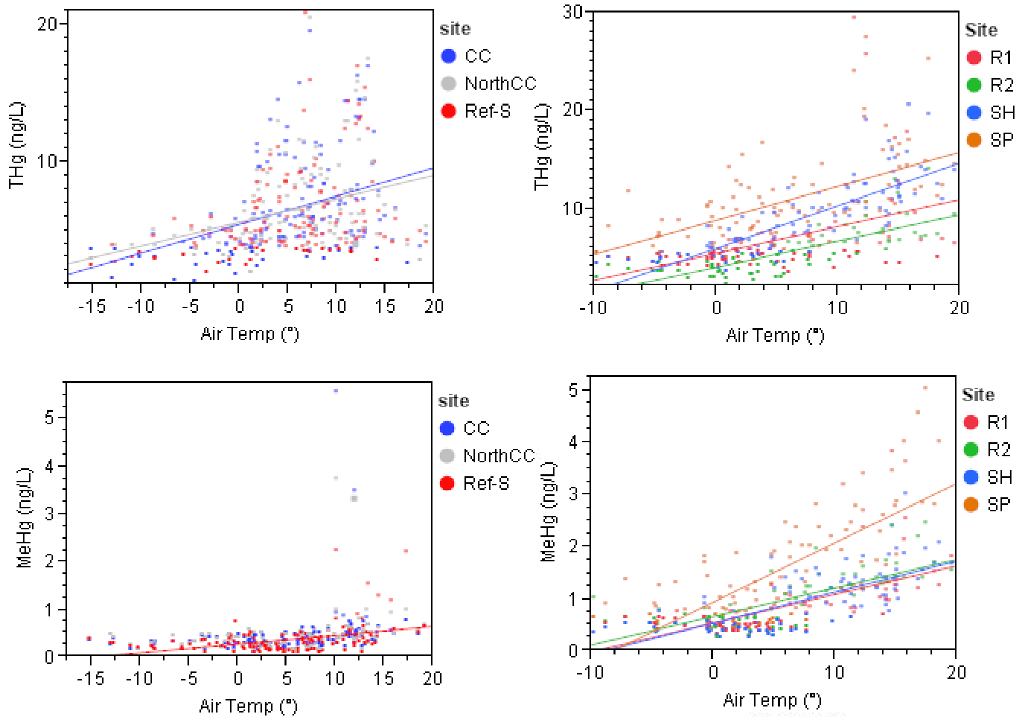


Figure 28: Correlation of THg and MeHg with air temperature for the sites at Balsjö and Örebro

At the sites in Balsjö, the correlation between THg, MeHg and weakly antecedent calculated air temperature was very weak (THg-air temperature: CC: r^2=0.14, NorthCC: r^2=0.12; MeHg-air temperature: Ref-S: r^2=0.15) (**Figure 28**). In Balsjö, THg showed no relationship towards the soil temperature at a depth of 15 cm. MeHg on the other hand revealed rather strong significant correlations with soil temperature (15 cm) for CC (r^2=0.40), NorthCC (r^2=0.39) and Ref-S (r^2=0.31).

The temperature range in which the highest THg (MeHg) concentrations occurred was approximately from 2 – 15 °C (10 – 15°C) for Balsjö and from 12 – 18°C (around 20°C) for Örebro. Furthermore, the sites in Örebro showed increasing THg and MeHg concentrations with increasing temperature, whereby the sites at Balsjö exhibited especially for THg more like cluster formation in a given temperature range (2 – 15 °C) (**Figure 28**).

The correlation of sqrtTHg with sqrtQ (square root (sqrt) transformation) was significant at the sites in Balsjö (CC: r^2=0.51, NorthCC: r^2=0.46, Ref-S: r^2=0.48, all $p<0.0001$) In Örebro, the logTHg-logQ relationship was weaker and only significant for R2 (R2: r^2=0.21; $p<0.0001$, **Figure 29**). The logMeHg-logQ regression was significant for NorthCC (r^2=0.10, p=0.0002) and Ref-S (r^2=0.18, $p<0.0001$). At Örebro the significant relationship of logQ and logMeHg was characterized by a comparatively high coefficient of determination (R1: r^2=0.55; R2: r^2=0.40; SH: r^2=0.38, SP: r^2=0.17, **Figure 29**).

Figure 29 shows that the highest MeHg concentrations occured during non-event flow both at Örebro and Balsjö. This observation was in general also true for the THg released in Örebro as most of the elevated concentrations occured below a flow of 5 mm/d. At Balsjö, the highest THg concentrations occured also below 5 mm/d, however, compared to Örebro a proportionally high amount of elevated THg concentrations were found above 5 mm/d. These observations support the calculations done under 3.3.1

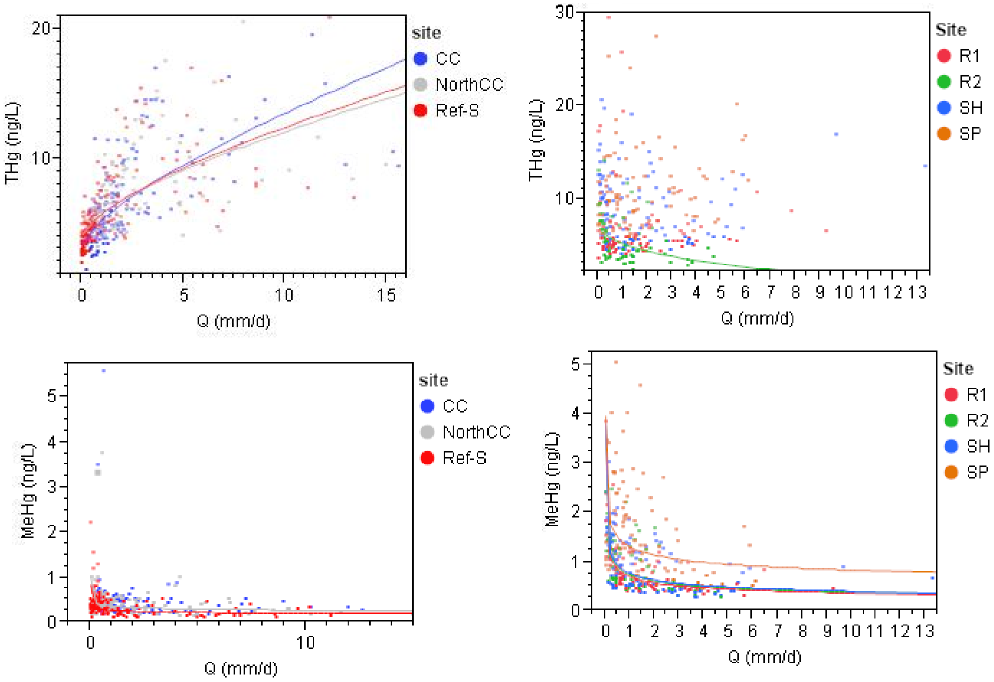


Figure 29: Correlation of THg and MeHg with flow (Balsjö and Örebro)

IV DISCUSSION

1. Temporal Variability of TOC, THg and MeHg

1.1 Variation of THg, MeHg and TOC concentrations over the year

The Balsjö sites were characterized by high THg and TOC concentrations in Spring and Summer in relation to high flow events that declined towards Autumn and were lowest in Winter (**Figure 9**). The pattern of seasonal THg and TOC concentration was quite homogenously distributed over the year, whereby highest THg and TOC stream concentrations occurred during Summer (at Ref-S during Summer and Autumn) and were linked in general to event flows (**Figure 6**). The elevated THg and TOC concentrations at Ref-S in Autumn were likely due to a higher biomass production compared to the partly clear cutted areas also in relation with higher deposition of Hg on the forest canopy. A higher concentration of THg and TOC with discharge in Summer was in line with highest annual temperatures stimulating microbiological activity, hence increasing decomposition of available organic matter accompanied by the highest annual mean precipitation (**Table 1**) that lead to increased flow, flushing surface near pores enriched with THg and TOC.

Lowest THg concentrations were found during Winter accounting for about 17- 19 % of the total annual mean concentrations in Balsjö. The rather high share of percentage THg and TOC concentrations in Winter could be related to the adaptation of the microbiological community to temperatures below zero and accumulation of DOM under the winter snowpack (Rilfors and Lindblom, 2002; Fahey et al., 1985). Furthermore, Kalbitz et al. (2000) stated that soil drainage conditions play an important role in understanding temperature effects on DOM release. The authors mentioned that the DOC concentrations in surface horizons reach very high levels in poorly drained soils irrespective the climatic conditions. This could be an explanation for the rather homogenous distribution of the THg, TOC and volume weighted concentrations at the Balsjö sites, especially at Ref-S and NorthCC, over the different seasons.

VWC peaked also for all sites in Balsjö in Summer and were lowest in Winter, however, VWC showed higher values than the mean concentrations. In Balsjö about 37 % of the total water flux occurred in Spring compared to 26 % in Summer (**Figure 3**). Summer months were characterized by precipitation induced flood events and highest annual THg concentrations that resulted in higher VWC in Summer compared to Spring.

In Örebro, high THg and TOC concentrations occuring during summer low flow (**Figure 10**) and locally during months with high runoff (**Figure 14**) were likely triggered *i. a.* by prior precipitation events. Selvendrian et al (2009) noted the same pattern as mentioned above and suggested two mechanisms that explain the TOC control on THg: (i) accelerated TOC composition during summer and (ii) “flushing” of TOC associated with elevated flow. The authors further continued that flushing does not necessarily imply pore water flushing but that the organic rich surface of a wetland would be sufficient to remain high TOC and THg concentration in the stream water after saturation due to raining events. Kalbitz et al. (2000) stated that high DOC concentrations in Summer are primarily linked to low water fluxes because of higher evaporation. The temperature effects on microbial activity were ranked by them as a secondary factor. Hence, in Örebro, higher microbial activity during Summer in relation to high temperatures associated with higher evapotranspiration might lead to a concentration of TOC and THg concentrations in the upper soil layers. It could be further hypothesized (especially for R1, SH and SP as R2 is rather wetland dominated) that these concentrated solutes were flushed from surface pores by precipitation events and transported to deeper soil layers and finally with the lateral ground water flow to the stream water.

In Winter, THg concentrations varied between 5 – 7 ng/L in Örebro and accounted for approximately 15 – 19 % of the annual concentrations. The Winter months in Örebro were rather mild (**Table 1**) suggesting a higher microbial activity under the snowpack.

VWC in Örebro followed the trend of the mean THg concentrations and peaked also during Summer and showed lowest values in Winter (**Figure 6**). High concentrations in Summer during low flow are weighted higher than lower concentrations during high flow in Winter.

High MeHg concentrations occurred at both major study sites in Summer, whereby the concentrations were highest in Örebro at site SP (**Figure 12, 13, 7**). In Balsjö, high MeHg concentrations were linked to hydrological processes and a greater net MeHg production within wetlands/soils during warm temperatures. High precipitation events prior to the measured peak MeHg concentrations in stream water probably lead to flushing of MeHg filled pore water and connected these “hot spots” hydrological with the stream water.

In Balsjö, peak MeHg concentrations up to 5.5 ng/L were only recorded during a very short time period in July/August (**Figure 12**). Selvendiran et al (2008) noted that higher MeHg concentrations were associated with the shallower part of the soil than with deeper depths. Factors like liable carbon, nutrients, abundance of methylating bacteria, warmer temperatures and anoxic conditions that are essential for methylation, are more associated to near surface processes (Selvendrian et al, 2008). Intense precipitation and higher temperatures prior to the exceptional high MeHg concentrations might be responsible for an increased OM degradation followed by flushing of near surface pores. It could be hypothesized that after the first flush of MeHg rich soil pore water newly produced MeHg was constantly diluted as the Balsjö sites were characterized by a rather high Summer flow (**Figure 3**). A rather low flow period before the recorded peak MeHg concentrations would support this theory. However, the measurements of peak MeHg concentrations in Balsjö were limited due to the fact that the manual sampling just caught the peaks “accidentally”, automatic sampling during this time period with e. g. ISCO samples would help to better understand MeHg dynamics in Balsjö.

In Örebro, low flow conditions during Summer increased the residence time of water within wetlands/soils leading to a longer interaction between soil pore water and other parameters favorable for methylation (Selvendiran et al., 2008; Shanley & Bishop, in press). The change of wetting events and dry periods (highest precipitation and highest temperatures in Örebro during Summer) is increasing DOC concentrations. Lundquist et al. (1999) mentioned three explanations for the increase of DOC concentrations after rewetting: (i) decreased utilization of DOC during dry periods by microorganisms, (ii) quicker turnover of microbial biomass and microbial products after rewetting and (iii) increased availability of sequestered carbon for microbial degradation due to disrupted soil structures. The detoriation of microbiological biomass after soil drying results in the release of hydrophilic neutrals and bases, whereby the release of hydrophobic organic acids (HPOA) are associated with wetter conditions (Christ & David, 1996). As site R1 and SH showed a quite good correlation between THg-TOC and even MeHg-TOC (**Table 4**), the release of hydrophobic DOC compounds probably after the increased availability of sequestered carbon or the decreased DOC utilization due to drying and rewetting cycles might be a plausible explanation. R2 (high correlation of THg-TOC and MeHg-TOC) incorporates a quite high amount of wetland area and hence, is thought to be a methylation "hot spot" due to increased degradation of terrestrial debris during the warm season, wetting and drying cycles shifting redox conditions and flushing events finally transporting MeHg to stream water. SP, however, showed a lower THg-TOC and MeHg-TOC correlation supporting the hypothesis that hydrophilic bacterial biomass might be released and transported down to deeper soil layers to a comparatively higher fraction compared to the other sites.

MeHg VWC peaked also for both major study sites in Summer and were lower than the mean concentrations (not for SP). This is in line with the expected results as the peak MeHg concentrations had a higher influence during low flow in Örebro and as comparatively lower MeHg concentrations were associated with a rather high flow in Balsjö.

1.2 Hydrologic and seasonal roles in terrestrial contribution of TC and THg to stream water TOC, THg and MeHg concentrations

Changing flow paths in the soil during event and non-event flows are likely to influence the quality and amount of organic carbon. DOC concentrations are higher in the upper soil layer and retained by sorption as well as biodegraded when percolating down to the mineral layers. Hence, under low flow conditions most DOC originates from the soil water of the mineral horizons or from surficial groundwater flow (Vidon et al. 2008; Aiken & Cotsaris, 1995). Dittman et al. (2010) observed a shift in DOC source and quality with changing flow paths. They noted that high flows where characterized by a shift to high aromatic DOC situated in the shallow parts of the soil. This also indicates a change in DOC sources towards terrestrial material, as higher plant biomass is richer in aromatic C than microbial sources. Research showed that most of the aromatic DOC compounds are located in the hydrophobic organic (HPOA) fraction (Dilling & Kaiser, 2002), which on the other hand is thought to have the highest capacity to bind mercury (Haitzer et al., 2003). In relation to chances of DOC source and quality with higher flow also a shift in THg source to more recently deposited mercury compared to the ones in deeper soil layers is suggested (Dittman et al., 2010).

The soil THg concentrations decreased with increasing depth associated with decreasing % TC for site CC in Balsjö and all sites in Örebro (**Figure 18**). This was also found by Alriksson (2001). Furthermore, THg concentrations decreased also with increasing distance from the river coinciding with lower organic matter content.

However, at NorthCC and Ref-S in Balsjö THg concentrations decreased with increasing depth, whereby % TC remained on a quite high level (~ 50 %). Furthermore, the THg/TC ratio showed a decreasing trend with increasing depth (**Figure 19**). This could be attributed to different DOC sources and qualities in the upper soil layers having a high share of hydrophobic organic fractions (HPOA, Vidon et al. 2008; Aiken & Cotsaris, 1995) or to the fact that Hg deposition occurred primarily in the upper soil layers. In Balsjö, liable THg and TOC concentrations increased towards the soil surface. As most of the mean THg concentrations occurred during high flow events (Q> 5 mm/d, **Figure 15)** the increased lateral flow moved to the upper soil layers, where degraded HPOA rich DOC together with "new" Hg was mobilized. Davidson & Janssens (2006) stated in their review that lower decomposition of organic matter in peat and wetlands during flooding is linked to lower oxygen concentration inhibiting the activity of phenol oxidase enzyme of microorganisms that is leading to the accumulation of phenolic compounds. High concentrations of phenolic compounds are known to inhibit the activity of hydrolase enzyms and hence reduce decomposition further. The higher production of phenolic compounds in the upper soil layers in the peat dominated sites in Balsjö might be responsible for the high storage capacity of mercury (**Figure 18**) and the decreasing THg/TC ratio with soil depth (**Figure 19**).

Taking into account that the correlation between TOC and flow was weaker than the THg-Q relationship in Balsjö other THg sources not in association with TOC might be considered especially under high flow. However, the stronger THg-Q relationship might also suggest that other sources of TOC were mobilized under event compared to base flow conditions.

At the sites in Örebro, the total mean THg concentrations were more attributed to low flow conditions (**Figure 15**). The soil profile for SH and R2 exhibited decreasing soil concentrations the closer to the river bank and showed a rather vertical profile at the 21 or 14 m sampling point (**Figure 18**).

Longer growing seasons in the southern regions lead to increased foliar uptake of Hg and at the same time increased mineralization and Hg flux from the soil due to favorable climatic conditions (Grigal, 2003; Fleck et al., 1999). This would be confirmed by the lower % TC especially in the upper soil layers compared to Balsjö. Interestingly, the THg/TC ratio showed an increasing trend with depth along with a lower C/N ratio in Örebro (see RIM analysis under 1.3). The increasing THg/TC ratio with depth would suggest that a proportionally high amount of THg was associated with a lower % of carbon compared to the upper soil layers and hence indicate a different carbon source or the association of mercury with other compounds. Microbial density is highest in the upper soil layers (Fierer et al., 2003). The mobilization of organic colloids in the forest floor is related to microbial activity (oxidative degradation of organic matter or production of microbial metabolites), that is depending on the soil environment (e. g. temperature, soil moisture content, availability of substrate, Guggenberger et al., 1998, Fierer et al, 2003). Compounds derived from microbiological sources are released to the soil solution (hydrophilic compounds, Soctt et al., 1998), which are known to have a lower binding capacity for mercury (Ravichandran, 2004). It could be speculated that the upper soil layer especially of SP was very rich in hydrophilic organic carbon with a proportionally reduced capacity to bind mercury. The top soil layer at SH consisted out of black, coal like soil and might not offered the necessary quality to bind mercury. R2 showed a different pattern and relatively high capacity to bind mercury in the upper soil layer as the stored THg concentrations at 0.5 and 3 m (**Figure 18**) were nearly the same compared to the ones in Balsjö, but showing a much lower % TC. The above mentioned reduced capacities of organic carbon to bind Hg in the top soil layer at site SP and SH associated with an effective mineralization of organic material might have lead to an increased Hg flux to lower soil layers.

Bourg & Schindler (1985) expected that Hg(II) is mostly controlled by organic matter and that in acidic waters mercury should be trapped in horizons where the organic compounds precipitate. In Örebro, THg was transported most likely in association with organic matter or in some cases as Hg-ion-complexes (e. g. $Hg(Cl)_{2,}$ in case of a high proportion of hydrophilic organic carbon content) into deeper soil layers, where depending on the pH and redox conditions precipitation of organic matter, adsorption of Hg on colloids or complexes with sulfide (HgS) occurred that “trapped” a fraction of THg. Anderson (1979) showed that the only effective sorbent in acid soils (pH < 4.5 – 5) is organic material compared to iron oxides and clay minerals in neutral soils. As the mobility of mercury increases in soils with low organic matter content with decreasing pH making translocations within the soil profile increasingly likely (Schuster, 1991), the trapped THg fraction in deeper soil layers not only associated to organic material might be a possible source for the high mercury concentrations during low flow. However, to further assess the mobilization, transport and adsorption of THg in deeper soil layers more information about the soil solution chemistry, redox potential and pH is needed.

In Örebro and Balsjö the MeHg concentrations were mainly linked to low flow conditions, (**Figure 15)** indicating again that the residence time of water within the soil played a major role in the overall MeHg production.

1.3 RIM model results and link to other observations

The RIM_{static} model visualized the effect of flow and showed in general a good NSC for the modeled THg concentrations in Balsjö as well as for the MeHg concentrations in Örebro (not site SP, **Table 5** appendix). The model efficiency was lower for the TOC concentrations compared to the THg concentrations in Balsjö. These findings were confirmed by the bivariante analysis of THg-Q, TOC-Q (data not shown) and MeHg-Q for Balsjö and Örebro (**Figure 29**). The higher influence of flow on the THg compared to TOC concentrations was also visible in the time series analysis as THg concentrations followed the flow pattern well. Furthermore, although the THg-TOC relationship was significant with a rather good r^2-value (**Table 4**) for the Balsjö sites, a higher correlation of the THg-Q compared to the THg-TOC relationship indicated that different fractions of TOC might be mobilized according to different flow pattern or that a mobilization with other mechanisms than organic matter could have occurred. Furthermore, the rather weak sqrtTOC-sqrtQ relationship (CC: r^2= 0.33, NorthCC: r^2=0.24 and Ref-S: r^2=0.25) suggested that flow did only explain about 25 – 30 % of the variability in TOC concentrations in Balsjö. The model residuals of RIM_{static} from Balsjö and Örebro correlated in general very well with temperature and showed no correlation with flow suggesting that flow was a very important variable controlling THg, TOC and MeHg dynamics, however not the only variable influencing organic matter and mercury dynamics. The correlation of TOC, THg and MeHg with soil and air temperature was stronger for the sites in Örebro than Balsjö indicating that the seasonal influence was more dominant in the catchments in Örebro. This observation was also supported by PLS (**Figure 20, 21, 22, 23**) and Pearson bivariant analysis (**Figure 29**).

As the two parameter RIM showed not much improvement compared to the one parameter models with regard to the NS factor, overall best results were achieved with $RIM_{dyn}c0$ (**Table 5**, appendix). In $RIM_{dyn}c0$ the seasonal change was achieved by moving the static THg, MeHg and TOC profiles (constant f-factor) to a higher or lower concentration level (seasonal variation in c_0).

All $RIM_{dyn}c0$ modeled MeHg concentrations had a negative f-factor suggesting that the dilution of the MeHg soil solution increased the higher the flow (**Table 7, Figure 17**). The simulated dilution effect was not so strong at site SH compared to CC (**Figure 17**) indicating a higher net MeHg production at SH. The highest MeHg concentrations occurred at low flow, which is in line with the calculations done in this study (e. g. **Figure 15**). The NSC values for

MeHg of the sites in Balsjö were low for CC and NorthCC (0.14, 0.22) but higher for Ref-S (0.51) as Ref-S showed as the only site in Balsjö a significant logMeHg-logQ relationship.

The f-value was somewhat close to zero for TOC and THg at the sites in Örebro indicating a rather vertical soil solution profile, whereby the f-factor for site R1, SH and R2 was negative, leading to the assumption that a higher dilution of TOC and THg concentrations occurred with increasing flow. The Balsjö catchments showed higher f-values compared to the Örebro sites which suggested decreasing THg and TOC concentrations with increasing depth. The differences in soil solution profiles for Balsjö and Örebro help to explain the variability of TOC and THg concentrations at Balsjö and Örebro and were supported by similar findings for the soil analysis (dry fraction, **Figure 18**) and time series analysis **(Figure 15, 9-14**). From the $RIM_{dyn}c0$ results it could be expected that THg and TOC concentrations will not vary much with changing flow paths as the soil solution profiles of THg and TOC were nearly constant with depth in Örebro (**Figure 17**). The lack of a correlation between THg (TOC) and flow (**Figure 29**) for the sites in Örebro (not R2) suggested also chemostatic behavior (Winterdahl et al. 2011). Winterdahl et al. (2011) suggested that the delivery of TOC concentrations via lateral groundwater flow independent of runoff levels could be an additional explanation for the rather vertical soil solution profile in Örebro. This could be true for site R2 (highest negative f-value for TOC, **Table 8**) as the uphill ground water flow is forced through peatlands/wetlands. The positive TOC-Temperature and the weak logTOC-logQ (logTHg-logQ, **Figure 29**) relationship (logTOC-logQ would suggest partial overland flow) supports the hypothesis of superficial ground water flow generating stream runoff (Winterdahl et al., 2011). On the other hand across all sites in Balsjö a dilution of Na^+ and an increase of TOC and THg concentrations with flow occurred during high flow events indicating a shift from the lower soil layer to the upper soil horizons.

Hence, due to the differences in the soil solution profiles in Balsjö compared to Örebro similar variations of flow paths within the soil would result in large changes in TOC and THg concentrations in Balsjö (Winterdahl et al., 2011). Consequently, the variation of flow paths in the soil seemed to be more important in Balsjö.

In the $RIM_{dyn}c0$ the offsets and amplitudes of the simulated c_0 concentrations showed in general regional specific trends between Balsjö and Örebro, with concentrations peaking during Summer. Furthermore, similar regional values of c_0-base concentration for e. g. MeHg (**Figure 26**) in the applied $RIM_{dyn}c0$ model lead to the hypothesis that future models could built up on a regional scale by adopting one single c_0 concentrations for all models. If this would be feasible statements about regional TOC, THg and MeHg dynamics could be made based on a few measurements. However, this hypothesis should be confirmed with a synoptic setup of sampling sites all over Sweden.

1.4 Effect of antecedent flow and temperatures

PLS analysis indicated that weakly calculated antecedent flow and temperatures had a high influence on THg and MeHg concentrations in Balsjö and Örebro (**Figure 20, 21, 22, 23**). In this study the weekly calculated mean fluxes and mean temperatures prior to the measured THg, MeHg or TOC concentrations had in general a higher influence on these concentrations than the daily measured values. This indicated that the initial conditions of the watershed prior to event flows were highly important for the event itself. Schiff et al (1998) found similar results, namely that antecedent wetness of a watershed prior to event flows might be important for DOC concentrations in the soil solution and stream water. Raymond & Saiers (2010) noted that temperature and antecedent discharge influence short term processes on DOC export (e. g. dissolution, microbial activity) as well as long term processes (e. g. primary production, soil OM pools). The authors furthermore highlighted the different time scales (from event time scales of hours, days or weeks to climate time scales of decades) controlling THg, TOC and MeHg concentrations in stream water. However, closer assessments of the sites in Balsjö and Örebro prior to event flows need to be done in order to better understand mercury and organic carbon dynamics. This gains also importance in the light of climate change as with a better understanding of the factors that influence the "status quo" more realistic prediction about the future changes with changing climate in the terrestrial and aquatic watershed could be made.

1.5 THg, MeHg and TOC export in Balsjö and Örebro

It is important to study the biochemical response of forested watersheds to event flows as a significant portion of the annual water and chemistry flux might be released during that time (Dittman et al., 2010; Babiarz et al., 1998). Hydrologic fluxes were higher for THg and TOC during months with high flow resulting in a flow driven export in Balsjö (Selvendiran et al., 2008). Hence, in Balsjö the export was highest in Spring coinciding with snow melt. The THg Spring flux accounted for about 40 % of the annual total THg export. In Örebro however, the export of THg was more equally distributed over the vegetation periods with highest fluxes for R1 in Winter, SH in Autumn and SP in Summer (**Figure 8**). Site R1 showed a mainly flow driven export as the highest seasonal flow occurred during Winter (2.17±1.53 mm/d). The export at SP and SH could be not only explained with flow alone as the Örebro sites were characterized by Winter high flow (**Figure 3**). Temperature driven export seemed to play an important role especially at SP. The MeHg export over the study period varied between 2.22 – 6.60 µg/d*ha and 7.68 – 19.49 µg/d*ha in Balsjö and Örebro, respectively (**Table 3**). The highest export at both sites occurred in Summer, whereby about 45 % of the MeHg export occurred in July/August in Balsjö, compared to only about 30 % or less in Örebro. Precipitation induced Summer floods played a higher role in Balsjö connecting different MeHg hot spots to the stream water.

The THg, MeHg and TOC fluxes over the study period of the Balsjö and Örebro catchments varied strongly between the catchments, but were highest at SP (THg: 137.89±103.37 µg/d*ha; TOC: 405.50±418.55 g/d*ha; MeHg: 19.49 µg/d*ha, **Table 3**). Selvendrian et al. (2008) reported that THg fluxes in literature varied between about 25 – 161 µg/d* and Grigal (2002) assessed the THg exports from a variety of different watersheds, whereby 75 % of the observations laid within 27 – 82 µg/d*ha. Raymond & Saiers (2010) reported total annual DOC fluxes of about 63 g/d*ha and Laudon et al. (2004) reported TOC fluxes from seven catchments in Sweden varying between 96 – 208 g/d*ha. Grigal (2002) reported that 80 % of the pooled MeHg fluxes from literature were below 4 µg/d*ha. Explanations of substantially higher MeHg flux values lie in watershed characteristics (Grigal, 2002). Selvendrian et al. (2008) presented MeHg fluxes from other studies with greater % wetlands ranging from approximately 5 – 15 µg/d*ha. Louis et al. (1996) reported MeHg fluxes from about 0.2 – 6.8 µg/d*ha and THg fluxes from about 27 – 63 µg/d*ha for various types of catchments (Upland, riverine wetland, etc.) with different kind of wetlands and contents (0 – 25.2 %).

At the sites in Örebro MeHg, THg and TOC means fluxes were substantially higher compared to the literature values. Especially site SP showed exceptional high MeHg, THg and TOC fluxes (**Table 3**) indicating that catchments specific processes were responsible for the observed high exports. In Balsjö site CC showed higher THg, MeHg and TOC fluxes than the other sites probably attributed to a higher mean specific discharge. The mean values reported for the THg, MeHg and TOC fluxes in Balsjö were mainly in the upper range of the reported literature data.

2. Parameters influencing mercury mobilization, methylation and transport

1.1 THg and MeHg concentrations in relation to other studies

The range of THg and MeHg concentrations varied from 1.19 – 20.8 ng/L and 0.09 – 5.55 ng/L in Balsjö and from 2.2 – 29.3 ng/L and 0.26 – 5.01 ng/L in Örebro. Although the upper range of the MeHg concentrations in Balsjö and Örebro were similar, it should be noted that extreme values occurred in Balsjö only during a very short time period each year leading to overall much lower mean MeHg concentrations compared to the ones in Örebro (**Table 2**). Povari & Verta (2003b) found MeHg concentrations between 0.03 – 3.8 ng/L and THg concentrations between 0.84 – 24 ng/L in several boreal forest catchments in Finland. The range of MeHg and THg concentrations at the mire outlet (subcatchment) in the Svartberg catchment in northern Sweden varied between 0.1 – 1.4 ng/L and 2.1 – 6.0 ng/L, whereby the MeHg concentration range was lower for the other subcatchments in Svartberg having a lower share of wetlands (Lee et. al, 1995). Other studies reported THg concentrations ranging from 0.65 - 3.9 ng/L as well as from 1.1 – 6.9 ng/L (Regnell et al., 2009) and from 0.5 – 11.8 ng/L (Selvendiran et al., 2008), whereby MeHg concentrations varied from 0.01 – 0.8 ng/L (Selvendiran et al., 2008) and from <0.06 – 1.10 as well as from 0.08 – 1.0 ng/L (Regnell et al., 2009).

Comparing the range of MeHg and THg concentration from Örebro with the concentrations reported in literature, it could be noticed that the values in Örebro were very high. Especially the MeHg concentration exceeded the reported MeHg values in literature by far indicating that Örebro and especially SP was a methylation hot spot. For the sites in Balsjö the concentrations for MeHg and THg were in general in line with the reported data from literature.

1.2 Organic carbon as a vehicle for THg and MeHg

Dissolved and particulate organic carbon are important factors for the transport of mercury (Dittman et al., 2010). The strong THg-TOC (**Table 4**) relationship indicated that the transport of THg was primarily driven by TOC. In Örebro 54 – 85 % and in Balsjö 62 – 72 % of the variation in THg concentrations could be explained by TOC. The importance of organic carbon in THg mobilization was also shown by other studies (e.g. Selvendrian et al., 2008, Skyllberg et al., 2009). However, NorthCC, Ref-S (Balsjö) and especially SP (Örebro) showed a lower coefficient of determination compared to the other sites suggesting other important mechanisms that influence THg transport (**Table 4**). Skyllberg et al. (2009) proposed that Hg mobilization increased with increased HS^- concentrations under the formation of e. g. soluble $Hg(SH)_2$, HgS_2H^- and HgS_2^{2-} complexes. Furthermore the authors suggested that ionic Hg could be mobilized as HgS (s), FeS (s) or under suboxic conditions in association with polysulfides. During methylation sulfate is reduced to sulfide and hydrogen sulfide (Schulze & Mooney, 1993) which might in turn increase the mobilization of THg. Hence, it could be hypothesized that at SP the high mobilization of THg might be also driven by the formation of soluble Hg-sulfide complexes. However, further research about mercury specification in the stream water to confirm or reject this assumption is needed.

The THg/TOC ratio was consistent for the sites in Balsjö and most sites in Örebro (**Table 2**) with about 0.3 ng THg per mg TOC. Site SP in Örebro however, showed a THg/TOC ratio up to about 0.4 ng THg per mg TOC. Grigal (2002) reported average slopes of about 0.2 ng THg per mg DOC in catchments in the northern hemisphere and Dittman et al. (2010) reported slopes of 0.3 in their study. The similarity in slopes of the sites reported in this study (not SP) and the ones in literature (e.g. Dittman et al., 2010) suggest a strong universal correlation between THg and the TOC. About 80 % of DOM consists out of humic substances that are grouped in seven fractions based on their properties (hydrophobic acids, bases, neutrals; hydrophilic acids, bases and neutrals and transphilic organic matter) (Ravichandran, 2004; Leenherr & Croue, 2003). Filtered THg is mainly associated with the hydrophobic organic acid (HPOA) fraction of DOC, which has a fairly consistent share of about 50 % of total DOC during all flow conditions and seasons (Dittman et al., 2009, Dittman et al., 2010). Dittman et al. (2010) hypothesized that the constant percentage of HPOA of total DOC and the close association of filtered THg with HPOA lead to similar slopes of the THg-DOC relationship across sites. The slope is likely to change, when the fraction of HPOA of total DOC differs (Dittman et al., 2010). As SP showed a higher slope than all other sites, a higher percent HPOA of TOC could be suggested. However, as the correlation between TOC and THg was rather weak at SP ($r^2=0.54$) compared to the other sites this hypothesis might not be the only explanation. The higher THg/TOC ratio and the lower coefficient of determination of the THg-TOC relationship at SP might support the suggested hypothesis that THg mobilization could be driven by other factors than TOC.

The transport of MeHg to surface water was likely facilitated by TOC for the Örebro sites (**Table 4**). Hence, at R2 and SH more than 80 % of the MeHg variability could be explained with TOC. As MeHg peaked either before or after TOC peaked, other important mechanisms influence MeHg transport at SP and R1 might be present at this sites. Skyllberg et al. (2008) proposed dissolved (e. g. MeHgSH) and colloidal inorganic sulfides (FeS(s)) as other mobilization mechanism for MeHg from soil to stream water. Furthermore, the weakly significant correlation of MeHg with TSS for site SP (positive, $r^2=0.18$, $p<0.0001$) and R2 (positive, $r^2=0.14$, $p=0.0014$) indicated that at these two sites also particle induced MeHg transport seemed to be a factor that need to be considered.

Significant positive MeHg-Abs filt/TOC correlations for Örebro (**Figure 20**) indicated a higher MeHg production and transport the higher the colored fraction of TOC.

The strong MeHg-THg correlation (**Figure 24**) and the PLS results (**Figure 22**) indicated that THg had a strong influence on MeHg production in Örebro. The MeHg-THg/Abs filt relationship was weakly negative and significant for site R2 and SH, showing, the higher the amount of THg attached to the colored fraction of TOC the lower the amount of bioavailable uncharged Hg-complexes for methylation. High THg and MeHg concentrations occurred at around the same time in summer and as the THg/Abs filt did not change with increasing MeHg concentrations at SP other mechanisms responsible for the solubility of THg need to be considered that might contribute to the extremely high mean MeHg concentration compared to all other sites. The Abs filt/TOC ratio was about the same for all sites in Örebro and Balsjö, indicating that the fraction of colored TOC was similar in the northern and southern sites. Having in mind that the THg/TOC and THg/ Abs filt ratio was elevated for site SH and SP compared to the other sites (**Table 2**), it is supporting the hypothesis that THg might be mobilized with other sources than TOC which was mainly visible for site SP.

In Balsjö all sites showed neither a correlation between MeHg-TOC, MeHg-TSS, MeHg-Abs filt/TOC, MeHg-Fe/TOC nor for MeHg-THg. It could be hypnotized that other factors, especially seasonal factors like temperature were missing prerequisite for a high MeHg production.

The MeHg/THg ratio was much higher at the sites in Örebro compared to the ones in Balsjö (**Table 2**). In Örebro, SP and R2 showed that about 17 – 18 % of the mercury was present as MeHg. Grigal (2002) stated in his review that the ratio of MeHg to THg in soil water is varying between 0.15 – 15 %, which placed the noted MeHg/THg ratios of R2 and SP in stream water in the upper range of reported values in literature. R2 was rather dominated by wetlands and high methylation has been linked to semi-anoxic systems with a high accumulation of C (Grigal, 2003, Skyllberg et al., 2003). Although the anoxic condition at SP was not assessed in this study it could be very likely that SP was characterized by highly reduced environments favoring methylation processes.

2.1 Influence of iron and sulfate on MeHg production

At Balsjö, sulfate, iron and Fe/TOC showed no correlation with MeHg. However, according to PLS-analysis (**Figure 23**), especially Fe and Fe/TOC had a high importance on MeHg concentrations. When excluding the extreme peaks in Summer from the original data set of Balsjö, MeHg revealed a significant weak negative relationship to sulfate (NorthCC and CC) and a significant weak positive correlation to Fe for all sites. This might indicate that the extreme values that occur just for very short time period each year during July/August might be influenced by different factors than the rest of the data set.

At Örebro all sites had a significant negative correlation of MeHg with sulfate and a positive one with iron and Fe/TOC. Skyllberg et al. (2009) found also a negative correlation between sulfate and MeHg (exponential) and a positive one between MeHg and Fe (exponential). Gilmour & Henry (1991) stated that below the optimal sulfate concentration (~20 – 50 mg/L) for methylation by SRB in sediments, sulfate becomes limiting for methlyation and above the mentioned concentration the methylation process is inhibited. High sulfide concentrations due to sulfate reduction might limit Hg methylation by the formation of less bioavailable Hg-S complexes (Benoit et al., 1999). Compeau & Barta (1985) found in their study that the methylation potential for SRB was hightest under sulfate limiting conditions. This might explain the negative relationship between MeHg-sulfate found in this study.

In Örebro, the significant difference in the sulfate concentrations between all seasons, especially Summer and Winter having the lowest and hightest sulfate concentration respectively, might be associated to a higher sulfate reduction during the warm season and hence increased MeHg production (Skyllberg et al., 2009). The positive relationship of MeHg and sulfate in Winter for R1 (significant) and R2 (not significant) might indicate that sulfate reduction could be a limiting process during this season. Site SP showed the highest MeHg concentration of all sites (**Table 2**) and at the same time presented the lowest coefficient of determination for the correlations of sulfate and Fe/TOC with MeHg among the Örebro sites. It seemed that SP had the highest intercept and steepest slope in most presented correlations suggesting that an interplay of different parameters influence MeHg levels. It could be hypothized that all factors necessary for a high MeHg production were present at site SP, *i. a*. high sulfate reduction in summer. For site R1 and SH the strong correlation between MeHg and sulfate or Fe/TOC suggests that both had might have high influence on MeHg concentrations.

Sulfate concentrations were higher in Örebro, whereas the Fe/TOC ratio was higher at the Balsjö sites. The higher sulfate concentration in surface water in Örebro compared to Balsjö might be also related to a higher share of atmospheric SO_4^{2-} deposition in southern Sweden (Rhode, 1972) which coincidenced with higher atmospheric Hg deposition in southern compared to northern Sweden (Munthe et al., 2007). It has been shown in literature that sulfate addition to wetlands and surface water is able to increase the methylation potential (Watras et al., 2006; Jeremiason et al., 2006).

The parameter Fe represents the total Fe concentration in the stream and is the sum of Fe(II) (dominant under acidic conditions, soil mobilized) and Fe(III) which is often complex by NOM $(Fe(OH)_{3-n}^{n+}$. When making the presumption that Fe (III) is rather conservative and 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). A probably higher Fe(II) production associated with iron reduction could be present in Balsjö. Furthermore, the higher iron concentration in Balsjö could also lead to the formation of insoluble FeS, that reduced the pool of uncharged and bioavailable mercury complexes (Sedlak & Ulrich, 2009).

2.2 Effect of pH

According to PLS analysis, the pH-value had a high influence on THg concentrations in Balsjö, but not in Örebro. Furthermore, PLS analysis indicated that the pH correlated only negatively with THg concentrations at NorthCC (**Figure 21**). However, all sites in Balsjö showed a strong relationship between logTHg-logpH and logTOC-logpH. Leng & Nies (1999) found in laboratory studies that the optimum pH for methylation was 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 natural organic matter (e. g. TOC) is causing natural acidity which is an important factor for the lower pH in stream water in northern Sweden (Laudon et al., 1999). In this study up to 84 % of the pH variability could be explained by TOC in Balsjö. In Örebro, only SP showed a weak correlation between logTHg-logpH and logTOC-logpH indicating that the acidity in the southern catchments might be among other factors influenced by anthropogenic sulfur deposition. R1 and SP exhibited a weakly positive correlation between MeHg and pH. Interestingly, high methylation occurred until pH values higher than 6 at site R1 and SP. At site SH and R2 the highest methylation rates occurred below pH 5. As mercury specification is very much dependent on pH, it seemed that enough bioavailable THg complexes (e. g. HgS, $HgCl_2$, $Hg(OH)_2$), not in association with TOC, must be present at R1 and SP that sustained high methylation at increased pH-values. However, more research regarding pH dependent specification of Hg in the stream water is needed to assess the methylation process in Örebro and Balsjö.

3. Estimation of THg and MeHg concentration in stream water

As sampling is mostly focused on high flow events, it is difficult to capture the wide variations of Hg concentration in stream water. The strong link of THg with organic matter and in some cases also MeHg-TOC might be used to capture Hg dynamics during event and non event flows (e. g. this study, Dittman et al., 2010; Skyllberg et al., 2009). Research has shown that THg is mostly bound to the UV_{254} fraction of TOC (Dittman et al., 2009), which in this study could be approximated with the colored humic fraction and hence absorption. If THg and TOC are more associated with the dissolved phase, (filtered) absorption measurement (420 nm, UV_{254}) is a method to measure the (colored) organic matter content. For particulate linked carbon and mercury, turbidity measurements proved to be effective (Whyte & Kirchner, 2000). Hence, these analytical methods could be used as a first estimate of MeHg and THg concentration in water as they could be easily applied in the field as real time measurements. Better estimates of Hg concentrations on a finer time scale will lead to a better understanding of Hg dynamics and Hg budgets (Dittman et al., 2010). Furthermore, absorption as well as turbidity measurement are quite simple and much cheaper compared to the analytical laboratory methods used for MeHg and THg analyses.

In this study the possibility to use absorption measurement as estimation for mercury concentration was supported by the rather high coefficient of determination of the THg-Abs filt regression of the sites in Örebro and Balsjö (**Table 4**). The slope analysis of the THg-Abs filt relationship revealed that in Balsjö the slopes of the regression lines of all sites did not differ significantly whereas only the slopes of the treated in Örebro revealed no significant difference indicating that the treatment might have a higher effect in Örebro than in Balsjö.

However, it should be noted that the slopes of all treated sites in Örebro and Balsjö were in the same range and hence a treatment specific approach towards absorption measurement should be further assessed.

The relationship between THg-TOC was somewhat stronger for the sites in Balsjö, whereby the THg-Abs filt was overall stronger for the sites in Örebro.

4. Differences in response of treated and reference sites

Watershed characteristics like topography, size and the amount of wetlands strongly influence TOC, THg and MeHg dynamics (Grigal, 2002). In this study watershed specific differences (e. g. soil type, hydrologic flow paths, amount of wetlands, seasonal variation in temperature and flow) in the TOC, THg, and MeHg chemistry between Balsjö and Örebro were found. Also, forest treatment seemed to have an effect on the chemistry dynamics. In Balsjö, Sörensen et al. (2009a) reported a rather small increase or even decline in MeHg and THg concentrations in the treated compared to the untreated catchments after clear cut which were lower than increases in TH and MeHg concentrations reported in other studies after forest treatment (e. g. Povari et al., 2003a). In Örebro, no increase in THg, TOC and MeHg concentrations after site preparation and stump harvest was noticed (monitoring period started after the sites were logged) and even a significant decrease in MeHg and THg concentrations at SH and a significant decrease of MeHg in SP in relation to R1 could be found (Eklöf et al., in prep.). However, when comparing THg, TOC and MeHg concentrations (**Table 2**) as a snapshot without taking into account the pre-treatment history of the respective catchments, they showed significant higher THg, MeHg and TOC concentrations in the treated sites in Örebro and significant higher MeHg concentrations in the treated sites in Balsjö (Wilcoxon test, $p<0.05$). As differences in MeHg, TOC and THg concentrations are rather large between the sites in Örebro (also before site preparation and stump harvest took place) it could be possible that already the initial logging was responsible for the increase in concentrations in the treated areas (Eklöf et al., in prep.).

Logging activities lower the evapotranspiration resulting in raising water tables that saturate the upper organic rich soil layers (Kreutzweiser et al., 2008). This might have more effect on watersheds with less moist soils compared to ones that are already characterized by wetlands or histosoils. Furthermore, increasing water tables might also increase the hydrologic connectivity between soil solution and stream water and lead to increasing inorganic sulfide concentrations due to changes in the redox potential (Bishop et al., 2009).

The catchments in Örebro would be more affected by the above named changes due to logging activities than the ones in Balsjö not only from the soil property perspective but also from the climatic conditions favoring higher microbial growth and decomposition of organic material and hence increasing likely the export of mercury.

Differences in response to mercury and carbon dynamics of treated and reference sites were also shown by the different slopes in the THg-Abs filt relationship (**Table 4**). The slopes for the reference sites in Balsjö and Örebro were similar. However, R1 showed much higher slope for the THg-Abs filt regression line which could be explained with the fact that R1 was partially flooded by a beaver influencing hydrology and chemistry dynamics. The slope of the THg-Abs filt correlation of the treated sites was also in the same range indicating that the composition of TOC might have changed due to treatment activities.

5. Implications of climate change on carbon and mercury dynamics

The stored mercury and carbon concentrations in the soil were much higher in Balsjö compared to Örebro (**Figure 25**). Grigal (2003) attributed the higher SOM and Hg pool in the soil to shorter mineralization periods and further stated that these pools have a higher potential for hydrologic export. Mineralization is expected to be higher in warmer climates leading to an increased Hg and TOC flux from the soil (Grigal, 2003). Overall, a wetter and warmer climate due to climate change is predicted to occur in northern Sweden (SWECLIM, 2001). Köhler et al. (2009) modeled that DOC concentrations might increase by 15 % due to a warmer and wetter climate. This would have huge implications on THg dynamics and finally ecosystems. However, Agren et al. (2010) showed that winter climate plays an important role in elevated DOC concentrations during snowmelt due to e. g. physical (frost damaging cells and fine roots) and biological (adaptation of microorganisms to lower temperatures) forces acting in Winter. They further stated that the effect of the future climate on DOC concentrations in stream water depend on the combined effect of winter temperatures, and the timing, duration and depth of snow accumulation. Forecasting DOC and THg dynamics under changing climatic conditions is very challenging, extremely complex and leads sometimes to different results. However, there are indications that climate change might increase the DOC and THg export due to increased mineralization in northern Sweden having huge implications on human and ecosystem health.

V CONCLUSIONS AND OUTLOOK

This study strengthened the hypothesis that the TOC and mercury variability in northern Sweden are more influenced by flow, whereby temperature plays a higher role in the southern catchments. RIM model results, PLS, Pearson and time series analysis confirmed this theory.

45.5 % and 26.9 % of the THg concentrations in Balsjö and Örebro were attributed to high flow conditions which symbolizes the different hydrologic and climatic responses of the different major study sites in relation to catchment characteristic properties (e. g. amount of wetland, size, hydrologic pattern). Furthermore, it could be hypothesized that the large variation in response of sites regarding forest treatments lies in the different soil properties and characteristics and hence organic carbon quality and source formed over centuries by different climatic conditions. In Balsjö, the lack of correlation between MeHg and hardly every parameter, besides temperature suggested that high temperatures could be a factor increasing the methylation potential.

Furthermore, this study showed that the weekly calculated antecedent flow and temperature, so to say the condition of the watershed prior to events were highly important for the concentration of MeHg, TOC and THg on the respective event.

Across all sites, it was shown that organic matter is in most cases the number one factor explaining mercury dynamics. TOC in Balsjö and absorption (420 nm) in Örebro were able to best explain the variability of mercury. It was also shown that the MeHg transport was associated with TOC in general and especially with the colored fraction of TOC (absorption, 420 nm) for the sites in Örebro indicating the importance of organic matter in the mercury cycle. It was highlighted that the quality and source of organic matter is extremely important when linking OM to the storage, mobilization and transport of mercury.

THg and % TC soil storage was higher in Balsjö compared to Örebo, however, stream water THg, MeHg and TOC concentrations were higher in Örebro. Hence, higher turnover of biomass in Örebro is expected to be in close association with higher temperatures, precipitation and a rather homogenous flow pattern. The RIM models with their fairly easy set up proved to effectively model not only TOC, but THg and MeHg concentrations in stream water. RIM_{static} showed in general good results for TOC and THg models in Balsjö which were flow dominated. $RIM_{dyn}c0$ incorporating a seasonal component in varying c_0-base concentration over the year improved the model performance drastically in Örebro and also in Balsjö. $RIM_{dyn}c0$ soil solution profiles of the sites in Örebro and Balsjö supported the time series analysis and the soil analysis of the dry fraction done in this study.

Future research should make a closer assessment of the microbiological community and their byproducts (e. g. hydrophilic carbons) – also in comparison between Balsjö and Örebro. Overall the different TOC fraction under event and non-event flow within the soil and stream water should be analyzed before and after forest treatment as the knowledge about the fractions of TOC that mobilize and transport mercury are highly important in understanding the mercury cycle and hence mitigate its effects. Also, the influence of the antecedent watershed conditions on TOC, THg and MeHg concentrations should be closer examinated.

In order to assess the peak MeHg concentrations for further assessment, ISCO sampling over the respective period in July/August should be done. Furthermore, modeling of groundwater flow for all seasons could be done in order to assess how, when and where the subsurface flow crosses certain soil layers.

The $\mathrm{RIM}_{\mathrm{dyn}}$c0 approach should be further applied to a variety of study sites in order to test the hypothesis that adapting the same c0- base concentration on a regional scale would be feasible and hence simplify the necessary input data for the simulations.

VI REFERENCES

Aastrup, M., Johnson, J., Bringmark, E., Bringmark, L. & Iverfeldt (1991) ‚Occurance and transport of mercury within a small catchment Area’ Water, Air and Soil Poll. 56, 155 - 167

Agren, A., Haei, M., Köhler, S., Bishop, K. & Laudon, H. (2010), ‚Long cold winters give higher stream water dissolved organic carbon (DOC) concentrations during snowmelt‘, Biogeosciences Discuss. 7, 4857 - 4886

Aiken, G.R. & Cotsaris, E. (1995), ‘Soil and hydrology: their effect on NO;, JAWWA 87, 36 - 45

Alexandersson, H., Karlstroem, C. and Larsson-McCann, S. (1991) ‘Temperature and Precipitation in Sweden 1961–90. Reference Normals (in Swedish)’, SMHI Meteorology, 81, pp. 1–87. (In Swedish)

Alriksson, A. (2001), ‘Regionalvariability of Cd, Hg, Pb and C concentrations in different horizons of Swedish forest soils’, Water, Air and Soil Pollu.: Focus 1, 325 - 341

Amaral, A.L. & Ferreira, E.C. (2005), ‘Activated sludge monitoring of a wastewater treatment plant using image analyses and partial least squares regression”, Analytica Chimica Acta 544, 246 - 253

Andersson, A. (1979), 'Mercury in soils', in O. Nriagu (ed.), The Biogeochemistry of Mercury in the Environment. Elsevier, North-Holland Biomedical Press, Amsterdam, The Netherlands, pp. 79-112.

Anderson, D.W., Saggar, S., Betanny, J.R. & Stewart, J.W.B. (1981) ‚Particle size fraction and their use in studies of soil organic matter:I. The nature and distribution of forms of carbon, nitrogen, and sulfur’, Soil Sci. Soc. Am. J. 45, 767 - 772

Babiarz, C., Hurley, J., Benoit, J.M., Schafer, M.M., Andren, A.W. & Webb, D.A. (1998) ‘Seasonal influences on partitioning and transport of total and methylmercury in rivers from contrasting watersheds’ Biogeochemistry 41, 237 - 257

Benoit, J.M., Gilmour, C.C., Mason, R.P. & Heyes, A. (1999), ‘Sulfide controls on mercury speciation and bioavailability for methylating bacteria in sediment pore waters” Environ. Sci Technol. 33, 951 - 957

Bishop, K., Lee, Y-H., Pettersson, C. & Allard, B. (1995), ‘Methylmercury output from the Svartberget catchment in northern Sweden during spring flood’, Water Air Soil Pollut. 80, 445 - 454

Bishop K. & Lee, Y-H. (1997) ‘Catchments as a source of mercury/methylmercury in boreal surface waters’, in Sigel, H. & Sigel A. (Eds) ‘Mercury and its effects on environment and biology metal ions in biological systems’, Volume 34, Marcel Dekker

Bishop, K. Lee, Y.-H. Munthe, J., & Dambrine, E. (1998), ‘Xylem sap as a pathway for total mercury and methylmercury transport from soils to tree canopy in the boreal forest’, Biogeochemistry 40, 101 – 113

Bishop, K., Seibert, J., Köhler, S. & Laudon, H. (2004) ‘Resolving the Double Paradox of rapidly mobilized old water with highly variable responses in runoff chemistry‘, Hydrol. Process. 18, 185 – 189

Bishop, K., Allan, C., Bringmark, L., Garcia, E., Hellsten, S., Högbom, L., Johansson, K., Lomander, A., Melli, M., Munthe,J., Nilsson, M., Porvari, P., Skyllberg, U., Sorensen, R., Zettererg,

T. & Akerblom, S (2009) ‘The effects of Forestry on Hg bioaccumulation in nemoral/boreal waters and recommendations for good silvicultural practice’ Ambio 38, 373 - 380

Bourg, A.C.M. & Schindler, P.W. (1985), 'Control of trace metals in natural aquatic systems by the adsorptive properties of organic matter' in T.D. Lekkas (ed.), Proc. 5th Int. Conf. Heavy Metals in the Environment, Athens (GR), Sept. 1985, pp. 97-99.

Branfireun, B.A., Heyes, A., & Roulet, N.T. (1996) ‘The hydrology and methylation dynamics of a Precambrian Shield headwater peatland’, Water Resour. Res. 32, 1785 - 1794

Carrubba, L. (2000), ‘Hydrologic modeling at the watershed scale using NPSM’, Journal of the american water resource association 36, 1237 – 1246

Chin, W.W. (1998), ‘The Partial Least Squares Approach to Structural Equation Modeling,’ in: Modern Methods for Business Research, G.A. Marcoulides (ed.), Lawrence Erlbaum Associates, pp. 295-336.

Clarkson, T.W (1987) ‘Metal Toxicity in the Central Nervous System’, Envir. Health Perspec. 75, 59 - 64

Clarkson, T.W (1997) ‘The Toxicology of Mercury’, Critical Reviews in Clinical Laboratory Science. 34(3), 369 - 403

Compeau, G. C. & Bartha, R. (1985) ‘Sulfate-reducing bacteria: principal methylators of mercury in anoxic estuarine sediment’, Appl. Environ. Microbiol. 50, 498-502

Christ, M. J., &. David, M.B. (1996) ‘Temperature and moisture effects on the production of dissolved organic carbon in a spodosol’, Soil Biol. Biochem. 28; 1191-1199.

Davidson, E.A & Janssens, I.A. (2006) ‘Temperature sensitivity of soil carbon decomposition and feedback to climate change’, Nature 440/9, 165 - 173

Devereux, R, Winfrey, M.R., Winfrey J. & Stahl, D.A. (1996), ‘Depth profile of sulfate-reducing bacterial ribosomal RNA and mercury methylation in an estuarine sediment”, FEMS Microbiol. Ecol. 20, 23 – 31

Dilling, J. & Kaiser, K. (2002), ‘Estimation of the hydrophibic fraction of dissolved organic matter in water samples using UV photometry, Water Res. 36, 5037 - 5044

Dittman, J.A., Shanley, J.B., Discoll, C.T., Aiken, G.R., Chalmars, A.T. & Towse, J.E (2009) ‘Ultraviolet absorbance as a proxy for total dissolved mercury in streams, Environ. Polut. 157, 953 - 1956

Dittman, J.A., Shanley, J.B., Discoll, C.T., Aiken, G.R., Chalmars, A.T., Towse, J.E. & Selvendiran, P. (2010) ‘Mercury dynamics in relation to dissolved organic carbon concentration and quality during high flow events in three northeastern U.S. streams’, Water Resources Research 46, W07522; 1 - 15

Drott, A., Lambertsson, E.B., & Skyllberg, U. (2007), ‘Importance of dissolved neutral mercuy sulfides for methyl mercury production in contaminated sediments”, Environ. Sci. Technol. 41, 2270 - 2276

Eklöf, K, Maili, M., Akerblom, S., & Bishop, K (2011) ‚Impact of stump harvest on the export of total mercury and methylmercury to aquatic ecosystems‘, in prep.

Eriksson, L., E. Johansson, N. Kettaneh-Wold N. & S.Wold. 1999. Introduction to Multi- and Megavariate Data Analysis Using Projection Methods (PCA & PLS). Umetrics AB, Umeå, Sweden: 490 pp.

Evans, C.D., Chapman, P.J., Clark, J.M., Monteith, D.T. & Cresser, M.S. (2006) ‘Alternative explanations for rising dissolved organic carbon export from organic soils’, Global Change Biology 12, 2044 - 2053

Fahey, T. J., J. B. Yavitt, A. E. Blum, and J. I. Drever. 1985. Controls of soil-solution chemistry in lodgepole pine forest ecosystems, Wyoming. In Planetary Ecology. D.E. Caldwell, J.A. Brierley and C.L. Brierley (eds.). Van Nostrand Reinhold, New York, pp. 473-484.

Fierer, N., Schimel, J.P & Holden, P.A (2003) ‚Variation in microbial community composition through two soil depth profiles‘, Soil Biology & Biochemistry 35, 157 - 176

Fitzgerald, W.F., Engstrom, D.R., Mason, R.P. & Nater, E.A. (1998) ‘The case for atmospheric mercury contamination in remote areas’, Envrion. Sci. & Technol 32, 1 - 7

Fleck, J.A., Grigal, D.F. & Nater, E.A. (1999) ‘Mercury uptake by trees: An observation experiment’, Water Air Soil Pollut. 115, 513 - 523

Grabs, T., (2010), ‘Water quality modeling based on landscape analysis: importance of riparian hydrology’, Department of Physical Geography and Quaternary Geology, Stockholm University, Dissertation

Gilmour, C. C. & Henry, E. A. (1991) ‘Mercury methylation in aquatic systems affected by acid deposition’, Environ. Pollut. 71, 131 - 169

Grigal, D.F (2002) ‘Inputs and outputs of mercury from terrestrial watersheds: a review’, Environ. Rev. 10, 1 - 39

Grigal, D.F. (2003) ‘Mercury sequestration in forest and peatlands: a review’ J. Environ. Qual. 32, 393 - 405

Grigal, D.F., Nater, E.A & Homann, P.S. (1994), ‘Spatial distribution patterns of mercury in an east-central Minnesota landscape’, 305 – 312 in Watras, C.J. & Huckabee, J.W. (eds) ‘Mercury pollution: Integration and synthesis, Lewis Publ., Boca Raton, FL

Guggenberger, G., Kaiser, K & W. Zech, W. (1998), ‘Organic Colloids in Forest Soils: 1. Biochemical Mobilization in the forest floor’, Phys. Chem. Earth 23, 141 - 146

Haitzer, M., Aiken, G. R. & Ryan, J (2003) ‘Binding of Mercury(II) to Aquatic Humic Sutbstance: Influence of pH and Source of Humic substances’, Environ Sci. & Technol 37, 2436 – 2441

Hakanson, L., Andersson, T & Nilsson, A (1990) ‘Mercury in fisch in Swedish lakes – linkages to domestic and European sources of emission’, Water Air Soil Pollut. 50, 171 – 191.

Hintelmann, H.; Harris, R.; Heyes, A.; Hurley, J. P.; Kelly, C. A.;Krabbenhoft, D. P.; Lindberg, S.; Rudd, J. W. M.; Scott, K. J. & St. Louis, V. L. (2002) ‘Reactivity and mobility of new and old mercury deposition in a boreal forest ecosystem during the first year of the METAALICUS study’ Environ. Sci. Technol. 36, 5034– 5040.

Hurley, J.P, Cowell, S.E., Shafer, M.M. & Hughes, P.E. (1998), ‘Partitioning and transport of total and methyl mercury in the lower fox river, Wisconsin”, Environ. Sci. Technol. 32, 1424 - 1432

Jeremiason, J.D., Engstrom, D.R., Swain, E.B., Nater, E.A., Johnson, B.M., Almendinger, J.E., Monson, B.A. & Kolka, R.K. (2006) ‘Sulfate Addition Increases Methylmercury Producation in an experimental wetland’, Environ. Sci. Technol. 40, 3800 - 3806

Johansson K, Aastrup, M., Andersson, A., Bringmark, L. & Iverfeldt, A. (1991) ‘Mercury in Swedisch forest soils and waters – assessment of critical load’, Water Air and Soil Pollution 56, 267 – 281

Johnson, D.W. (1995) ‘Role of carbon in the cycling of other nutrients in forested ecosystems’, 299 – 328, in McFee, W.W. & Kelly, J.M. (eds) ‘Carbon forms and functions in the soils, SSSA, Madison, WI.

Kalbitz, K, Solinger, S, Park, H.-H., Michalzik, B. & Matzner, E. (2000) ‚Controls on the dynamics of dissolved organic matter in soils: A review‘, Soil Science 165 (4), 277 - 304

Kerin, E.J., Gilmour, C.C., Roden, E., Suzuki, M.T. Coates, J.D. & Mason, R.P. (2006), ‘Mercury methylation by dissimilatory iron-reducing bacteria’, Applied and Environ. Microbiol. 72, 7919 - 7921

Kirchner, J.W. (2003), ‘A double paradox in catchment hydrology and geochemistry’, Hydrol. Process 17, 871–874

Köhler, S. J., Buffam, I., Seibert, J., Bishop, K. H., & Laudon, H. (2009) ‘Dynamics of stream water TOC concentrations in a boreal headwater catchment: Controlling factors and implications for climate scenarios’, J. Hydrol., 373, 44–56,

Kreutzweiser D.P., Hazlett, P.W., & Gunn, J.M. (2008), ‘Logging impacts on the biogeochemistry of boreal forest soils and nutrient export to aquatic systems: A rewiew”, Environ. Rev. 16, 157 - 179

Kuglerová, L. (2010), ‘Effects of Forest Harvesting on the Hydrology of Boreal Streams: The Importance of Vegetation for the Water Balance of a Boreal Forest’, Master thesis, Department of Forest Ecology and Management, SLU, Umeå

Lambertsson, L. & Björn, E. (2004), ‘Validation of simplified field-adapted procedure for routine determinations of methyl mercury at trace levels in natural water samples using species-specific isotope dilution mass spectrometry”, Anal. Bioanal. Chem., 380, p. 5.

Laudon, H., Köhler, S. & Buffam, I (2004) ‘Seasonal TOC export from seven boreal catchments in northern Sweden’, Aquat. Sci. 66, 223 - 230

Laudon, H., Köhler, S & Bishop K.H. (1999) ‘Natural acidity or anthropogenic acidification in the spring flood of northern Sweden?’, The Science of the Total Environment 234, 63 - 73

L-Beackström, G., Hanell, U. & Svensson, G (2004), ‘Baking Quality of Winter Wheat Grown in Different Cultivating Systems, 1992 – 2001: A Holistic Approach’ J. of Sust. Agri. 24 (1), 53 - 79

Lee, Y.H., Bishop, K., Pettersson, C., Iverfeldt, A. & Allard, B., (1995) ‘Subcatchment output of mercury and methylmercury at svartberget in northern Sweden’, Water, Air and Soil Pollution 80, 455 - 465

Leenheer, J.A. & Croue, J.-P. (2003), ‚Characterizing aquatic dissolved organic matter‘ Environmental Science Technology 37, 19A-26A

Leng, J.F. & Nies, L.F. (1999), ‘The relationship between anaerobic reductive dechlorination and biomethylation of mercury”, Adv. Environ. Res. 3, UI - 402

Lepori, F., D. Palm & B. Malmqvist. (2005),’Effects of stream restoration on ecosystem functioning: detritus retentiveness and decomposition’ J. Appl. Ecol., 42: 228-238

Louis, V.L.St., Rudd, J.W.M. Kelly, C.A., Beaty, K.G., Flett, R.J. & Roulset, N.T. (1996), ‘Production and Loss of Methylmercury and Loss of Total Mercury from Boreal Forest Catchments Containing Different Types of Wetlands’, Environ. Sci. Technol. 30, 2719 - 2729

Löfgren, S., Ring, E., von Brömssen, C., Sörensen, R & Högbom, L. (2009) ‚Short-term effects of clear-cutting on the water chemistry oft wo boreal streams in northern Sweden: A paired catchment study, AMBIO 38 (7), 347 - 356

Lundquist, E.J., Jackson, L.E, & Scow, K.M., (1999) ‘Wetdry cycles affect dissolved organic carbon in two California agricultural soils’, Soil Biol. Biochem. 31; 1031-1038.

Munthe, J. & Hultberg, H. (2004) ‘Mercury and Methylmercury in runoff from a forested catchment – concentrations, fluxes and Their response to Manipulations’, Water, Air & Soil Pol. 4, 607 – 618

Munthe, J., Wängberg, I., Rognerud, S., Fjeld, E., Verta, M., Porvari, P., & Meili, M. (2007) ‘Mercury in Nordic ecosystems’, Swedish environmental research institute, IVL report B1761

Nash, J.E. & Sutcliffe, J.V. (1970), ‘River flow forcasting through conceptional models part I – a discussion of principles’, Journal of Hydrology 10, 282 - 290

Oades, J.M. (1988) ‘The retention of organic matter in soils’ Biogeochemistry 5, 35 - 70

Padmavathiamma, P. K. & Li, L. Y. (2007), ‘Phytoremediation technology: Hyperaccumulationmetals in plants’, Water Air Soil Pollut 184, 105 - 126

Porvari P, Verta, M., Munthe, J & Haapanen, M. (2003a) ‘Forestry practices increase Mercury and Methyl Mercury output from Boreal Forest Catchments’, Envir. Sci. & Technol 37, 2389 - 2393

Porvari, P. & Verta, M. (2003b) ‘Total and methyl mercury concentrations and fluxes from small boreal forest catchments in Finland’, Environmental Pollution 123, 181-191

Ravischandran, M. (2004), ‘Interactions between mercury and dissolved organic matter – a review”, Chemosphere 55, 319 - 331

Raymond, P.A & Saiers, J.E. (2010), ‘Event controlled DOC export from forested watersheds’, Biogeochemistry 100, 197 - 209

Regnell, O., Watras, C.J., Troedsson, B., Helgee, A. & Hammer, T. (2009), ‘Mercury in a boreal forest stream – role of historical mercury pollution, TOC, temperature and water discharge’, Environ. Sci. Technol. 43, 3514 - 3521

Reuter J.H. & Perude, F.M. (1976) ‘Importance of heavy metal-organic matter interactions in natural waters”, Geochimcia et Csmochimca Acta 41, 325 - 334

Rhode, H. (1972) ‘A study of the sulfur budget for the atmosphere over Northern Europe’, Tellus 24, issue 2

Rilfors, L. & Lindblom, G. (2002) ‘Regulation of lipid composition in biological membranes – biophysical studies of lipids and lipid synthesizing enzymes’, Colloid. Surface. B. 26, 112–124,

Rosipal, R. & Krämer, N. (2006), ‘Overview and recent advances in Partial Least Squares’, 34 – 51, in Saudernser et al., (eds) SLSFS 2005, Springer-Verlag, Berlin, Heidelberg

Schiff, S. Arvena, R., Mewhinney, E., Elgood, R., Warner, B., Dillon, P, & Trumbore, S (1998), ‘Precambrian shield wetlands: hydrologic control of the sources and export of dissolved organic matter’, Climate Change 40 (2), 167 - 188

Schroeder, W.H. & Munthe, J (1998) ‘Atmospheric mercury – an overview”, Atmospheric Environment 32, 809 – 822

Schroeder, W.H., Yarwood, G. & Niki, H. (1991) ‚Transformation processes involving mercury species in the atmosphere – results from a literature survey‘, Water, Air and Soil Pol. 56, 653 - 666

Schulze, E.-D. & Mooney, H.A. (1993), ‘Biodiversity and ecosystem function‘, Springer-Verlag, pp.88–90

Schuster, E., (1991), ‘The Behavior of mercury in the soil with special emphasis on complexation and adsorption processes – A review of the literature’, Water, Air and Soil Poll. 56, 667 - 680

Schuster, P.F., Shanley, J.B., Marvin-Dipasquale, M., Reddy, M.M., Aiken, G.R., Roth, D.A., Taylor, H.E., Krabbenhoft, D.P. & DeWild, J.F. (2008) ‘Mercury and organic carbon dynamics during runoff episodes from a northeastern USA watershed’, Water Air and Soil Pol 187, 89 - 108

Scott, M. J., Jones, M.N, Woof, C. & Tipping, E. (1998), ‘Concentrations and fluxes of dissolved organic carbon in drainage water from an upland peat system’, Environ. Int. 24; 537-546.

Sedlak D.L. & Ulrich, P.D. (2009), ‘Control of mercury methylation in wetland through iron addition”, UC Water Resource Center, Technical Completion Report for Project No. WR1012

Seibert, J., Grabs, T., Köhler, S., Laudon, H., Winderdahl, M. & Bishop, K. (2009), ‚Linking soil- and stream-water chemistry based on a Riparian Flow-Concentration Integration Model’, Hydrol. Earth Syst. Sci. 13, 2287 - 2297

Selvendrian, P., Driscoll, C.T., Bushey, J.T & Montesdeoca, M.R. (2008), ‘Wetland influence on mercury fate and transport in a temperate forested watershed’, Environmental Pollution 154, 46 - 55

Shanley, J.G., Mast, M.A., Campbell, D.H., Aiken, G.R., Krabbenhoft, D.P., Hunt, R.H., Walker, J.F., Schuster, P.F., Chalmers, A., Aulenbach, B.R., Pters, N.E., Marvin-DiPasqualte, M., Clow, D.W. & Shafer, M.M. (2008) ‘Comparison of total mercury and methyl mercury cycling at five sites using the small watershed approach’, Environ. Pollut. 154, 143 - 154

Shanley, J.B. & Bishop, K. (2010), ‘Hg cycling in terrestrial watersheds”, Chapter 10, in press

Skyllberg, U., Qian, J., Frech, W., Xia, K & Bleam, W.F. (2003) ‘Distribution of mercury, methyl mercury and organic sulfur species in soil, soil solution and stream of a boreal forest catchment”, Beiogeochemistry, 64, 53 - 76

Skyllberg, U., Westin, M.B., Meili, M. & Björn, E. (2009), ‘Elevated concentrations of methyl mercury in streams after forest clear-cut: A consequence of mobilization from soil or new mehtylation?’, Environ. Sci. Technol. 43, 8535 – 8541

Sörensen, R., Meili, M., Lambertsson, L., Brömssen, C. & Bishop, K. (2009a), ‘The effect of forest harvest operations on mercury and methylmercury in two boreal streams: relatively small changes in the first two years prior to site preparation’, Ambio 38, 364 – 371

Sörensen, R., Ring, E., Meili, M., Högbom, L., Seibert, J., Grabs, T., Laudon, H. & Bishop, K (2009b) ‚Forrest harvest increases runoff most during low flows in two boreal streams’, AMBIO 38 (7), 357 - 363

Swedish National Forest Inventory (2010) ‘Broadleaf dominated forest – proportion of productive forest land’, period 2005 – 2009, available at: http://efdac.jrc.ec.europa.eu/ (taken 28.03.2010)

SWECLIM, 2001. Ökad säkerhet i klimatfrågan, Norrköping, SMHI.

Temnerud, J. (2002), ‘The colour of water a sense of humus’, Man-Technology-Environment Research Center, Department of Natural Sciences, Örebro University

Troedsson, T. & Wiberg, M (1986) ‘Soil Map of Sweden, (Sheet 2)’, available at: http://eusoils.jrc.ec.europa.eu/library/maps/country_maps/metadata.cfm?mycountry=SE, European Commission, 2010 (taken 28.03.2010)

Ullrich, S.M., Tanton, Trevor, T.W. & Abdrashitova, S.A. (2001), ‘Mercury in the aquatic environment: A review of factors affecting methylation”, Critical Reviews in Environmental Science and Technology 31, 241 - 293

U.S.E.P. (2002) ‘Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry”, Method 1631, Revision E. – Washington, EPA (EPA-821-R-02-019)

US EPA (2007), ‘Method 7473 – Mercury in Solids and solutions by thermal decomposition, amalgamation and atomic absorption spectrophotometry”, available at: http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/7473.pdf (taken 15.05.11)

Venäläinen, A., H. Tuomenvirta, M. Heikinheimo, S. Kellomaki, H. Peltola, H. Strandman & H. Vaisanen, (2001) ‘Impact of climate change on soil frost under snow cover in a forested landscape’, Climate Res. 17, 63–72

Watras, C. J.; Morrison, K. A.; Regnell, O. & Kratz, T. K. (2006) ‘The methylmercury cycle in Little Rock Lake during experimental acidification and recovery’ Limnol. Oceanogr. 51, 257– 270.

Whyte, D.C & Kirchner, J.W. (2000) ‘Assessing water quality impacts and cleanup effectiveness in streams dominated by episodic mercury discharges, Sci. Total Environ. 260, 1 - 9

Winterdahl, M., Temnerud, J., Futter, M.N., Löfgren, S. & Bishop, K. (2011), ‘Riparian zone influence on stream water total organic carbon concentrations at the Swedish Integrated Monitoring sites‘, manuscript

Wold, S., Sjöström, M. & Eriksson, L. (2001), ‘PLS-regression: a basic tool of chemometrics’, Chemometrics and intelligent Laboratory Systems 58, 109 – 130

VII APPENDIX

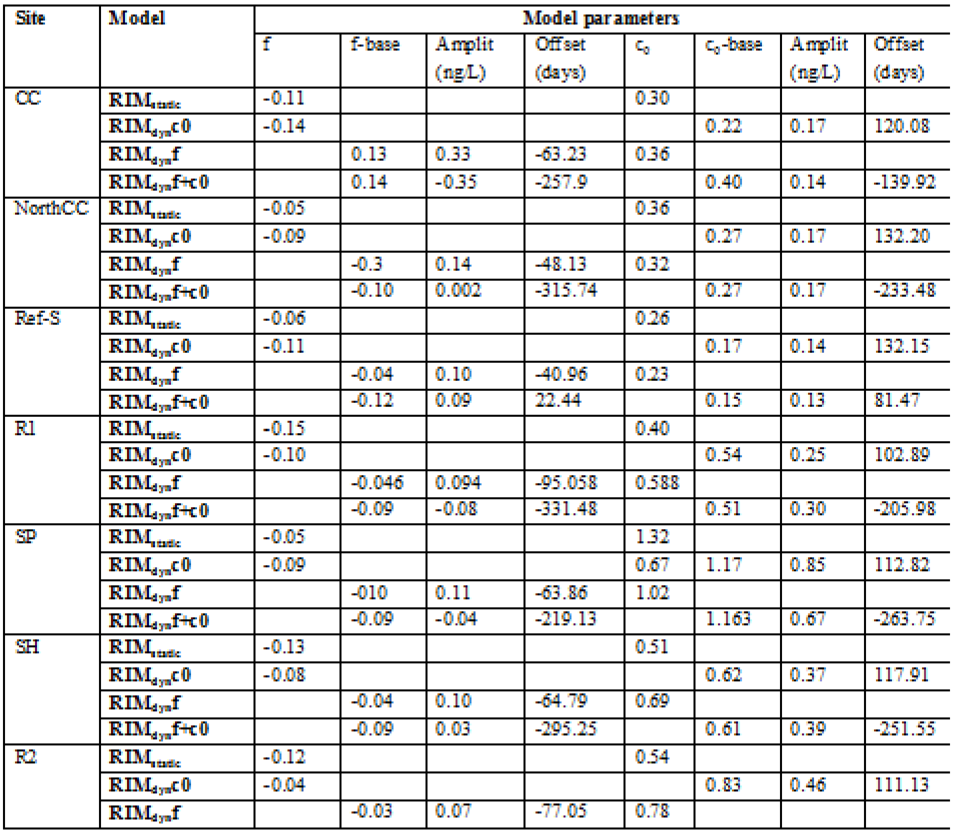
Table 5: Nash-Sutcliffe coeficient (NSC) for the RIM models in Balsjö and Örebro, improvement of model shown from RIM$_{static}$ to RIM$_{dynamic}$ and from one to two parameter model

Site	Parameter	RIMstatic	RIMdync0	RIMdynf	RIMdynf+c0	RIMstatic -> RIMdynamic	1 -> 2 parameter
CC	MeHg	0,03	0,14	0,18	0,19	0,15	0,01
CC	THg	0,52	0,68	0,55	0,70	0,16	0,02
CC	TOC	0,35	0,60	0,44	0,62	0,25	0,03
NorthCC	MeHg	0,03	0,22	0,20	0,22	0,18	0,00
NorthCC	THg	0,44	0,63	0,45	0,68	0,19	0,06
NorthCC	TOC	0,26	0,60	0,34	0,63	0,34	0,03
Ref-S	MeHg	0,12	0,51	0,60	0,62	0,48	0,02
Ref-S	THg	0,46	0,61	0,47	0,77	0,15	0,16
Ref-S	TOC	0,35	0,63	0,45	0,65	0,29	0,02
R1	MeHg	0,58	0,72	0,74	0,83	0,16	0,09
R1	THg	0,03	0,28	0,28	0,36	0,26	0,08
R1	TOC	0,01	0,41	0,26	0,44	0,39	0,04
SP	MeHg	0,07	0,76	0,65	0,77	0,68	0,01
SP	THg	0,01	0,39	0,23	0,51	0,37	0,12
SP	TOC	0,07	0,59	0,35	0,66	0,52	0,06
SH	MeHg	0,40	0,81	0,67	0,81	0,41	0,00
SH	THg	0,07	0,72	0,61	0,76	0,65	0,04
SH	TOC	0,07	0,87	0,67	0,87	0,80	0,01
R2	MeHg	0,34	0,73	0,54	0,75	0,39	0,02
R2	THg	0,30	0,71	0,65	0,76	0,41	0,05
R2	TOC	0,20	0,84	0,69	0,84	0,64	0,00

Table 6: Model parameters for the THg RIM models for Balsjö and Örebro

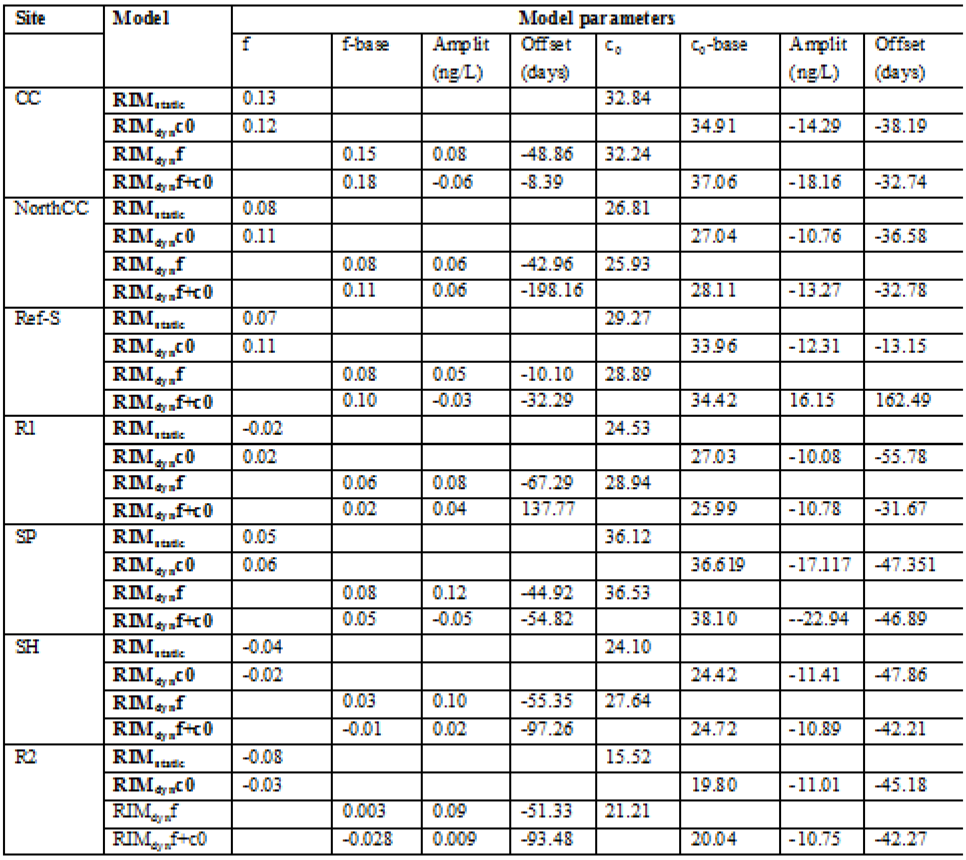
Site	**Model**	**Model parameters**							
		f	f-base	Amplit (ng/L)	Offset (days)	c_0	$c_0$base	Amplit (ng/L)	Offset (days)
CC	**RIM$_{static}$**	0.18				10.12			
	RIM$_{dyn}$c0	0.20					9.61	-4.00	-52.11
	RIM$_{dyn}$f		0.20	-0.08	102.12	10.11			
	RIM$_{dyn}$f+c0		0.22	0.06	-172.43	8.13	10.31	-4.22	-41.59
NorthCC	**RIM$_{static}$**	0.14				9.15			
	RIM$_{dyn}$c0	0.17					8.69	-3.50	-47.83
	RIM$_{dyn}$f		0.15	-0.03	46.54	9.31			
	RIM$_{dyn}$f+c0		0.15	-0.10	-40.26		8.79	-4.18	-49.99
Ref-S	**RIM$_{static}$**	0.11				9.70			
	RIM$_{dyn}$c0	0.15					10.17	-3.55	-30.04
	RIM$_{dyn}$f		0.12	0.03	-28.31	9.57			
	RIM$_{dyn}$f+c0		0.08	-0.050	-83.483		7.69	-2.96	-62.30
R1	**RIM$_{static}$**	-0.04				5.89			
	RIM$_{dyn}$c0	0.03					7.98	-3.91	-79.08
	RIM$_{dyn}$f		0.10	0.15	-84.66	8.13			
	RIM$_{dyn}$f+c0		0.09	0.1061	-95.94		8.32	-3.00	-57.70
SP	**RIM$_{static}$**	0.02				11.48			
	RIM$_{dyn}$c0	0.04				4.87	12.55	-4.38	-66.07
	RIM$_{dyn}$f		0.05	0.09	-74.89	12.072			
	RIM$_{dyn}$f+c0		0.05	0.08	184.98		12.81	6.84	147.41
SH	**RIM$_{static}$**	-0.05				7.32			
	RIM$_{dyn}$c0	-0.01					8.10	-4.16	-67.92
	RIM$_{dyn}$f		0.06	0.13	-73.65	9.25			
	RIM$_{dyn}$f+c0		0.03	0.05	-98.34		8.52	-3.52	-54.34
R2	**RIM$_{static}$**	-0.01				3.30			
	RIM$_{dyn}$c0	-0.03					4.76	-2.32	-74.92
	RIM$_{dyn}$f		0.02	0.10	-83.32	5.15			
	RIM$_{dyn}$f+c0		-0.002	0.05	-133.72	8.13	5.08	-2.29	-47.06

Table 7: Model parameters for the MeHg RIM models for Balsjö and Örebro



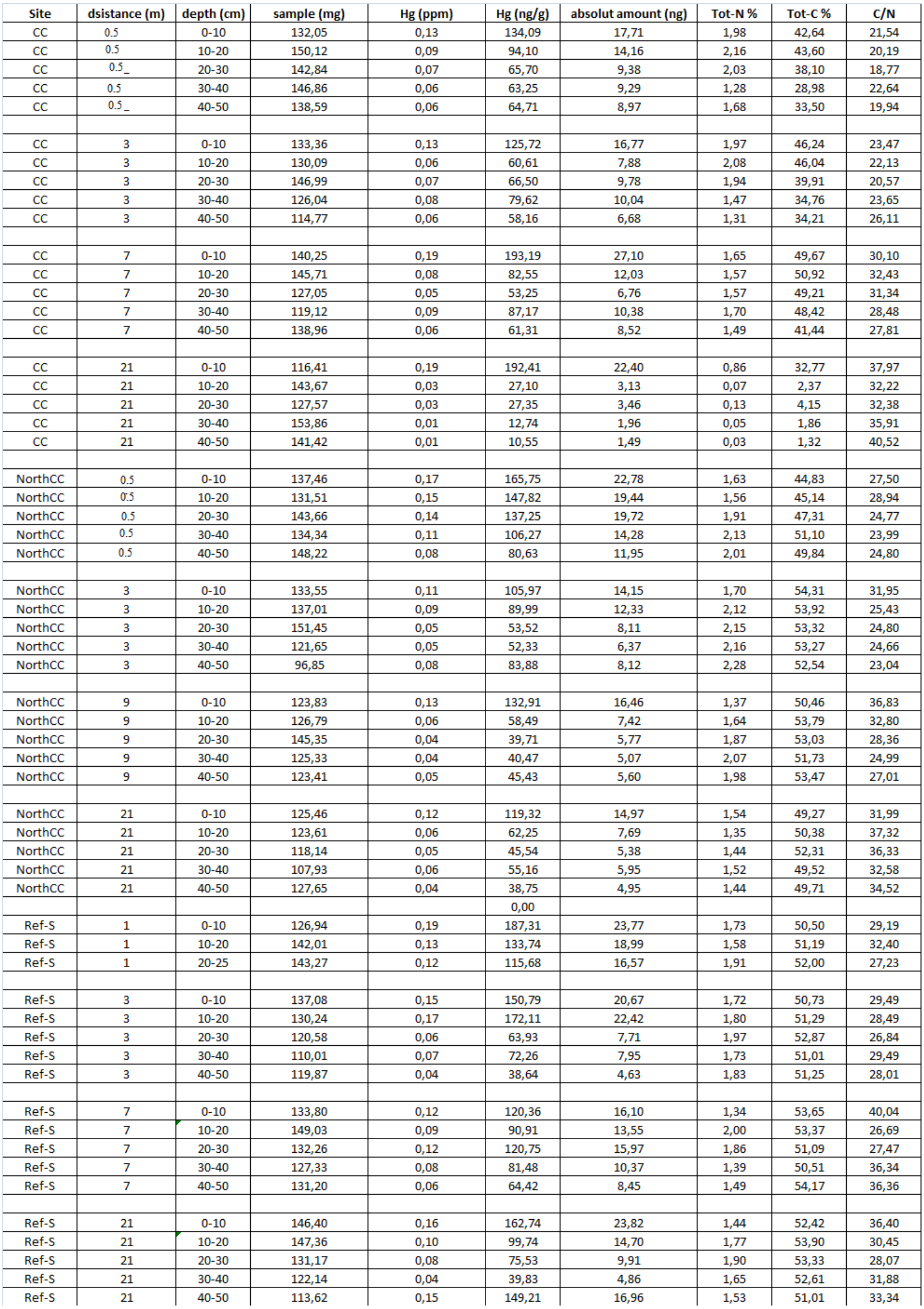
Site	Model	Model parameters							
		f	f-base	Amplit (ng/L)	Offset (days)	c$_0$	c$_0$-base	Amplit (ng/L)	Offset (days)
CC	**RIM$_{static}$**	-0.11				0.30			
	RIM$_{dyn}$c0	-0.14					0.22	0.17	120.08
	RIM$_{dyn}$f		0.13	0.33	-63.23	0.36			
	RIM$_{dyn}$f+c0		0.14	-0.35	-257.9		0.40	0.14	-139.92
NorthCC	**RIM$_{static}$**	-0.05				0.36			
	RIM$_{dyn}$c0	-0.09					0.27	0.17	132.20
	RIM$_{dyn}$f		-0.3	0.14	-48.13	0.32			
	RIM$_{dyn}$f+c0		-0.10	0.002	-315.74		0.27	0.17	-233.48
Ref-S	**RIM$_{static}$**	-0.06				0.26			
	RIM$_{dyn}$c0	-0.11					0.17	0.14	132.15
	RIM$_{dyn}$f		-0.04	0.10	-40.96	0.23			
	RIM$_{dyn}$f+c0		-0.12	0.09	22.44		0.15	0.13	81.47
R1	**RIM$_{static}$**	-0.15				0.40			
	RIM$_{dyn}$c0	-0.10					0.54	0.25	102.89
	RIM$_{dyn}$f		-0.046	0.094	-95.058	0.588			
	RIM$_{dyn}$f+c0		-0.09	-0.08	-331.48		0.51	0.30	-205.98
SP	**RIM$_{static}$**	-0.05				1.32			
	RIM$_{dyn}$c0	-0.09				0.67	1.17	0.85	112.82
	RIM$_{dyn}$f		-010	0.11	-63.86	1.02			
	RIM$_{dyn}$f+c0		-0.09	-0.04	-219.13		1.163	0.67	-263.75
SH	**RIM$_{static}$**	-0.13				0.51			
	RIM$_{dyn}$c0	-0.08					0.62	0.37	117.91
	RIM$_{dyn}$f		-0.04	0.10	-64.79	0.69			
	RIM$_{dyn}$f+c0		-0.09	0.03	-295.25		0.61	0.39	-251.55
R2	**RIM$_{static}$**	-0.12				0.54			
	RIM$_{dyn}$c0	-0.04					0.83	0.46	111.13
	RIM$_{dyn}$f		-0.03	0.07	-77.05	0.78			

Table 8: Model parameters for the TOC RIM models for Balsjö and Örebro



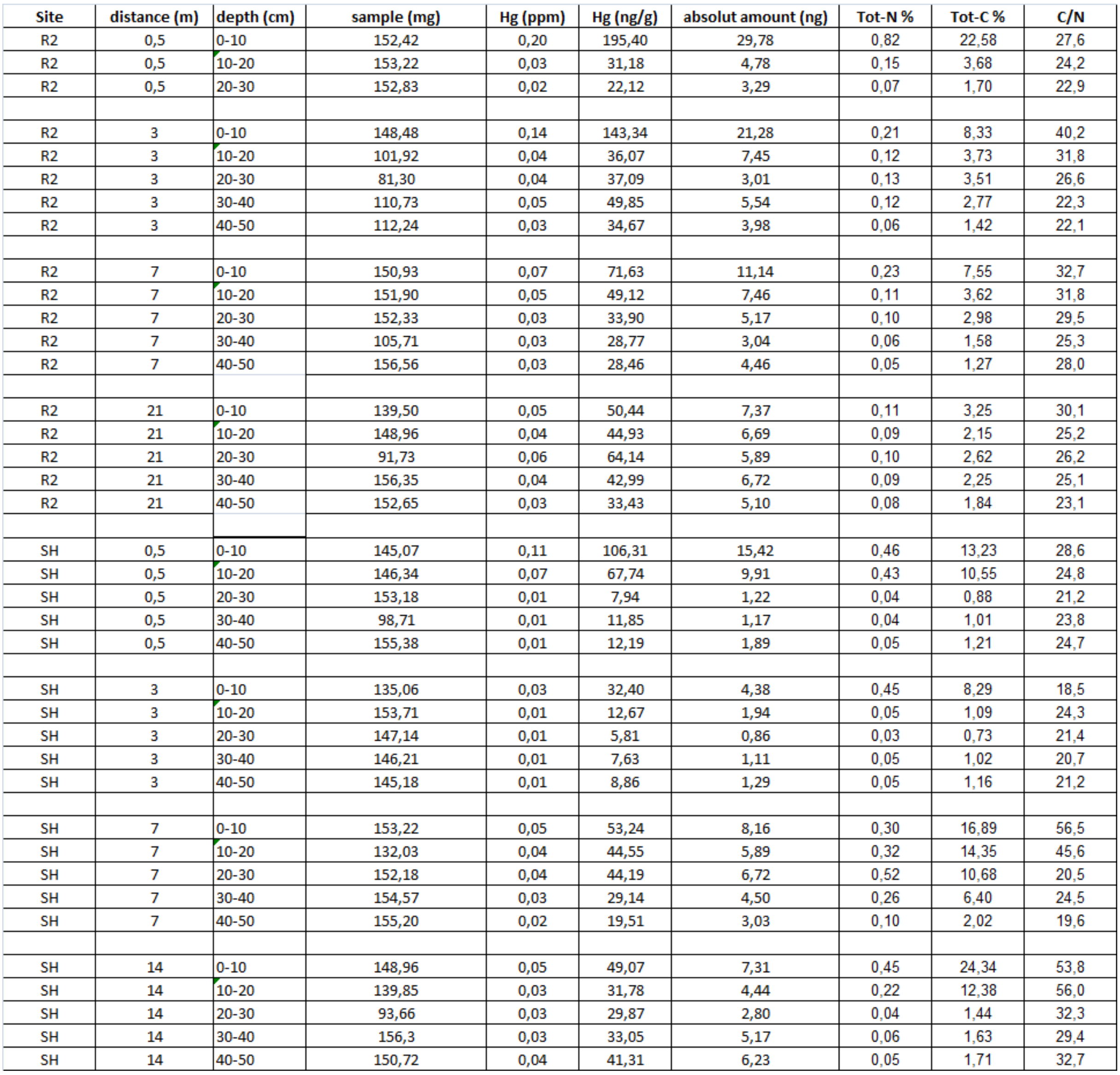
Site	Model	Model parameters							
		f	f-base	Amplit (ng/L)	Offset (days)	c$_0$	c$_0$-base	Amplit (ng/L)	Offset (days)
CC	**RIM$_{static}$**	0.13				32.84			
	RIM$_{dyn}$c0	0.12					34.91	-14.29	-38.19
	RIM$_{dyn}$f		0.15	0.08	-48.86	32.24			
	RIM$_{dyn}$f+c0		0.18	-0.06	-8.39		37.06	-18.16	-32.74
NorthCC	**RIM$_{static}$**	0.08				26.81			
	RIM$_{dyn}$c0	0.11					27.04	-10.76	-36.58
	RIM$_{dyn}$f		0.08	0.06	-42.96	25.93			
	RIM$_{dyn}$f+c0		0.11	0.06	-198.16		28.11	-13.27	-32.78
Ref-S	**RIM$_{static}$**	0.07				29.27			
	RIM$_{dyn}$c0	0.11					33.96	-12.31	-13.15
	RIM$_{dyn}$f		0.08	0.05	-10.10	28.89			
	RIM$_{dyn}$f+c0		0.10	-0.03	-32.29		34.42	16.15	162.49
R1	**RIM$_{static}$**	-0.02				24.53			
	RIM$_{dyn}$c0	0.02					27.03	-10.08	-55.78
	RIM$_{dyn}$f		0.06	0.08	-67.29	28.94			
	RIM$_{dyn}$f+c0		0.02	0.04	137.77		25.99	-10.78	-31.67
SP	**RIM$_{static}$**	0.05				36.12			
	RIM$_{dyn}$c0	0.06					36.619	-17.117	-47.351
	RIM$_{dyn}$f		0.08	0.12	-44.92	36.53			
	RIM$_{dyn}$f+c0		0.05	-0.05	-54.82		38.10	--22.94	-46.89
SH	**RIM$_{static}$**	-0.04				24.10			
	RIM$_{dyn}$c0	-0.02					24.42	-11.41	-47.86
	RIM$_{dyn}$f		0.03	0.10	-55.35	27.64			
	RIM$_{dyn}$f+c0		-0.01	0.02	-97.26		24.72	-10.89	-42.21
R2	**RIM$_{static}$**	-0.08				15.52			
	RIM$_{dyn}$c0	-0.03					19.80	-11.01	-45.18
	RIM$_{dyn}$f		0.003	0.09	-51.33	21.21			
	RIM$_{dyn}$f+c0		-0.028	0.009	-93.48		20.04	-10.75	-42.27

Table 9: THg soil storage, TC and TN (%) of the soil sampling in Balsjö



Site	dsistance (m)	depth (cm)	sample (mg)	Hg (ppm)	Hg (ng/g)	absolut amount (ng)	Tot-N %	Tot-C %	C/N
CC	0.5	0-10	132,05	0,13	134,09	17,71	1,98	42,64	21,54
CC	0.5	10-20	150,12	0,09	94,10	14,16	2,16	43,60	20,19
CC	0.5	20-30	142,84	0,07	65,70	9,38	2,03	38,10	18,77
CC	0.5	30-40	146,86	0,06	63,25	9,29	1,28	28,98	22,64
CC	0.5	40-50	138,59	0,06	64,71	8,97	1,68	33,50	19,94
CC	3	0-10	133,36	0,13	125,72	16,77	1,97	46,24	23,47
CC	3	10-20	130,09	0,06	60,61	7,88	2,08	46,04	22,13
CC	3	20-30	146,99	0,07	66,50	9,78	1,94	39,91	20,57
CC	3	30-40	126,04	0,08	79,62	10,04	1,47	34,76	23,65
CC	3	40-50	114,77	0,06	58,16	6,68	1,31	34,21	26,11
CC	7	0-10	140,25	0,19	193,19	27,10	1,65	49,67	30,10
CC	7	10-20	145,71	0,08	82,55	12,03	1,57	50,92	32,43
CC	7	20-30	127,05	0,05	53,25	6,76	1,57	49,21	31,34
CC	7	30-40	119,12	0,09	87,17	10,38	1,70	48,42	28,48
CC	7	40-50	138,96	0,06	61,31	8,52	1,49	41,44	27,81
CC	21	0-10	116,41	0,19	192,41	22,40	0,86	32,77	37,97
CC	21	10-20	143,67	0,03	27,10	3,13	0,07	2,37	32,22
CC	21	20-30	127,57	0,03	27,35	3,46	0,13	4,15	32,38
CC	21	30-40	153,86	0,01	12,74	1,96	0,05	1,86	35,91
CC	21	40-50	141,42	0,01	10,55	1,49	0,03	1,32	40,52
NorthCC	0.5	0-10	137,46	0,17	165,75	22,78	1,63	44,83	27,50
NorthCC	0.5	10-20	131,51	0,15	147,82	19,44	1,56	45,14	28,94
NorthCC	0.5	20-30	143,66	0,14	137,25	19,72	1,91	47,31	24,77
NorthCC	0.5	30-40	134,34	0,11	106,27	14,28	2,13	51,10	23,99
NorthCC	0.5	40-50	148,22	0,08	80,63	11,95	2,01	49,84	24,80
NorthCC	3	0-10	133,55	0,11	105,97	14,15	1,70	54,31	31,95
NorthCC	3	10-20	137,01	0,09	89,99	12,33	2,12	53,92	25,43
NorthCC	3	20-30	151,45	0,05	53,52	8,11	2,15	53,32	24,80
NorthCC	3	30-40	121,65	0,05	52,33	6,37	2,16	53,27	24,66
NorthCC	3	40-50	96,85	0,08	83,88	8,12	2,28	52,54	23,04
NorthCC	9	0-10	123,83	0,13	132,91	16,46	1,37	50,46	36,83
NorthCC	9	10-20	126,79	0,06	58,49	7,42	1,64	53,79	32,80
NorthCC	9	20-30	145,35	0,04	39,71	5,77	1,87	53,03	28,36
NorthCC	9	30-40	125,33	0,04	40,47	5,07	2,07	51,73	24,99
NorthCC	9	40-50	123,41	0,05	45,43	5,60	1,98	53,47	27,01
NorthCC	21	0-10	125,46	0,12	119,32	14,97	1,54	49,27	31,99
NorthCC	21	10-20	123,61	0,06	62,25	7,69	1,35	50,38	37,32
NorthCC	21	20-30	118,14	0,05	45,54	5,38	1,44	52,31	36,33
NorthCC	21	30-40	107,93	0,06	55,16	5,95	1,52	49,52	32,58
NorthCC	21	40-50	127,65	0,04	38,75	4,95	1,44	49,71	34,52
					0,00				
Ref-S	1	0-10	126,94	0,19	187,31	23,77	1,73	50,50	29,19
Ref-S	1	10-20	142,01	0,13	133,74	18,99	1,58	51,19	32,40
Ref-S	1	20-25	143,27	0,12	115,68	16,57	1,91	52,00	27,23
Ref-S	3	0-10	137,08	0,15	150,79	20,67	1,72	50,73	29,49
Ref-S	3	10-20	130,24	0,17	172,11	22,42	1,80	51,29	28,49
Ref-S	3	20-30	120,58	0,06	63,93	7,71	1,97	52,87	26,84
Ref-S	3	30-40	110,01	0,07	72,26	7,95	1,73	51,01	29,49
Ref-S	3	40-50	119,87	0,04	38,64	4,63	1,83	51,25	28,01
Ref-S	7	0-10	133,80	0,12	120,36	16,10	1,34	53,65	40,04
Ref-S	7	10-20	149,03	0,09	90,91	13,55	2,00	53,37	26,69
Ref-S	7	20-30	132,26	0,12	120,75	15,97	1,86	51,09	27,47
Ref-S	7	30-40	127,33	0,08	81,48	10,37	1,39	50,51	36,34
Ref-S	7	40-50	131,20	0,06	64,42	8,45	1,49	54,17	36,36
Ref-S	21	0-10	146,40	0,16	162,74	23,82	1,44	52,42	36,40
Ref-S	21	10-20	147,36	0,10	99,74	14,70	1,77	53,90	30,45
Ref-S	21	20-30	131,17	0,08	75,53	9,91	1,90	53,33	28,07
Ref-S	21	30-40	122,14	0,04	39,83	4,86	1,65	52,61	31,88
Ref-S	21	40-50	113,62	0,15	149,21	16,96	1,53	51,01	33,34

Table 10: THg soil storage, TC and TN (%) values of the soil sampling in Örebro



Site	distance (m)	depth (cm)	sample (mg)	Hg (ppm)	Hg (ng/g)	absolut amount (ng)	Tot-N %	Tot-C %	C/N
R2	0,5	0-10	152,42	0,20	195,40	29,78	0,82	22,58	27,6
R2	0,5	10-20	153,22	0,03	31,18	4,78	0,15	3,68	24,2
R2	0,5	20-30	152,83	0,02	22,12	3,29	0,07	1,70	22,9
R2	3	0-10	148,48	0,14	143,34	21,28	0,21	8,33	40,2
R2	3	10-20	101,92	0,04	36,07	7,45	0,12	3,73	31,8
R2	3	20-30	81,30	0,04	37,09	3,01	0,13	3,51	26,6
R2	3	30-40	110,73	0,05	49,85	5,54	0,12	2,77	22,3
R2	3	40-50	112,24	0,03	34,67	3,98	0,06	1,42	22,1
R2	7	0-10	150,93	0,07	71,63	11,14	0,23	7,55	32,7
R2	7	10-20	151,90	0,05	49,12	7,46	0,11	3,62	31,8
R2	7	20-30	152,33	0,03	33,90	5,17	0,10	2,98	29,5
R2	7	30-40	105,71	0,03	28,77	3,04	0,06	1,58	25,3
R2	7	40-50	156,56	0,03	28,46	4,46	0,05	1,27	28,0
R2	21	0-10	139,50	0,05	50,44	7,37	0,11	3,25	30,1
R2	21	10-20	148,96	0,04	44,93	6,69	0,09	2,15	25,2
R2	21	20-30	91,73	0,06	64,14	5,89	0,10	2,62	26,2
R2	21	30-40	156,35	0,04	42,99	6,72	0,09	2,25	25,1
R2	21	40-50	152,65	0,03	33,43	5,10	0,08	1,84	23,1
SH	0,5	0-10	145,07	0,11	106,31	15,42	0,46	13,23	28,6
SH	0,5	10-20	146,34	0,07	67,74	9,91	0,43	10,55	24,8
SH	0,5	20-30	153,18	0,01	7,94	1,22	0,04	0,88	21,2
SH	0,5	30-40	98,71	0,01	11,85	1,17	0,04	1,01	23,8
SH	0,5	40-50	155,38	0,01	12,19	1,89	0,05	1,21	24,7
SH	3	0-10	135,06	0,03	32,40	4,38	0,45	8,29	18,5
SH	3	10-20	153,71	0,01	12,67	1,94	0,05	1,09	24,3
SH	3	20-30	147,14	0,01	5,81	0,86	0,03	0,73	21,4
SH	3	30-40	146,21	0,01	7,63	1,11	0,05	1,02	20,7
SH	3	40-50	145,18	0,01	8,86	1,29	0,05	1,16	21,2
SH	7	0-10	153,22	0,05	53,24	8,16	0,30	16,89	56,5
SH	7	10-20	132,03	0,04	44,55	5,89	0,32	14,35	45,6
SH	7	20-30	152,18	0,04	44,19	6,72	0,52	10,68	20,5
SH	7	30-40	154,57	0,03	29,14	4,50	0,26	6,40	24,5
SH	7	40-50	155,20	0,02	19,51	3,03	0,10	2,02	19,6
SH	14	0-10	148,96	0,05	49,07	7,31	0,45	24,34	53,8
SH	14	10-20	139,85	0,03	31,78	4,44	0,22	12,38	56,0
SH	14	20-30	93,66	0,03	29,87	2,80	0,04	1,44	32,3
SH	14	30-40	156,3	0,03	33,05	5,17	0,06	1,63	29,4
SH	14	40-50	150,72	0,04	41,31	6,23	0,05	1,71	32,7

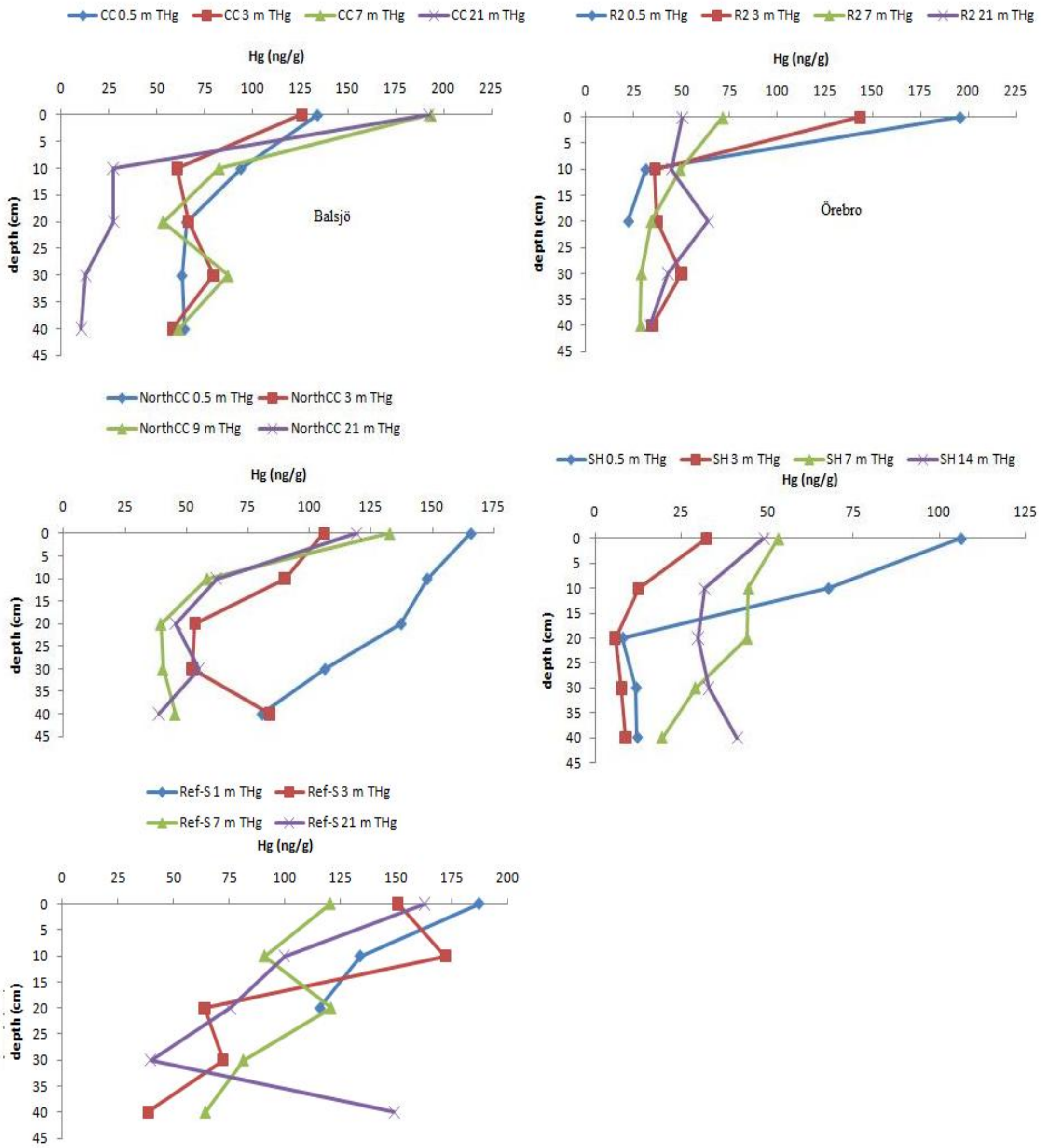


Figure 30: Soil THg profiles for the sites in Balsjö (left) and Örebro (right)