Methylmercury in runoff from forested catchments: Characterisation of three catchments prior to logging

Malin Bernhardsson

Department of Environmental Assessment
Swedish University of Agricultural Sciences
Box 7050 SE 750 07 Uppsala

Supervisors: Kevin Bishop, Department of Environmental Assessment, Swedish University of Agricultural Sciences and Guy Kirk, National Soil Resources Institute, Cranfield University.
This report presents an MSc theses in Soil Science, carried out in cooperation between the Department of Environmental Assessment, Faculty of Natural Resources and Agricultural Sciences, SLU and Cranfield University at Silsoe. The work has been supervised and reviewed by supervisors, and been approved by the examinator. However, the author is the sole responsible for the content.
Methylmercury in runoff from forested catchments: Characterisation of three catchments prior to logging
Cranfield University at Silsoe

Malin Bernhardsson

MSc Environmental Water Management

Academic Year: 04/05

Methylmercury in runoff from forested catchments:
Characterisation of three catchments prior to logging

Abstract

High mercury concentrations in freshwater fish compose a serious environmental problem in Sweden and a threat to human health. Mercury is accumulated in the food chain as methylmercury which is a potential nervous toxin, especially harmful for prenatal life. Due to anthropogenic emissions, mercury concentration in the atmosphere has increased, which has led to faster deposition rates and a storage of mercury in forest soils. Inorganic mercury is transformed into methylmercury by sulphur reducing bacteria in anoxic environments like wetlands and lake sediment and enters aquatic systems by runoff. Lately studies have shown that catchments subject to forestry practices have had an increased methylmercury load in runoff compared to undisturbed catchments. In Balsjö, northern Sweden a project is started to study the impacts of forestry on mercury levels in three forested catchments. This study is part of the baseline assessment as a characterisation of the study area with respect to mercury occurrence. Methyl- and total mercury concentrations in soil pore water have been measured using isotope dilution, gas chromatography-inductively coupled plasma mass spectrometry. The results have been compared with results from other studies in Sweden and show very low concentrations in the Balsjö area which may be due to the way the sampling was carried out. There were no significant differences in pre-treatment conditions between the catchments. Methylmercury concentrations are not controlled by total mercury but rather by the potential for methylation within the catchment. The lack of relationship between methylmercury concentrations seen in soil and water shows that it is not a simple equilibrium but indicates that other factors are involved where the binding to organic material could be one.
Acknowledgements

I would like to thank my supervisors, Prof. Kevin Bishop (Swedish university of Agricultural Sciences) and Prof. Guy Kirk (Cranfield University) for ideas, advice and support during my work on this thesis.

I also would like to acknowledge the Department for Analytical Chemistry at Umeå University where all analysis were made and thank Dr. Lars Lambertsson for supervision in the analysis.

Finally thanks to Rasmus Sörensen for help and support in field work and data analysis.
## Contents

1 Introduction and objectives.................................................................1

2 Background information........................................................................3

2.1 The mercury cycle...........................................................................3

2.2 Bioaccumulation and human exposure...........................................4

2.3 Methylation by sulphur reducing bacteria.......................................5

2.4 Methylmercury in terrestrial runoff- importance of wetlands...........6

2.5 Organic material – carrier of methylmercury...................................7

2.6 Effects of acid deposition.................................................................8

2.7 Impacts of forestry............................................................................9

2.8 Mercury levels in Swedish fish........................................................10

3 Methodology.......................................................................................12

3.1 Study site and sampling procedure................................................12

3.2 Analytical methods..........................................................................13

3.3 Comparisons to other studies.........................................................15

4 Results and Discussion......................................................................16

4.1 Groundwater ..................................................................................16

4.2 Importance of the riparian zone......................................................16

4.3 Groundwater levels.........................................................................17

4.4 Runoff...............................................................................................17

4.5 The Balsjö area compared to southern Sweden..............................20

4.6 Relations between methylation rates and methylmercury concentrations.................................................................22

4.7 Increased methylation rates after logging.......................................24

5 Conclusions.......................................................................................26

6 References..........................................................................................28

Appendix................................................................................................30
List of tables and figures

Fig 1.1. The Balsjö study area located in north-eastern Sweden.........................................................2
Fig 2.1 Location of major mercury emission sources in Sweden (Håkansson et al. 1988).....................3
Fig 2.2 Mercury levels (mg/kg) in forest soil, from (Meili, 2001)..........................................................4
Fig 2.3 Sulphate deposition in Sweden, concentrations in precipitation (mg/l) (IVL 2004)...............9
Fig 2.4 Mercury concentration (mg/ kg) in1-kg pike (Munthe et al 2004)...........................................11
Fig 3.1 Scematic map of the Balsjö study area. In A the two different watersheds are shown with the V- notch weirs marked and in B it is shown how the groundwater pipes used for sampling and measuring of groundwater levels are installed along transects perpendicular to the stream. From Ring and Högbom (2005).................................................................................................................................13
Fig 4.1 Groundwater methylmercury concentrations seen at different distances from the stream.........16
Fig 4.2 Methylmercury concentration relative groundwater depth..................................................17
Fig 4.3 Runoff measured from WSF and WS7 during spring 2005.....................................................17
Fig 4.4 Total mercury in runoff during spring 2005 for the three study catchments .........................18
Fig 4.5 Methylmercury concentrations in runoff during spring 2005 for the three study catchments.....18
Fig 4.6 Methylmercury in soil pore water and runoff within WSF, WS9 and WS7..............................18
Fig 4.7 Methylmercury concentrations in soil pore water similar to concentrations in runoff. From Bergman et al. (in review)..............................................................................................................19
Fig 4.8 Number of sampled sites in southern Sweden with a particular methylmercury concentration...20
Fig 4.9 Variation of methylmercury concentrations measured at two soil depths in mires across southern Sweden (Bishop et al unpublished), and average concentrations seen in the Balsjö area..................................................21
Fig 4.10 Methylmercury concentrations in peat pore water at two sampling depths relative soil sulphur content in the studied mires in southern Sweden........................................................................22
Fig 4.11 Methylmercury concentrations in peat pore water at the two sampling depths relative total mercury content in peat soil in the studied mires in southern Sweden...........................................22
Fig 4.12 Peat methylmercury content relative methylation rate..........................................................23
Fig 4.13 Methylmercury concentrations in soil pore water relative methylation rate..........................23
Fig 4.14 Methylmercury concentrations in soil pore water relative methylmercury in peat soil. Data by Bishop et al. (unpublished)...............................................................................................................23
Fig 4.15 No correlation between methylmercury and TOC in soil pore water. Data by Bishop et al (unpublished)............................................................................................................................................24

Table 4.1 Methyl- and total mercury concentrations (average values in brackets) found in Balsjö (this study), Vindeln (Lee et al. 1995), (Bishop et al. 1995), Degerö (Bergman et al. XXXX) and Southern Sweden (Bishop et al. unpublished)..................................................................................................24
List of symbols

MeHg: Methylmercury, measured in ng/l in water samples.

Hg tot: Total mercury, measured in ng/l in water samples.

DOC: Dissolved organic carbon, measured in mg/l in water samples.

TOC: Total organic carbon, measured in mg/l.
1 Introduction and objectives

High mercury levels in freshwater fish have been an environmental problem in Sweden for many years. It was first believed to be acid rain in combination with mercury deposition that caused the high concentrations in fish (Håkansson et al 1990), but the complexity of the problem was revealed when it was discovered that also fish from lakes in remote areas with very low levels of mercury and acid deposition contained high levels of mercury. Another part of the complexity is that even though mercury occurs in different chemical forms (species), it is only bioaccumulated in the food chain as methylmercury which is an organic form of mercury (Bloom 1992). Methylmercury is the most toxic form of mercury and becomes a hazard to human health when it occurs in high concentration in fish (WHO 1991). Today thousands of Swedish lakes contain fish with mercury concentrations above the recommended guidelines for human consumption.

Many studies on the subject have been carried out since the problem was discovered resulting in a lot of new knowledge on factors controlling mercury levels in fish. There are though still uncertainties regarding for example biological transformation of mercury species and the mechanisms behind mercury output from catchments. The impacts of forestry is another interesting subject since there are indications that forestry practices may increase methylmercury output from watersheds (IVL 2002), but the issue needs to be studied further to understand the effects. Since forestry is an important industry in Sweden covering large areas of the country many lakes may be affected by this which makes the issue important.

In Balsjö, north-eastern Sweden, a study on forestry’s impact on methylmercury concentrations in peat porewater and catchment runoff is started. Within two watersheds, forested areas will be subject to different treatments. One will be totally clear-cut and one will be clear-cut with buffer strips along the stream which is the common environmental consideration taken at forest harvesting in Sweden according to best management practice. One area will be left as a control area to observe background levels. The aim of the study is to investigate the impact of forestry practices on methylmercury levels in soil pore water and runoff. The logging will take place during
the winter 05/06. This study is part of the baseline assessment of the experimental area which location in Sweden is shown in figure 1.1. It is the aim of this study to make a characterisation of the Balsjö study area with respect to mercury occurrence. The main objectives are to investigate how methylmercury concentrations in runoff correspond to the methylmercury concentrations found in groundwater, and possible connections between groundwater levels and methylmercury concentrations.

The hypothesis that has been tested in this thesis was whether there are any pre-treatment differences between the study catchments. This information is crucial since the three catchments will be subject to different treatments and impacts of the treatments will be evaluated. Therefore potential pre-treatment conditions must be well characterised.

Methylmercury and total mercury concentrations in peat pore water have been measured and evaluated together with mercury concentrations in runoff that have been measured outside this study. To look into how the methylmercury occurrence in this area corresponds to methylmercury occurrence in other areas in Sweden the results have been compared with data from other studies. Patterns and variation between different areas have been evaluated in context of factors controlling mercury methylation.
2 Background information

2.1 The mercury cycle

Mercury exists in three oxidation states; elemental mercury (Hg$^0$), mercurous mercury (Hg$^+$) and mercuric mercury (Hg$^{2+}$, hereafter referred to as inorganic mercury). In nature it occurs in the earth’s crust bound in inorganic compounds like mercury oxide (HgO) and cinnabar (HgS). Elemental mercury is most often found as a gas in the atmosphere where it is very stable with a residence time of about one year. Mercury is naturally emitted from volcanoes, soil and water surfaces, but also from anthropogenic sources like combustion of fossil fuels, burning of waste and mining activities. Due to its long residence time in the atmosphere which is about one year mercury can travel long distances away from the emission source before being deposited which makes it a global pollutant (UNEP 2002). Oxidised forms of mercury have shorter residence time in the atmosphere which leads to faster deposition rates in heavily populated and industrial areas where emissions occur at higher rates which means that mercury is both a global and regional pollutant (Lindqvist 1994). See fig 2.1 for locations of areas of high mercury deposition rates in Sweden. Emissions in the areas are due to production of metals, paper pulp and fossil fuels. According to Hylander and Meili (2003) anthropogenic emissions of mercury have at least doubled global atmospheric mercury deposition rates although it is varying between regions.

![Fig 2.1 Location of major mercury emission sources in Sweden (Håkansson et al. 1988)](image)

Mercury enters the terrestrial and aquatic environments with wet and dry deposition, mainly in oxidised form as inorganic mercury. Once deposited it often forms
compounds with anions like chloride (Cl⁻) and hydroxide (OH⁻), or binds to sites on organic material. Mercury deposited on soil is stored in the soil before being transported with the help of runoff mechanisms to streams and lakes. Total mercury concentrations in the most upper part of the soil can be used as a measure on atmospheric deposition (see figure 2.2 for spatial variation in Sweden), while concentrations in deeper part of the profile also are depending on the geology at the site. Under anaerobic conditions like in wetlands or at lake bottoms the different mercury species are either immobilised by the formation of cinnabar, or are biologically transformed to methyl- (CH₃Hg⁺), dimethyl- ((CH₃)₂Hg) or elemental mercury. New mercury species formed enter the water column where methylmercury is available for biomagnification while the majority of the elemental- and dimethylmercury is emitted to the atmosphere (UNEP 2002).

![Fig 2.2 Mercury levels (mg/kg) in forest soil, from Meili, (2001).](image)

### 2.2 Bioaccumulation and human exposure

The major part of mercury input to aquatic systems has been found to be inorganic mercury (Hg²⁺), but the form that bioconcentrates in the food web is organic mercury, almost entirely as monomethylmercury (CH₃Hg). Bloom (1992) found in a study on both marine and freshwater fish and invertebrate species that for all species included in the study, more than 95% of the mercury present in fish and invertebrate tissue was
methylmercury. By tight binding to sulphide groups in proteins, methylmercury easily bioaccumulates in the food chain. Through food-chain biomagnification the highest levels of methylmercury are found in predatory species like freshwater trout (Salmo trutta) and northern pike (Esox lucius). Marine species like tuna, swordfish and shark have also been found to have high mercury concentrations. The bioconcentration factor (ratio of the concentration of methyl mercury in fish tissue to the concentration in water) is usually between 10 000 and 100 000 (WHO 1991).

Methylmercury is a powerful toxin causing disorders in the central nervous system with a lethal dose of 0.2 g. Prenatal life is most sensitive to methylmercury exposure. The substance easily pass the placental barrier and negative effects on the neuronal development in fetus after exposure to methylmercury has been recorded, as well as decreased brain size (WHO 1991).

Consumption of fish and seafood is the main pathway for methyl mercury to enter the human body. There is a guideline level for tolerable weekly intake of 0.3 mg mercury/week of which no more than 0.2 mg should be methylmercury. Advisory guidelines say that fish for human consumption should not have mercury concentrations above 0.5-1.0 mg Hg/kg fish tissue (wet weight) (WHO 1972). Adverse health effects associated with methylmercury have been seen for example in Japan in the 1950:s where about 3000 people were poisoned from consumption of fish and seafood with high levels of methylmercury discharged from a chemical plant (Japanese Ministry of the Environment 2002). In Iraq in the 1970:s over 6000 people were hospitalised and more than 400 people died after eating bread baked with flour from seed grains dressed with a methylmercury fungicide (Bakir et al. 1973).

2.3 Methylation by sulphur reducing bacteria

As mentioned above, inorganic mercury undergoes biological transformation into methylmercury. In a study by Compeau and Barta (1985) sulphate reducing bacteria in anoxic sediment were identified as the principal methylators of inorganic mercury. The transformation takes place in anaerobic environments like wetlands and aquatic sediments. That is today the generally accepted explanation on how inorganic mercury
is transformed into methylmercury even though there are uncertainties whether there are other, yet unknown methylators as well. In addition, a number of aerobic and anaerobic bacterial strains have been recognised as able to degrade, or demethylate methylmercury to elemental or inorganic mercury which means that what is called methylation of mercury in the environment is a net methylation; methylation – demethylation. There is however still no clear, generally accepted reason found why bacteria methylate and demethylate mercury (Benoit et al. 2003).

2.4 Methylmercury in terrestrial runoff - importance of wetlands
Since sulphur reducing bacteria were identified as methylators, several studies on methylmercury occurrence, controlling factors and loads in runoff have been carried out. According to Rudd (1995) in a review on sources of methylmercury to freshwater systems there are three sources of methylmercury to freshwater ecosystems: precipitation, runoff from wetlands and in-lake methylation. Each three of them may be important sources mostly depending on the watershed to lake area. Usually catchment runoff is the dominant source since only a small fraction of the mercury in atmospheric deposition is methylmercury why methylation within the watershed is thought to be of greater importance (Benoit et al 2003).

St. Louis et al (1994) showed in a study on methylmercury loads in runoff from subcatchments of different character that wetlands have a great importance for the methylmercury loads in watershed runoff. They found that yields of methylmercury from wetland portions of catchments were 26–79 times higher than from upland areas. The major part of the methylmercury in runoff was internally produced within the wetland since the output was a lot larger than the input. These results support the theory that sulphur reducing bacteria in anaerobic environments are mercury methylators since wetlands contain large volumes of saturated soils where sulphur reducing bacteria are found. Also studies from Finland and Sweden have shown clearly higher loads of methylmercury in runoff from peatland catchments and peatland part of catchments than from upland, mineral soil catchments (Porvari and Verta 2003; Lee et al 1995).
French et al (1999) studied the influence of different physical and chemical factors on mercury in aquatic sediment in lakes without industrial inputs. They found in the study that watershed area to lake area ratio (WA:LA) was the most important factor influencing the mercury concentrations. This illustrates the importance of terrestrial runoff as pathway for mercury transportation to aquatic systems.

Methylmercury occurrence in surface water is seldom found to be correlated to total mercury occurrence. Many studies from different regions on methyl- and total mercury concentrations in fresh water have shown the lack of relationship between methylmercury and total mercury, for example St. Louis et al. (1994) and Porvari and Verta (2003). This lack of relationship tells that mechanisms of mercury species transformation, of transferring from soil to runoff and from sediment to the water column are very complex and driven by several factors that need to be understood.

### 2.5 Organic material – carrier of methylmercury

Authors of several studies, (Garcia and Carignan 1999, 2000; Meili et al. 1991; Benoit et al 2003) have found positive correlations between organic matter (total organic carbon (TOC), dissolved organic carbon (DOC), dissolved humic matter and particulate humic matter) and methylmercury loads to aquatic systems. Organic material is an important carrier of methylmercury in runoff since the compound often is bound to sites on the organic material. An exception in this pattern has been seen in northern Sweden during spring flood when DOC and total mercury concentrations increased but methylmercury concentrations decreased. This suggests that methylmercury concentrations are determined by factors other than total mercury and organic material during spring flood which is an important hydrological event since it in northern Sweden constitutes a great part of the annual runoff (Bishop et al. 1995a).

Input of fresh organic material to the system is crucial for mercury methylation since microbial activity requires a carbon source of good quality (Benoit et al. 2003). As already mentioned, in-lake methylation also is an important source of methylmercury to lakes. For in-lake methylation the amount of organic material in sediment is an important factor as concluded by Lambertsson and Nilsson in Lambertsson (2005).
According to the authors the major controlling factors for net methylation of inorganic mercury are the input of new organic material and the redox potential, which to a great extent is determined by the content of organic material in the sediment since a high content of organic material in the sediment maintains a low redox potential which is essential for sulphate reduction and therefore also mercury methylation.

2.6 Effects of acid deposition

It was, as mentioned in the introduction earlier believed that low pH due to acid deposition in combination with high mercury deposition rates was the reason for the elevated mercury concentrations found in fish. As outlined it is now shown that soil biota plays a major part, but acid deposition does also affect methylation of mercury. Branfireun et al (2001) added in a Swedish study during three years sulphate (Na₂SO₄) and nitrate (NH₄NO₃) to peat soil in amounts equivalent to the deposition rates in southern Sweden during the 1980s with the objective to determine effects of long-term deposition of acid precipitation on peat pore water methylmercury. The results revealed that addition of sulphate increased methylmercury concentrations to up to six times the background levels while no significant effect was seen from nitrate addition. This is thought to demonstrate that acid rain dominated by SO₄²⁻ stimulates bacterial methylation of inorganic mercury since available sulphate is crucial for sulphur reduction and by that also mercury methylation. The effect is also amplified by a fluctuating water table since the deposited sulphur can be reduced/oxidised several times depending on groundwater level. Acid rain dominated by NO₃-N will not have the same effect since there are no links between nitrogen and mercury known as there are between sulphur and mercury. Sulphur deposition has decreased all over Sweden during the years 1990 to 2000 and the open field deposition 2001 was on average 46.2 % of the deposition in 1991 (IVL 2004). The map in figure 2.3 shows sulphate concentrations in precipitation in different parts of Sweden. Along the northern coast soils are naturally rich in sulphur which also is an important contributing sulphur source.
2.7 Impacts of forestry

Forestry is a very important industry in Sweden and it covers large areas over the whole country but is especially widespread in the northern part. Research on environmental impacts of forestry has already been investigating its effects on sediment and nutrient transport for many years. Now also the impacts on methyl- and total mercury output from catchments subject to forestry practices are being studied. There are indications that clear cutting of forest may increase methyl- and total mercury input to lakes receiving runoff from such logged catchments.

Clear-cutting of forested catchments is well known to bring elevated ground water levels and increased soil moisture as a result of removing the transpiration and interception of the trees. These effects lead to increased runoff from the watershed, and also increased loads of sediment and nutrient loads leaving the watershed (Hobbie and Likens 1973).

Regarding mercury, elevated groundwater levels and increased soil water content imply an increased area of saturated soils, and also a raise of the water level in wetland parts of the logged catchment which means that former aerobic sites become anaerobic and that may enhance methylation. Usually low lying areas close to streams become saturated and can therefore easily contribute to the methylmercury loads in the stream. Porvari et al (2003) found in a study from Finland that methyl- and total mercury loads in runoff were significantly higher after than before clear-cutting a forested catchment.
Other practices like burning of forest do not seem to affect methylmercury loads to lakes significantly. Garcia and Carignan (1999) studied methylmercury in zooplankton from lakes with recently logged, burned or undisturbed watersheds. The results showed no significant differences between methylmercury concentrations in zooplankton from lakes with burned catchments and reference catchments. Methylmercury concentrations in zooplankton from lakes with recently logged catchments were slightly, but significantly higher than in zooplankton from the other lakes. The same authors found in a later study on total mercury concentrations in northern pike (Garcia and Carignan 2000), that the mercury concentrations in pike were significantly higher in fish from lakes with logged catchments than in fish from lakes with burned or undisturbed catchments. Mercury concentrations in pike were also strongly correlated to methylmercury in zooplankton. In both studies methylmercury loads were positively correlated to DOC concentrations in runoff.

2.8 Mercury levels in Swedish fish
Mercury (methylmercury) concentrations in 1 kg pike vary between different parts of the country according to the pattern shown in figure 2.4. A recent study showed that there are lakes in the north-eastern part of Sweden containing fish with mercury concentrations between 2.5 and 3.0 mg/kg (Fellbrink 2002). Håkansson et al. (1990) state that there are about 10 300 Swedish lakes with fish mercury concentrations above 1 mg/kg which makes it a widespread serious environmental problem in Sweden.
The storage of mercury in soil is itself a problem since the soil now after decades of elevated mercury deposition rates not is a place for mercury retention but instead acts as a source of mercury to streams and lakes. This means that even if mercury emission were immediately and totally stopped, mercury levels in fish would still remain high for a long time (Bishop and Lee 1997). There is also a risk that soil biota will be affected by the toxic properties of mercury resulting in disturbances in decomposition of organic material and nutrient cycling which also could have economic consequences for forestry (Meili et al 2003). Highest methylmercury concentrations have been found in the top soil immediately below the water table. In runoff events with shallow water tables the highest flux is concentrated to the depth just below the groundwater table which means that those high methylmercury levels are being transported from the soil to streams and lakes (Bishop et al. 1995b; Bergman et al. in review).
3 Methodology

3.1 Study site and sampling procedure

The study site includes two small watersheds 0.54 and 0.26 km² in size with the larger one divided into two sections. The northern part of the larger catchment is the control area, called WSF (watershed forest), and the southern part that will be logged with buffer strips left along the stream is called WS9 (watershed 9). The smaller catchment which is to be totally clear cut is called WS7 (watershed 7). Both catchments are vegetated by coniferous, mainly spruce forest. The annual air temperature is about 0.6°C and the annual precipitation is about 554 mm. The catchments are drained by first order streams that seem to have been straightened to some extent during the first half of the 20th century when ditching of the area also was carried out to improve the properties of the soil for forestry. The soil type is mainly peat soil and to a large extent covered by blueberry, except for the riparian zone which is a few meters wide where sphagnum mosses dominated the ground vegetation (Ring and Högbom 2005). V-notch weirs are installed in the streams for flow measurements and for better control of the water quality measurements. A schematic map of the area is shown in figure 3.1. Groundwater pipes were installed along transects perpendicular to the streams reaching from the edge of the stream to 40-60 m away from it prior to the study and have been used for measuring groundwater depth and groundwater sampling. Groundwater depths have been measured and stream water has been sampled and analysed for mercury in all three catchments biweekly outside this study to characterise the pre-treatment conditions of the site. In the mercury analyses the same analytical methods were used as for groundwater samples that have been analysed in this study (3.2). Stream runoff is continually measured using data loggers every 30 minutes and measured manually biweekly. The groundwater samples were taken from the groundwater pipes using a Teflon pump. The pipes were emptied and left to refill 24 h before the sampling to ensure representative samples. The samples were kept dark at 4°C in the time between sampling and analyses (< 1 week). To remove particulate organic material all samples
were filtered. Due to the large amount of organic material filtering had to be done in two steps. First the samples were filtered with a coarse cellulose filter before the second filtering which was done with a 0.45 µm nitrocellulose filter (Millipore).

3.2 Analytical methods

The analyses were carried out at the Department for Analytical Chemistry at Umeå University, Umeå. The concentrations of methylmercury and inorganic mercury in the samples were determined by using an Isotope Dilution Gas Chromatography with Inductively Coupled Plasma Mass Spectrometry ((ID) GC-ICP-MS) method. The general principle in isotope dilution is that a known amount of a compound that is chemically identical to the analyte except being labelled with an enriched isotope (isotopomer) is added to the sample (generally referred to as “spiking” the sample). This results in an isotope abundance ratio between isotopomer and analyte (reference) that
deviates from the natural abundance ratio that in nature is very stable. By first separating the different mercury species using gas chromatography and then measuring the experimental isotope ratio in the spiked sample with mass spectrometry, the analyte concentration can be determined (Lambertsson 2005).

The filtered samples were spiked with $\text{Me}^{200}\text{Hg}^+$ and $\text{Hg}^{2+}$ and left for 24 h to equilibrate. The mercury species in the samples were then ethylated by adding a derivatisation reagent (sodium tetraethylborate buffered to pH 4.9 with acetate buffer) to create the volatile compounds $\text{MeHgEt}$ and $\text{Et}_2\text{Hg}$. The sample was then purged in a 125 ml glass gas wash bottle with helium gas for nine minutes and the mercury species were trapped in quartz tubes packed with Tenax. The Tenax tubes were connected to a gas chromatograph with a 15 m capillary column. By heating the Tenax to 200°C the ethylated mercury species were desorbed and transferred to the column. The gas chromatograph was connected to an ICP-mass spectrometer where mass to charge ratio ($m/z$) 198, 200 and 202 were monitored. $^{202}\text{Hg}$ was used as the reference isotope. The mercury species concentrations were calculated according to equation 1:

\[
C_x = C_y \times \frac{m_y M_x}{m_x M_y} \times \left( R_B \times f_x(2\text{Hg}) - f_x(1\text{Hg}) \right) / \left( f_x(1\text{Hg}) - R_B \times f_x(2\text{Hg}) \right)
\]

where $C_x$ is the unknown analyte concentration and $C_y$ the concentration of the isotopomer standard that is added to the sample; $m_y$ and $m_x$ are the mass of the added isotopomer and the mass of the sample; $M_y$ and $M_x$ are the relative molar masses of the standard and the sample; $R_B$ is the measured isotope ratio; $f_x(2\text{Hg})$ and $f_x(1\text{Hg})$ are the fractions of isotopes $^{2}\text{Hg}$ and $^{1}\text{Hg}$ in the standard (from isotopomer standard specifications); and $f_x(1\text{Hg})$ and $f_x(2\text{Hg})$ are the fractions of isotopes $^{2}\text{Hg}$ and $^{1}\text{Hg}$ in the sample (Sargent et al. 2002).

The advantage of the method are the low detection limit (0.007 ng/l for methylmercury and 0.06 ng/l for inorganic mercury) and that methyl- and inorganic mercury can be analysed simultaneously. The disadvantages are the high costs of running analyses which often sets the limit for the number of samples that can be analysed in a study and that samples have to be pre-treated before analyses can be run. Methylmercury concentrations measured with the method described above have been compared to
concentrations measured using another method at IVL, Swedish Environmental Institute, Gothenburg and the average difference between the methods can be regarded as zero since it was below detection limit.

3.3 Comparisons with other studies
The results have been compared with results from other studies on methyl- and total mercury occurrence in both northern and southern Sweden. The two studies from northern Sweden (Vindeln and Degerö) are performed in areas that receive similar deposition rates while the study area across southern Sweden receive more mercury and sulphate in deposition.
4 Results and Discussion

4.1 Groundwater

The total mercury concentrations in soil pore water ranged between 0.39 and 13.41 ng/l. Methylmercury, which is only a small fraction of total mercury, was found at concentrations between 0.02 and 0.59 ng/l. The average methylmercury concentrations in the three catchments (WSF, WS9 and WS7) were 0.07, 0.16 and 0.17 ng/l respectively. Student’s t-test showed that the differences between the three catchments were not significant. There was no correlation between methylmercury and total mercury concentrations which was not unexpected since as mentioned above that lack of relationship has been noticed in several studies (St. Louis et al. 1994), (Porvari and Verta 2003).

4.2 Importance of the riparian zone

The highest methylmercury concentrations were found in samples taken within six meters from the stream, shown in figure 4.1. The riparian zone is an area high in microbial activity making intense methylation possible. In Bishop et al. (1995) the riparian zone was recognised as a potential source of methylmercury since containing concentrations of methylmercury far higher than soil outside the riparian zone. In that study most of the soil samples were however taken in podsol soil except for the riparian zone which was organic rich peat. In this study the main soil type in the whole area is peat which means that the difference in methylation potential at different distances from the stream should be smaller, but could possibly still have an impact.

![Fig 4.1 Groundwater methylmercury concentrations seen at different distances from the stream.](image-url)
4.3 Groundwater levels

There were no significant differences in average groundwater levels between the sites near the stream (<10 m) and the sites further away from the stream (>10 m). Average groundwater depth in the three study areas did not differ significant from each other. Methylmercury concentrations relative groundwater depth is shown in figure 4.2. In neither of the three study catchments methylmercury concentrations were related to groundwater depth.

![MeHg/Groundwater depth graph](image)

Fig 4.2 Methylmercury concentration relative groundwater depth.

4.4 Runoff

Runoff from WSF and WS7 during the period varied as shown in fig 4.3. As can be seen in the figure the two catchments are hydrologically very similar except for the higher flow from WS7.

![Stream flow spring 2005 graph](image)

Fig 4.3 Runoff measured from WSF and WS7 during spring 2005

During the spring 2005 (April, May) methyl- and total mercury (MeHg and Hg tot) concentrations in runoff varied as shown in fig 4.4 and 4.5. The three study catchments (WSF, WS) and WS7) have similar methyl- and total mercury output, the very small
differences in runoff mercury concentrations observed during the study period were not significant. Methyl- and total mercury in runoff from the WS9 and WS7 catchments were not correlated to stream flow.

![Total Hg in runoff spring 2005](image)

**Fig 4.4** Total mercury in runoff during spring 2005 for the three study catchments.

![MeHg in runoff](image)

**Fig 4.5** Methylmercury concentrations in runoff during spring 2005 for the three study catchments.

One of the main questions in this study was if methylmercury concentrations in soil pore water were corresponding to methylmercury concentrations in runoff. As shown in

![MeHg (mean values)](image)

**Fig 4.6** Methylmercury in soil pore water and runoff whithin WSF, WS9 and WS7.
figure 4.6 average methylmercury concentrations were lower in groundwater than in runoff in all three study areas. The difference in concentration between soil pore water and runoff can possibly be explained by the way the sampling was carried out. Bishop et al. (1995) studied methyl- and total mercury concentrations in soil pore water at defined soil depths in a forested catchment located in northern Sweden. Methylmercury concentrations in the soil profile were found to range between 0.1 and 1.5 ng/l (Hg tot 5 – 40 ng/l) with the highest concentrations in the top 10 cm of the soil profile. The concentrations in the upper layers of the soil profile were corresponding well to the concentrations measured in runoff. In that study samples were taken at well defined depths by centrifugation of soil samples. Another study which also was carried out in northern Sweden by Bergman et al. (in review) on the impact of sulphur addition to soil on methylmercury concentrations gave similar results. Highest methylmercury concentrations were seen in the top ten cm below the water table and decreased with increasing depth. This pattern was seen in both plots that received extra sulphur and the control plots. In that study as well, concentrations in the top layers corresponded well to runoff concentrations as shown in figure 4.7. In this study the sampling was not done at defined depths. The samples taken from the groundwater pipes could have originated from any part of the soil profile that was penetrated by the groundwater pipe. Most probably the water originated from the deeper parts since the pipes were emptied to a depth of up to one meter below ground level. With this way of sampling it is not certain that the concentrations seen in soil pore water give a true picture of what amounts of mercury
that is being transported to the stream. Since this study showed lower concentrations in soil pore water than in runoff it is possible that the samples originated from greater soil depths with lower methylmercury concentrations as an effect of hydraulic gradients that was created as the groundwater pipes were emptied. Concentrations may be higher in the upper part of the soil profile where input of fresh organic material is faster leading to higher microbial activity which could be revealed by further studies with samples taken at defined soil depths.

4.5 The Balsjö area compared to Southern Sweden
A survey of methyl- and total mercury concentrations in mires across southern Sweden was carried out 2003 (Bishop, Meili and Nilsson 2003). In the survey 18 mires were included and they were among other parameters sampled for total mercury in peat, methylmercury in peat and peat pore water, methylation and demethylation rates in peat, and sulphur content in peat. Groundwater levels were also recorded. The mires were chosen to be located along a mercury deposition gradient from the west coast to the east coast of southern Sweden to make it possible to evaluate impacts of atmospheric mercury deposition.

Concentrations of methylmercury in peat pore water ranged between 0.22 and 2.63 ng/l with an average concentration of 1.14 ng/l in the top 20 cm of the soil profile which is noticeably higher than concentrations found in the Balsjö area where concentrations ranged between 0.02 and 0.59 ng/l. In figure 4.8 it can be seen that at 15 cm depth one third of the mires had methylmercury concentrations above the mean value of 1.14 ng/l.

![Fig 4.8 Number of sampled sites in southern Sweden with a particular methylmercury concentration.](image)
Factors that can help explain the higher methylmercury concentrations in southern than northern Sweden include higher mercury deposition rates, higher sulphate deposition rates and the fact that all samples were taken in mires with water table levels varying between 8 cm below the soil surface and 7 cm above the soil surface. The high water table levels indicate large areas of soil were saturated, which means conditions for mercury methylation were good, especially in combination with high sulphur deposition rates. Sampling technique could again be of importance, as they were in comparisons between the Balsjö study area and the other sites in northern Sweden. In the study from southern Sweden methylmercury was sampled at two depths and variation between the depths is shown in fig 4.9 together with the average concentrations seen in the three Balsjö study catchments beside.

![MeHg concentrations](image)

**Fig 4.9** Variation of methylmercury concentrations measured at two soil depths in mires across southern Sweden (Bishop et al. unpublished), and concentrations seen in Balsjö.

Methylmercury concentrations seem to be related to soil sulphur content as shown in figure 4.10 but the connection is not significant ($r^2 = 0.29$ $p = 0.06$). Methylmercury concentrations were not correlated to total mercury content in the peat soil as shown in figure 4.11. Neither were there any connections between water table level and methylmercury concentrations in peat pore water.
4.6 Relations between methylation rates and methylmercury concentrations

The conditions for methylation of mercury are only one of the complex factors controlling methylmercury in fresh water. The mobility and transfer of methylmercury between soil and water are also crucial but poorly understood. The complexity is illustrated by the data from the survey in southern Sweden by Bishop et al. (unpublished). Figures 4.12 and 4.13 show methylmercury in peat soil which is controlled by methylation rate ($r^2 = 0.62$ $p= 0.002$) while methylmercury concentrations in soil pore water are not related to methylation rate. Methylmercury in soil pore water is not correlated to methylmercury in peat soil either, as shown in figure 4.14, which indicates that the relationship between methylmercury in soil and methylmercury in soil pore water is not a simple equilibrium but rather controlled by factors that are not yet clearly understood. How methyl- and inorganic mercury are bound to organic material could be one factor, especially if there are differences between mercury species, or between particulate and dissolved organic material.
Fig 4.12 Peat MeHg content relative methylation rate. Data from Bishop et al. (unpublished)

Fig 4.13 MeHg concentrations in soil pore water relative methylation rate. Data from Bishop et al. (unpublished)

Fig 4.14 MeHg in soil pore water relative MeHg in peat soil. Data from Bishop et al. (unpublished)

Fig 4.15 show methylmercury concentration relative TOC concentrations in soil pore water in the mires in southern Sweden studied by Bishop et al. (unpublished). Methylmercury and TOC are not correlated, which also was noticed by Bishop et al. (1995 a) when studying methylmercury and TOC in northern Sweden during spring flood (see appendix C for methylmercury relative TOC in the Balsjö area).
Fig 4.15 No correlation between methylmercury and TOC in soil pore water. Data by Bishop et al (unpublished material).

In table 4.1 the Balsjö area mercury data is compared to mercury data available from the other studies mentioned above. Methylmercury concentrations in soil pore water are lower than in all other studied areas. Both methyl- and total mercury concentrations in runoff are slightly lower than found in Vindeln (Lee et al 1995).

Table 4.1 Methyl- and total mercury concentrations (average values in brackets) found in Balsjö (this study), Vindeln (Lee et al. 1995), (Bishop et al. 1995), Degerö (Bergman et al. in review) and Southern Sweden (Bishop et al. unpublished).

<table>
<thead>
<tr>
<th></th>
<th>Hg tot (ng/l)</th>
<th>MeHg (ng/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Balsjö</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil pore water</td>
<td>0.40-14.3 (3.25)</td>
<td>0.02-0.59 (0.15)</td>
</tr>
<tr>
<td>Runoff</td>
<td>1.78-13.1 (4.85)</td>
<td>0.09-0.49 (0.24)</td>
</tr>
<tr>
<td><strong>Vindeln</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil pore water</td>
<td>5-40</td>
<td>0.3-1.5</td>
</tr>
<tr>
<td>Runoff</td>
<td>2.5-5 (3.64)</td>
<td>0.1-0.6 (0.42)</td>
</tr>
<tr>
<td><strong>Degerö</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil pore water</td>
<td>0.3-30</td>
<td>(0.6)</td>
</tr>
<tr>
<td><strong>Southern Sweden</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil pore water</td>
<td></td>
<td>0.22-2.63 (1.14)</td>
</tr>
</tbody>
</table>

4.7 Increased methylation rates after logging?
Regarding the question whether forestry practices increase the methylmercury loads to lakes the studies on the subject so far have been focused on the amounts in runoff and concentrations seen in fish and invertebrates. Something that has not yet been studied is methylation rates in soil prior to and after logging have been carried out. After clear cutting of forest soil moisture increases. Also soil temperatures are prone to increase due to more solar radiation reaching the ground and an increase in the release of nutrients is often seen. Wetness and temperature are parameters that are important for
soil biota and how the activity of sulphur reducing bacteria and mercury methylation is affected would be interesting to see. Are methylation rates increased after logging or are the bigger loads in runoff only due to larger areas of saturated soil where methylation is possible and increased runoff?

The project in Balsjö aims to better understand the impacts of forestry on methylmercury occurrence in the boreal zone. The results from this study indicate that there are no pre-treatment differences between the study catchments. It is though worth mentioning that with the rather small number of samples used in this study (Appendix), small differences are difficult to discover and further studies might reveal small differences between the catchments that were too small to observe in this study. If the impacts of forestry are better understood chances are better to find a way to manage the problem. Forestry is though only a small part of the problem. As long as mercury and sulphur are emitted at today’s rates we are going to see high mercury concentrations in fish in the future as well.
5 Conclusions

Methylmercury concentrations in soil pore water found in the Balsjö study area are considerably lower than concentrations found in other studies from sites in northern Sweden. They do not correspond with concentrations found in runoff which is an indication that the low concentrations seen in this study can be due to the sampling procedure. High methylmercury concentrations are often found high up in the soil profile just below the water table and with the sampling technique used in this study it is likely that samples originated from deeper depths where methylmercury concentrations are lower. Average total mercury concentrations in runoff are slightly higher in Balsjö than seen in studies from Vindeln, north-eastern Sweden, but average methylmercury concentrations in runoff are slightly lower which indicate lower methylation potential in the Balsjö area than in Vindeln.

Methylmercury concentrations in soil pore water did not seem to have any connections to groundwater levels, but differences between groundwater levels at different sampling sites in this study were very small and prone to be insignificant. Compared to southern Sweden the methylmercury concentrations in soil pore water in the Balsjö study area are also very low. Again the sampling technique can be of importance for the low concentrations seen in soil pore water, but methylmercury concentrations in Southern Sweden are likely to be higher because of higher deposition rates of both mercury and sulphur. The link between sulphur deposition and methylmercury concentration via sulphur reducing bacteria is known from several studies and the concentrations of methylmercury in mires in southern Sweden seemed to increase with increased peat sulphur content. Concentrations in soil pore water did not seem to vary with either total mercury or methylmercury content in peat and neither to methylation rate in peat.

The processes behind methylation of mercury, transport by catchment runoff and uptake in fish are very complex. Due to the large mercury storage in soils, total mercury is in excess and is not the limiting factor for methylmercury occurrence. This means that other factors than mercury deposition are important for methylmercury occurrence in freshwater and freshwater fish. The potential for methylation within catchments is rather what is controlling methylmercury concentrations and factors like soil moisture and
sulphate concentrations in soil pore water are important. The transfer of methylmercury from soil to water and how and by what that is controlled is also something that needs further studying to make it possible to understand the patterns of methylmercury occurrence. The relationship between methylmercury concentrations in soil and concentrations in soil pore water is not an equilibrium but rather controlled by other factors involved that are not clearly understood. Binding of mercury species to particulate and dissolved organic material is an example.

More studying of impacts from forestry practices on methylmercury levels in forested areas is recommended and should not include loads in runoff only, but also methylation rates prior to and after logging. In the Balsjö area it is recommended to measure mercury in water from centrifugation of soil samples at defined depths instead of groundwater sampling from pipes for future studies to ensure precise measurements.

Methods for analysing mercury occurrence in fresh water should be further developed to reduce the high costs of running analysis. High costs can reduce the number of studies on mercury due to lack of funding which will affect the gain of knowledge. It will take a considerable time before we totally understand the mercury problem but no matter what the controlling factors for methylation and release of methylmercury to freshwater are, the input of mercury to the environment must be reduced to make less mercury available for future methylation.
6 References


Garcia, E., Carignan, R. (2000): Mercury concentrations in northern pike (Esox lucius) from boreal lakes with logged, burned or undisturbed catchments. Canadian Journal of Fisheries and Aquatic Sciences, 57 (Suppl 2): 129-135


Lambertsson, L. (2005): Mercury species transformations in marine and biological systems studied by isotope dilution mass spectrometry and stable isotope tracers. Department of Chemistry, Umeå University, Umeå, Sweden


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


Internet sources


Appendix

Appendix A: Balsjö runoff data

Appendix B: Balsjö groundwater data

Appendix C: Methylmercury relative sulphur and total organic carbon in the Balsjö area
### Appendix A

#### Balsjö runoff data

<table>
<thead>
<tr>
<th>Sampling date</th>
<th>MeHg ng/l</th>
<th>Hgtot ng/l</th>
<th>Flow (l/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSF 06/04/2005</td>
<td>0,20</td>
<td>3,16</td>
<td></td>
</tr>
<tr>
<td>WSF 14/04/2005</td>
<td>0,23</td>
<td>4,85</td>
<td>1,34</td>
</tr>
<tr>
<td>WSF 14/04/2005</td>
<td>0,16</td>
<td>4,44</td>
<td>1,65</td>
</tr>
<tr>
<td>WSF 14/04/2005</td>
<td>0,21</td>
<td>4,82</td>
<td>4,81</td>
</tr>
<tr>
<td>WSF 19/04/2005</td>
<td>0,26</td>
<td>4,58</td>
<td>6,94</td>
</tr>
<tr>
<td>WSF 26/04/2005</td>
<td>0,12</td>
<td>3,51</td>
<td>9,96</td>
</tr>
<tr>
<td>WSF 10/05/2005</td>
<td>0,12</td>
<td></td>
<td>3,45</td>
</tr>
<tr>
<td>WSF 19/05/2005</td>
<td>0,30</td>
<td>5,61</td>
<td></td>
</tr>
<tr>
<td>WSF 03/06/2005</td>
<td>0,32</td>
<td>2,76</td>
<td></td>
</tr>
<tr>
<td>WSF 14/06/2005</td>
<td>0,09</td>
<td>6,15</td>
<td></td>
</tr>
<tr>
<td><strong>Mean</strong></td>
<td><strong>0,20</strong></td>
<td><strong>4,33</strong></td>
<td></td>
</tr>
<tr>
<td>WS9 29/03/2005</td>
<td>0,44</td>
<td>13,62</td>
<td></td>
</tr>
<tr>
<td>WS9 06/04/2005</td>
<td>0,24</td>
<td>2,03</td>
<td></td>
</tr>
<tr>
<td>WS9 14/04/2005</td>
<td>0,23</td>
<td>3,89</td>
<td></td>
</tr>
<tr>
<td>WS9 19/04/2005</td>
<td>0,49</td>
<td>5,13</td>
<td></td>
</tr>
<tr>
<td>WS9 26/04/2005</td>
<td>0,29</td>
<td>5,07</td>
<td></td>
</tr>
<tr>
<td>WS9 10/05/2005</td>
<td>0,13</td>
<td>4,20</td>
<td></td>
</tr>
<tr>
<td>WS9 19/05/2005</td>
<td>0,24</td>
<td>4,44</td>
<td></td>
</tr>
<tr>
<td>WS9 03/06/2005</td>
<td>0,34</td>
<td>2,30</td>
<td></td>
</tr>
<tr>
<td>WS9 14/06/2005</td>
<td>0,15</td>
<td>5,19</td>
<td></td>
</tr>
<tr>
<td><strong>Mean</strong></td>
<td><strong>0,28</strong></td>
<td><strong>5,10</strong></td>
<td></td>
</tr>
<tr>
<td>WS7 29/03/2005</td>
<td>0,15</td>
<td>12,19</td>
<td></td>
</tr>
<tr>
<td>WS7 06/04/2005</td>
<td>0,24</td>
<td>2,22</td>
<td></td>
</tr>
<tr>
<td>WS7 14/04/2005</td>
<td>0,33</td>
<td>4,56</td>
<td>2,9</td>
</tr>
<tr>
<td>WS7 19/04/2005</td>
<td>0,41</td>
<td>4,59</td>
<td>4,96</td>
</tr>
<tr>
<td>WS7 26/04/2005</td>
<td>0,23</td>
<td>3,61</td>
<td>8,06</td>
</tr>
<tr>
<td>WS7 10/05/2005</td>
<td>0,19</td>
<td>4,67</td>
<td>19,37</td>
</tr>
<tr>
<td>WS7 19/05/2005</td>
<td>0,21</td>
<td>5,19</td>
<td>18,95</td>
</tr>
<tr>
<td>WS7 03/06/2005</td>
<td>0,22</td>
<td>2,35</td>
<td></td>
</tr>
<tr>
<td>WS7 14/06/2005</td>
<td>0,23</td>
<td>6,85</td>
<td></td>
</tr>
<tr>
<td><strong>Mean</strong></td>
<td><strong>0,25</strong></td>
<td><strong>5,14</strong></td>
<td></td>
</tr>
</tbody>
</table>
### Appendix B

#### Balsjö groundwater data

<table>
<thead>
<tr>
<th>Area</th>
<th>Sample ID</th>
<th>Distance from stream (m)</th>
<th>MeHg (ng/l)</th>
<th>Hg tot(ng/l)</th>
<th>Groundwater depth (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSF</td>
<td>2E</td>
<td>25,8</td>
<td>0,08</td>
<td>1,03</td>
<td>31,5</td>
</tr>
<tr>
<td>WSF</td>
<td>5A</td>
<td>0,5</td>
<td>0,07</td>
<td>1,10</td>
<td>22</td>
</tr>
<tr>
<td>WSF</td>
<td>5C</td>
<td>6,2</td>
<td>0,05</td>
<td>3,22</td>
<td>50,5</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td>0,07</td>
<td>1,78</td>
<td>34,7</td>
</tr>
<tr>
<td>WS9</td>
<td>11A</td>
<td>0,5</td>
<td>0,12</td>
<td>1,82</td>
<td>28</td>
</tr>
<tr>
<td>WS9</td>
<td>12A</td>
<td>0,5</td>
<td>0,06</td>
<td>1,02</td>
<td>37,5</td>
</tr>
<tr>
<td>WS9</td>
<td>11B</td>
<td>4</td>
<td>0,07</td>
<td>0,98</td>
<td>31</td>
</tr>
<tr>
<td>WS9</td>
<td>12E</td>
<td>44</td>
<td>0,04</td>
<td>0,81</td>
<td>20</td>
</tr>
<tr>
<td>WS9</td>
<td>Tr1A</td>
<td>10</td>
<td>0,21</td>
<td>2,26</td>
<td>51,5</td>
</tr>
<tr>
<td>WS9</td>
<td>Tr2A</td>
<td>10</td>
<td>0,39</td>
<td>3,10</td>
<td>54,5</td>
</tr>
<tr>
<td>WS9</td>
<td>Tr1B</td>
<td>15</td>
<td>0,06</td>
<td>1,14</td>
<td>35,2</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td>0,16</td>
<td>1,59</td>
<td>36,8</td>
</tr>
<tr>
<td>WS7</td>
<td>15C</td>
<td>6,2</td>
<td>0,08</td>
<td>11,56</td>
<td>19</td>
</tr>
<tr>
<td>WS7</td>
<td>17D</td>
<td>13</td>
<td>0,07</td>
<td>2,26</td>
<td>41,5</td>
</tr>
<tr>
<td>WS7</td>
<td>16D</td>
<td>13</td>
<td>0,13</td>
<td>1,92</td>
<td>49,5</td>
</tr>
<tr>
<td>WS7</td>
<td>16E</td>
<td>20,6</td>
<td>0,09</td>
<td>2,34</td>
<td>33,5</td>
</tr>
<tr>
<td>WS7</td>
<td>17E</td>
<td>20,6</td>
<td>0,02</td>
<td>0,39</td>
<td>30,5</td>
</tr>
<tr>
<td>WS7</td>
<td>17A</td>
<td>0,5</td>
<td>0,59</td>
<td>9,85</td>
<td>29</td>
</tr>
<tr>
<td>WS7</td>
<td>103</td>
<td>0,5</td>
<td>0,29</td>
<td>1,53</td>
<td>19</td>
</tr>
<tr>
<td>WS7</td>
<td>17B</td>
<td>2,6</td>
<td>0,06</td>
<td>1,07</td>
<td>21</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td>0,17</td>
<td>5,02</td>
<td>30,4</td>
</tr>
</tbody>
</table>
Appendix C
Methylmercury relative sulphur and total organic carbon in the Balsjö area.

Fig C1 Methylmercury concentrations relative sulphur concentrations in soil pore water in the Balsjö area.

Fig C2 Total mercury concentrations relative concentrations of TOC in runoff from the WSF study catchment.

Fig C3 Total mercury concentrations relative concentrations of TOC in runoff from the WS9 study catchment.

Fig C4 Total mercury concentrations relative concentrations of TOC in runoff from the WS7 study catchment.
**Fig C5** Methylmercury concentrations relative concentrations of TOC in runoff from the WSF study catchment.

**Fig C6** Methylmercury concentrations relative concentrations of TOC in runoff from the WS9 study catchment.

**Fig C7** Methylmercury concentrations relative concentrations of TOC in runoff from the WS7 study catchment.