



# Monitoring mercury in an urban environment, Umeå, Sweden

Representability and variability of mercury using forest moss biomonitors in an urban environment

Manuel Cañadas Fernandez

**Student**

Degree Thesis in Earth Science 15 ECTS  
Bachelor's Level  
Report passed: 16 March 2017  
Supervisor: Richard Bindler



## Abstract

The objective of my project was to determine variability and representability of mercury in the urban environment of Umeå in northern Sweden, based on applying the methods of forest moss biomonitoring (Swedish Environmental Protection Agency, ICP Manual). Mercury (Hg) is a common pollutant in urban environments released to the atmosphere by anthropogenic activities. Industrial, traffic and incineration activities are the main sources of this element. Mercury is easily transported through the atmosphere and cycles through terrestrial and aquatic ecosystems, tending to bioaccumulate in organisms. The aims of the study are: (1) determine the representability and variability of the method in a specific urban environment, based on more intensive analyses of a green area within the city boundaries of Umeå, northern Sweden. (2) influence of site-specific conditions on the concentration of mercury in mosses. (3) City-scale variability in relation to national forest moss biomonitoring data (IVL.se). Results of urban environment measurements do not differ much from the values of mercury concentration obtained sampling mosses far from the city, but it is subject to many factors that can alter results of the study. Most of these are meteorological factors and the difficulty of finding green zones close to cities with the suitable conditions to find mosses and perform a proper sampling process avoiding throughfall and litterfall. The conclusion is that the use of mosses is a representative and valuable method to obtaining information in an urban environment but is limited by mentioned factors.

Key Words: *Mercury, biomonitoring, moss, urban environment.*



# Table of contents

<b>1. Introduction</b> .....	<b>1</b>
<b>1.1 Small-scale temporal and spatial variability</b> .....	<b>2</b>
<b>1.2 Plot-scale factors influencing moss mercury concentrations</b> .....	<b>3</b>
<b>1.3 City-scale variability in moss mercury concentrations and regional comparison</b> .....	<b>3</b>
<b>2. Materials and Method</b> .....	<b>3</b>
<b>2.1 Field work for Small-scale temporal and spatial variability and Plot-scale factors</b> .....	<b>3</b>
<b>2.2 Field work City-scale variability in moss mercury concentrations and regional comparison</b> .....	<b>4</b>
<b>2.3 Laboratory work</b> .....	<b>5</b>
<b>2.4 Statistical analysis</b> .....	<b>6</b>
<b>3. Results</b> .....	<b>6</b>
<b>3.1 Small-scale temporal and spatial variability</b> .....	<b>6</b>
<b>3.2 Plot-scale factors influencing moss mercury concentrations</b> .....	<b>7</b>
<b>3.3 City-scale variability in moss mercury concentrations and regional comparison</b> .....	<b>8</b>
<b>4. Discussion</b> .....	<b>9</b>
<b>4.1 Small-scale temporal and spatial variability</b> .....	<b>9</b>
<b>4.2 Plot-scale factors influencing moss mercury concentrations</b> .....	<b>10</b>
<b>4.3 City-scale variability in moss mercury concentrations and regional comparison</b> .....	<b>11</b>
<b>5. Conclusion</b> .....	<b>11</b>
<b>Acknowledgment</b> .....	<b>12</b>
<b>Bibliography</b> .....	<b>12</b>



# 1. Introduction

Mercury (Hg) is a pollutant that can appear in the environment from human activities and natural sources from the earth. It can be found in elemental form (metallic mercury), inorganic (Hg<sup>2+</sup>) or organic (e.g., methyl-Hg), and all of them have different toxic effects (Cheng et al. 2013). Mercury emissions to the atmosphere by human activities are mainly related to mercury-containing impurities in fossil fuels, in mineral extraction and metallurgical processes (Lefticariu et al. 2011). The main source of this pollutant is the combustion of coal to produce electricity and heating. The mercury contained in the coal is emitted during combustion and almost half of the atmospheric emissions of mercury come from coal-fired power plants, industrial boilers and domestic use for heating and cooking (Rodríguez and Nanos, 2016). Other anthropogenic sources of mercury are hazardous waste incineration (hospital, electronics or metals) or breakage of products containing mercury inside of them (thermometers, switches, lamps, etc.) (Lindberg et al., 2007). This means that many urban processes release mercury to the atmosphere. Cities and industrial areas are susceptible to have elevated concentrations of this element around them. Another pernicious source of mercury to the atmosphere is wildfires. They release into the atmosphere mercury that was stored in soils (Homann et al., 2015; Turetsky et al., 2006; Woodruff and Cannon, 2010).

Mercury and mercury compounds constitute one of the chemical groups with the greatest impact on public health (Clarkson and Magos, 2006). Humans are exposed to this element from inhalation of toxic vapours with mercury and mostly by the diet, especially fish, is generally the main source of both inorganic and organic mercury. This pollutant arrives at aquatic ecosystems by atmospheric depositions to the surface of lakes and water bodies, then, it tends to bioaccumulate in the species that are at the top of the trophic chain (Johansson et al. 1991). Mercury is well known as an environmental pollutant that can cause significant damage to the central nervous system and organs like the kidney especially for pregnant women, infants and children (Clarkson and Magos, 2006).

Atmospheric deposition of this element is considered the most important load of mercury in ecosystems (Fitzgerald et al., 1998). The term atmospheric deposition encompasses the processes of wet, rain and snow, and dry deposition, the sedimentation of particles and the deposition of gasses. The fact that mercury deposition is more abundant closer to the main sources make the inhabitants and the ecosystems close to an urban area more exposed to this pollutant (Ross, 1990). Mercury can be easily transported through the atmosphere and cycle through terrestrial and aquatic ecosystems and during this process it tends to bioaccumulate in organisms (Wiener et al., 2003).

Mercury and other metals have been well studied in the natural environment, such as through forest moss biomonitoring (Swedish Environmental Protection Agency). It has been shown in some previous studies that mosses have the demonstrated ability to absorb and accumulate atmospheric pollutants, however, these studies have focused on more remote forested areas far from cities and major point sources (Berg and Steinnes, 1997; Ross, 1990). On the other hand, urban geochemistry papers have focused on identifying health risks due to the amount of contaminants in urban environments analyzing samples collected in areas near or inside the city (Johnson and Ander, 2008; Ljung et al., 2006). In my study I consider both types of research to make a successful biomonitoring process collecting mosses in areas close to an urban environment.

Biomonitoring consists in the use of an organism to acquire information of the environment. The organism used is called a bioindicator or biological monitor. There are differences between the term bioindicator or biological monitor. A Bioindicator refers to all organisms

that provide information of the quality of the environment, and biomonitors are the organisms that provide quantitative information about some factors of the environment (Markert et al., 2003). Biomonitoring investigations have some advantages in comparison with other methods used to study metal elements in the atmosphere. For example, pollution studies in India used particulate matter filters to collect atmospheric aerosols. This expensive and long-time method needs sophisticated technical equipment to obtain results (Chakraborty and Paratkar, 2006). Biomonitoring research using moss is one of the most effective with fewer cost solutions and it has been used in Europe since the pioneering work of Rühling and Tyler (1968). In Sweden, the use of mosses as biomonitors of metal deposition has been routinely studied by moss surveys since 1968 (Rühling and Tyler, 1995). These surveys are now performed every 5 years and provide valuable information on the relative spatial and temporal changes of trace metal deposition, long-distance spread of emissions and local emissions sources.

The fact that mosses do not have roots and cuticles requires them to find nutritive elements only in wet and dry atmospheric deposition (Chakraborty and Paratkar, 2006). This means that mosses only obtain mercury from atmospheric depositions and not from the soils, insulating this type of pollution for the study and discarding soils like a source of mercury for mosses. Nutrients and pollutants elements from the atmosphere are deposited in the moss cuticle as an aqueous solution, gaseous form or attached to small particles. Ion exchange is the physiological-chemical process that moss use to uptake the atmospheric elements. In the ion exchange process, cations and anions become attached to the functional organic groups in the cell wall primarily through chelation (Chakraborty and Paratkar, 2006). The efficiency of this process is affected by the competition for number and type of free cation exchange sites. Other factors that have influence in this uptake method are the age of the cells, their reaction to desiccation, the growing condition of the moss, temperature, precipitation, pH and composition of the pollutants (Tyler, 1990). Mosses have been recognized as practicable biomonitors in the evaluation of temporal trends in heavy metal accumulation (Harmens et al., 2008), and also in spatial variations (Schroder et al., 2008).

The overall objective of this study was to determine the variability of mercury in the urban environment based on applying the methods of forest moss biomonitoring (Swedish Environmental Protection Agency, ICP Manual).

### **1.1 Small-scale temporal and spatial variability**

The first aim of the study was to determine the representability and variability of the method in a specific urban environment, based on more intensive analyses of a forested area within the city boundaries of Umeå, northern Sweden. To analyze representability, I collected and analyzed moss samples *Hylocomium splendens* and *Pleurozium schreberi* from 10 plots within the same forested site, which were repeatedly sampled in 3 different weeks in order to determine if there are variances in the concentration of this element in distinct, but close in time, measurements. I analyze if there is variance between the 3 values of concentration obtained at the same sites but in different weeks and I compare the concentrations of mercury obtained in each week between them.

I also assess the small-scale spatial variability within the 10 plots I sampled in the intensive study site. The standard protocol for sampling of forest mosses for biomonitoring targets non-urban areas, and furthermore with a minimum 300 m away from roads, industries and villages and a minimum of 100 m from smaller roads and houses. In an urban environment these will likely be much closer to the sampling locations, which might have an influence even at a smaller spatial scale.

### **1.2 Plot-scale factors influencing moss mercury concentrations**

To assess the influence of site-specific conditions on the concentration of mercury in mosses, I sampled moss collected in different places in order to determine if the growth surface and environmental conditions affect pollutant absorption. The sites are: under a young spruce, under an old spruce, under a young pine, under an old pine, close to a pathway and under a dead tree. The protocols require a distance of at least 3 m from the nearest projecting canopy and a forest opening of at least 10 m diameter; however, in an urban environment with a limited extent of forested areas and thus a limited availability of suitable open areas, it may be difficult to select optimal sampling locations. Within this part of the study, I also divided the moss into two sections (green-new section and brown-old section) in order to determine if there are differences in concentrations of mercury depending on the section of the moss.

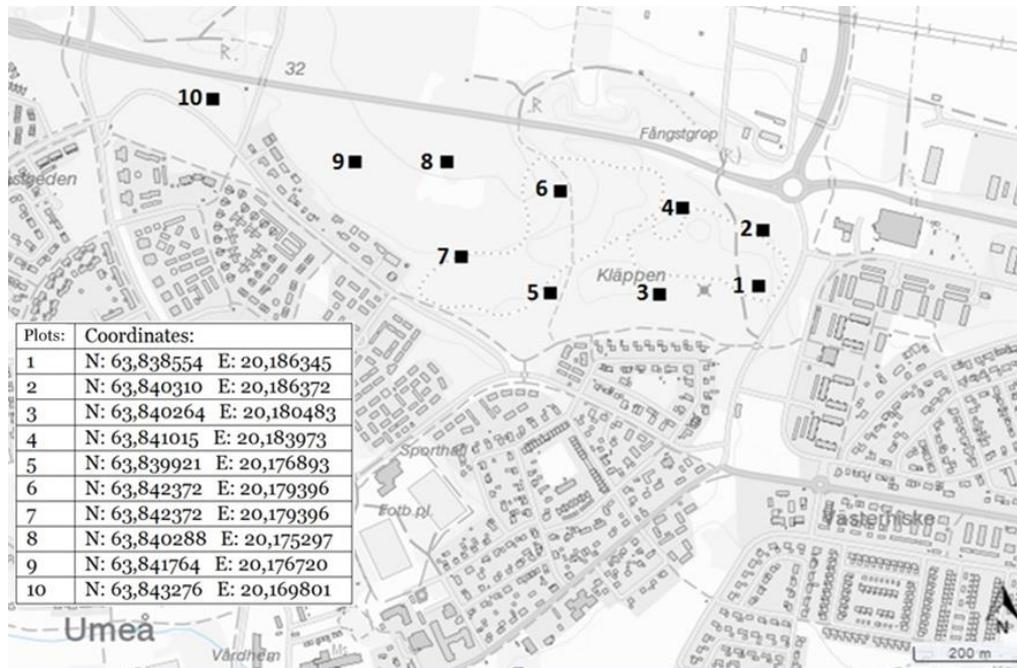
### **1.3 City-scale variability in moss mercury concentrations and regional comparison**

Finally, using my results and additional data collected within the course 'Field methods in geocology', I assess the mercury concentration levels in relation to national forest moss biomonitoring data (IVL.se), and more specifically I compare 12 urban environments sampled and analyzed within Umeå (with 10 sampled plots per site) in order to determine if there are differences between sites. The data on mercury concentrations in Umeå are then compared with supplementary forest moss monitoring data of 17 samples collected in close proximity to Umeå from 1995 to 2015 (IVL.se).

## **2. Materials and Method**

### **2.1 Field work for Small-scale temporal and spatial variability and Plot-scale factors**

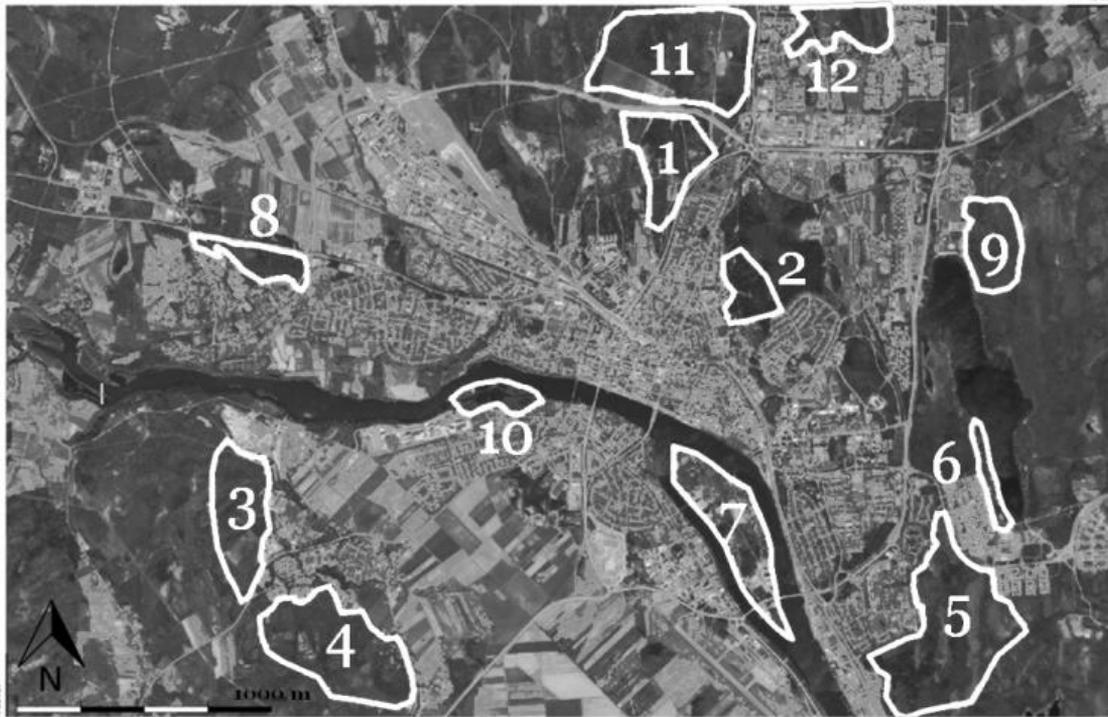
For my small-scale study, It was conducted an observational survey of a total cohort of 48 samples of moss focused only in a specific coniferous wooded area close to the city of Umeå, Sweden. This sampling site was a ~800 by 400 m continuous forested area in the northwest part of the city of Umeå, about 5 kilometers from the central town. This green area is surrounded by an important road (E12) and a really populated residential area (Umedalen). I performed the sampling process in 3 different weeks during October and November of 2016. I divided the wooden area in 10 plots where moss samples were collected (Fig. 1). In the city-wide study described further below, this intensive site is site number 8 (Fig. 2). In each plot I covered a radius of 50 m taking 6-10 moss sub-samples combined as one sample. In two of those plots duplicates samples were taken per week. The division principle was conceived to fully cover all the wooden area close to the city and the possibility to find both types of moss in all plots, *Hylocomium splendens* and *Pleurozium schreberi*. The first week 10 samples (Table 1) and 2 replicates were collected in the area. The second week samples were collected in the same 10 plots and 12 samples for the variability study were collected in plot 6 (Table 2). The last week, again 10 samples and 2 replicates were collected in the same location of the plots and a total of 6 samples more were collected for the green-brown section variability study in the plots number 1, 5 and 7, (Table 3).



**Fig. 1:** Location and coordinates of sampling plots in a green area in the northwest part of Umeå. Black square represents the location of the different sites. Moss samples of species *Hylocomium splendens* and *Pleurozium schreberi* were collected covering a radius of 50 m in each site. Figure for (1) small-scale temporal and spatial variability study.

## 2.2 Field work City-scale variability in moss mercury concentrations and regional comparison

The city-scale variability study was conducted collecting samples of moss in 12 periphery wooded areas close to the city of Umeå, Sweden. 12 students performed the sampling process in October of 2016. Each student collected 10 samples (one of them duplicate) in each study area, finally obtaining 132 mosses samples for the study of the spatial variety (Table 4). Study areas were chosen following the same criteria of possibility to find both types of moss and criteria of proximity to the city in order to fully cover a representative area of Umeå (Fig. 2). The site 8 in this study corresponds with the same green area used in the previous small-scale study. To conduct sampling process, students divided each of these areas in 10 different plots, which covered a radius of 50 m taking 6-10 moss sub-samples combined as one sample. In one of these plots, a duplicate sample was taken. I analyzed a supplementary 20 years data of concentrations of mercury monitoring in different forested sites further away from Umeå (IVL.se) (Table 5). During sampling process, I was careful to collect mosses in forest clearings to avoid throughfall from the forest canopy and cleaned the sample from soil and forest litter before being put into plastic bags (Ross, 1990).



**Fig. 2:** Location of 12 green areas close or inside Umeå. In each area, 10 samples of moss of species *Hylocomium splendens* and *Pleurozium schreberi* were collected. Site 8 correspond with the green area used in the small-scale study. Figure for (3) City-scale variability in moss mercury concentrations and regional comparison study

According to Chakraborty and Paratkar (2006), an organism has to meet specific requirements in order to be an appropriate biomonitor. The organism should be common in the study area and it should have low concentrations of trace elements naturally inside. The principal source of element uptake should be the atmosphere and the physiological mechanisms for uptake of depositional elements should be known for the researcher.

Mosses are cryptogams that grow in a humid environment and have been widely used as depositional trace-element biomonitors because they meet the above requirements as stated by Chakraborty and Paratkar (2006). Species of moss selected for use in this study were *Hylocomium splendens* and *Pleurozium schreberi*. The criteria for choosing these mosses were their abundance in the urban environment coniferous forest where the study took place and the fact that they are the same species of moss used in studies conducted far from urban environments (Ross, 1990; Berg and Steinnes, 1997). These species have others advantages, like that in *Hylocomium splendens* mosses a new segment grows every year making it easy to date. Dating is less exact for *Pleurozium schreberi* because it is a non-segmented moss, but also corresponds approximately to the same period. Only the green segment was used in the representability study (Ross, 1990). Another advantage of mosses in biomonitoring studies is their slow growth rate, which let them accumulate the mercury over a larger period. This is a useful property in order to know concentrations of this element on an integrated time period (Chakraborty and Paratkar, 2006).

### 2.3 Laboratory work

Moss samples were further cleaned and cut. I took care to remove remains of soil, needles and leaves of trees that are mixed with the mosses in the bag. Once this process was done, the samples were first ground and homogenized using a mixer and then dried at 35 °C all night long. The dry sample was pulverized using a coffee grinder and finally with a Retsch swing mill. This is the correct size status to be analyzed. The samples were weighed and analyzed for total Hg using a thermal desorption atomic absorption spectrometry (Milestone)

DMA-80) at 254nm, using a calibration curved developed from 3 standard reference materials. Standard reference material, internal reference material and replicate analyses were included approximately every 16 samples. Standards used for this analysis were LKSD-4, mess and apple material.

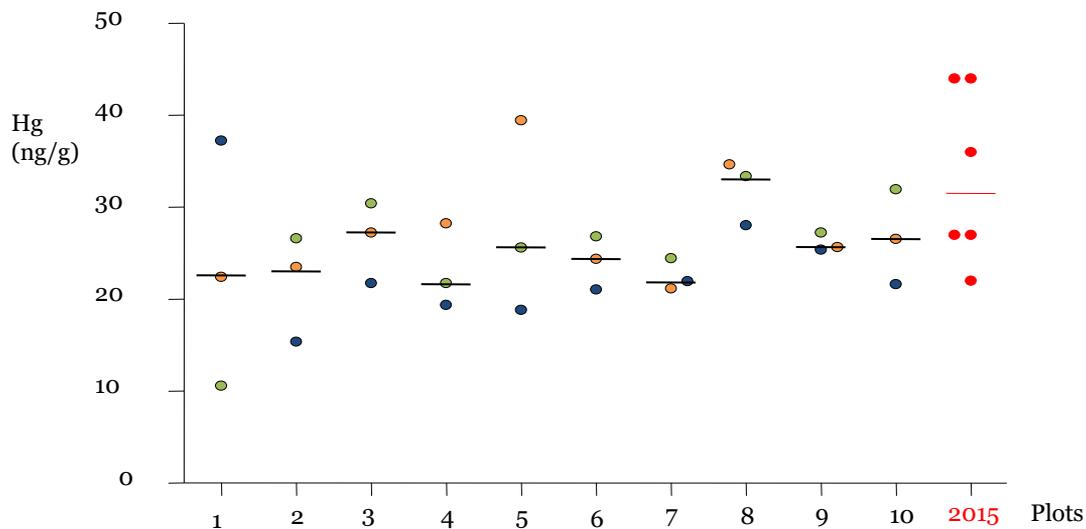
## 2.4 Statistical analysis

In statistical analysis, for the small-scale study, I used the non-parametric test of Friedman for related samples in order to compare the 3 values of mercury concentration collected in the same plot but in different weeks. To compare if there are variation in the concentration of mercury between the 3 weeks I will use again the non-parametric test of Friedman for related samples. For the city-scale variability study was used the test of analysis of variance (ANOVA) for comparison of means and standard deviations after objectify the sample of 12 sites followed a normal distribution (through Kolmogorov-Smirnov and Shapiro-Wilk Test). Processing and analysis of data were performed using SPSS v.15.0 statistical package.

## 3. Results

### 3.1 Small-scale temporal and spatial variability

Results obtained for representability and temporal trend analysis in the small-scale study reveal that no significant differences were detected in the mercury level analyzed in 2016 at the 10 plots ( $p=0.256$ ) (Fig. 3). The highest plot concentration average was 32.0 ng/g and the lowest average was 21.8 ng/g (Table 1). I analyzed in a more observational way the plots that are near the highway located on the north side of the green area (plot 4, average: 23.2 ng/g; plot 6, average: 24.1 ng/g; plot 8, average: 32.1 ng/g) and the plots near the urban zone (plot 1, average: 23.4 ng/g; plot 3, average: 26.5 ng/g; plot 5, average: 28.0 ng/g) in all weeks. The result is that the concentrations of mercury didn't show to be greater close to the road or the urban zone. In spite of this, the statistical comparison of the concentration of mercury between samples collected at 10 different plots but in same weeks (week 1, average: 23.1 ng/g; week 2, average: 27.3 ng/g; week 3, average: 26.0 ng/g) result that significant differences have been detected in the mercury levels of 2016 as a function of the measurement week ( $p= 0.014$ ). Mercury concentrations obtained in 2016 close to Umeå have small difference with the data of 2015 obtained in forests far from the city (Fig. 3)



**Fig. 3:** 10 plots mercury concentration in a green area close Umeå. Each black circle corresponds to the value of concentration in the same site but in a different week (3 values per site). Data of the week 1: dot color blue; week 2: dot color green; week 3: dot color orange. The black line corresponds to the average value of concentration in each plot. Red circles and red line correspond with the data of mercury concentration in Umeå at 2015 (IVL.se). Figure for (1) small-scale temporal and spatial variability study.

### 3.2 Plot-scale factors influencing moss mercury concentrations

For the variability study, results suggest that the brown section of mosses (old section) usually have a concentration of mercury higher than the green one (new section). It is easy to notice that in mosses collected in the plot 5 (green: 15.0 ng/g; brown: 42.9 ng/g) and plot 7 (green: 38.6 ng/g; brown: 53.8 ng/g) exists a huge difference of concentration between both parts of the moss, but in plot 1 (green: 28.1 ng/g; brown: 27.1 ng/g) there is little difference (Table 3). For the variability study of mercury concentration depending on the growth environment condition, results suggest that values collected under trees (young and old spruce/pines) usually are higher than the values of mosses collected close to a pathway or under a dead tree, being the average of these not superior to 36.0 ng/g of mercury and under trees species always higher and sometimes reaching 55.0 ng/g (Table 2).

**Table 1**

Data of mercury concentration obtained in a green area close to Umeå in three different weeks of October 2016 for (1) small-scale temporal and spatial variability study.

	Plot 1	Plot 2	Plot 3	Plot 4	Plot 5	Plot 6	Plot 7	Plot 8	Plot 9	Plot 10
Week 1 (ng/g)	37.3	15.4	21.8	19.4	18.9	21.1	22.0	28.1	25.4	21.7
Week 2 (ng/g)	10.6	26.6	30.4	21.8	39.5	26.8	24.5	33.4	27.3	32.0
Week 3 (ng/g)	22.4	23.5	27.3	28.3	25.6	24.4	21.2	34.7	25.7	26.6

**Table 2**

Data of mercury concentration obtained in different growth surfaces and environmental conditions for (2) Plot-scale factors influencing moss mercury concentrations study.

Dead tree	Hg (ng/g)	Y. spruce	Hg (ng/g)	O. spruce	Hg (ng/g)
1	31.7	1	40.4	1	33.0
2	40.6	2	45.2	2	59.4
Pathway	Hg (ng/g)	Y. pine	Hg (ng/g)	O. pine	Hg (ng/g)
1	34.0	1	52.9	1	46.3
2	36.7	2	58.3	2	33.0

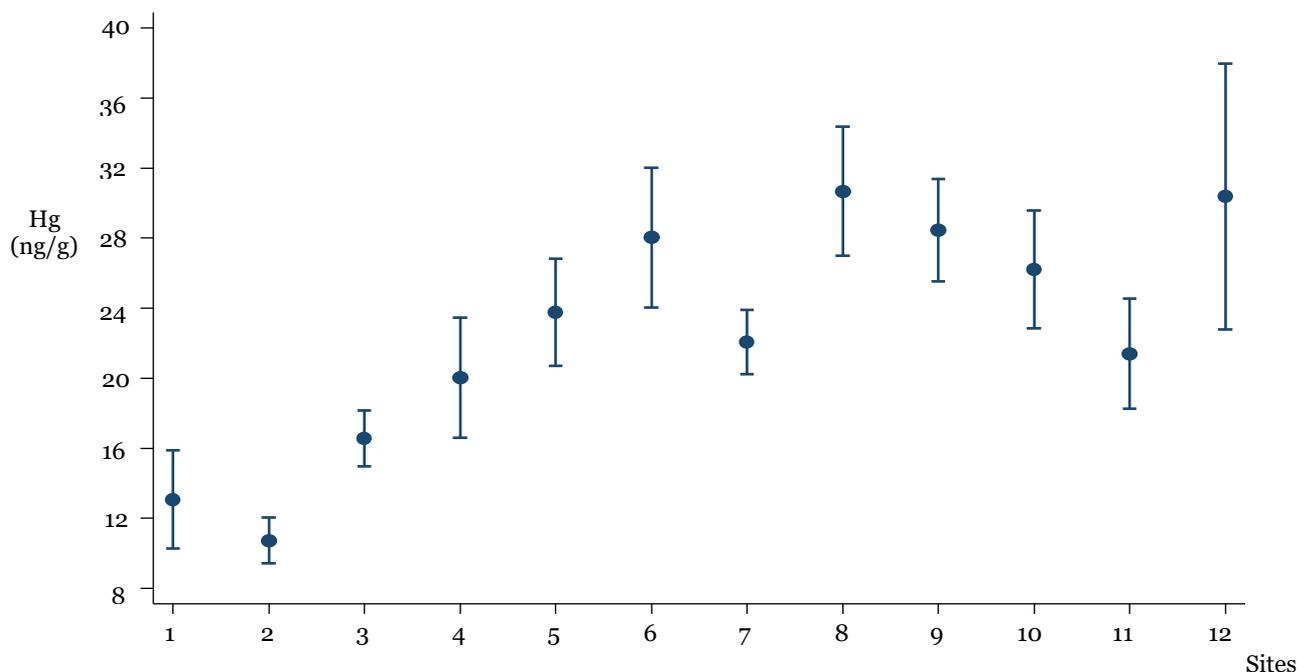
**Table 3**

Data of mercury concentration obtained in a different section (green-new; brown-old) of the mosses for (2) Plot-scale factors influencing moss mercury concentrations study.

Plot 1	Hg (ng/g)	Plot 5	Hg (ng/g)	Plot 7	Hg (ng/g)
Green 1	28.1	Green 5	15.0	Green 7	38.6
Brown 1	27.4	Brown 5	42.9	Brown 7	53.8

### 3.3 City-scale variability in moss mercury concentrations and regional comparison

For the city-scale study, the highest values were in site 8 (average: 30,68 ng/g) and 12 (average: 30,4 ng/g) and the lowest in site 2 (average: 10,7 ng/g) (Table 4). Comparison of the concentrations medians of mercury around the 12 wooden sites results in a different spatial variation between sites ( $p \leq 0,01$ )(Fig. 4). The analysis of the supplementary data (IVL.se) of last 20 years (1995, 2000, 2005, 2010 and 2015) results in significant differences between years ( $p= 0,032$ ). It is necessary to emphasize that the highest value appears in 1995 (average = 64.5 ng/g), the oldest year of the study (Table 5).



**Fig. 4:** Box plot diagram that represents the average and standard deviation of mercury concentrations measurements taken in the 12 green areas of Umeå (2016). Each area was divided in 10 plots where 1 sample of moss was collected (n=10). Figure for (3) City-scale variability in moss mercury concentrations and regional comparison study.

**Table 4**

Data of mercury concentration obtained in 12 green areas of Umeå for (4) City-scale variability in moss mercury concentrations and regional comparison study.

Site	Hg (ng/g)													Average
	19.1	25.2	13.8	11.6	11.0	12.1	8.6	15	13,4	8.1	7.8	11.2	-	
1	19.1	25.2	13.8	11.6	11.0	12.1	8.6	15	13,4	8.1	7.8	11.2	-	13.1
2	7.9	11.0	8.7	9.2	13.2	8.5	10.4	11.9	8.6	11.4	12.5	15.5	-	10.7
3	15.1	12.8	13.9	14.9	17.0	19.3	21.3	13.5	17.2	13.7	20.9	19.5	16.2	16.6
4	19.1	34.9	14.8	12.4	14.3	23.4	17.9	27.1	14.1	21.0	24.4	20.9	15.9	20.0
5	15.4	21.8	19.4	18.9	21.1	27.1	22.0	28.1	29.1	21.7	21.5	37.3	25.4	23.8
6	24.7	35.8	37.5	31.1	28.4	20.6	13.6	35.0	32.3	31.6	31.7	24.4	17.8	28.0
7	23.6	20.6	27.3	16.8	23.1	18.9	26.9	21.2	25.7	19.2	20.7	18.4	24.5	23.1
8	27.1	27.2	33.9	44.9	40.6	23.2	31.6	27.5	23.1	31.6	28.8	28.7	-	30.7
9	24.0	22.0	37.2	26.9	36.1	34.9	31.0	32.1	23.2	24.4	22.4	29.6	26.1	28.5
10	28.9	21.5	19.5	26.9	21.3	29.4	29.0	14.5	14.4	16.1	14.1	18.8	23.8	21.4
11	20.7	19.0	37.1	42.1	39.7	21.8	28.9	20.5	15.4	24.1	21.4	27.2	-	26.5
12	18.7	18.9	18.1	17.7	32.6	19.6	39.5	62.3	42.1	35.9	32.0	-	-	30.4

**Table 5**

20 years data of mercury concentration obtained in forest moss close to Umeå (4) City-scale variability in moss mercury concentrations and regional comparison study (IVL.se).

Year	Hg (ng/g)						Average
2015	36.0	26.0	27.0	22.0	44.0	27.0	30.3
2010	30.0	28.0	31.0	32.0	-	-	30.3
2005	8.0	14.0	13.0	-	-	-	11.6
2000	38.0	18.0	-	-	-	-	28.0
1995	79.0	50.0	-	-	-	-	64.5

## 4. Discussion

### 4.1 Small-scale temporal and spatial variability

According to the results obtained in my representability study, I can indicate that there are no differences in the concentration of mercury in 2016 at the 10 plot at my forested site where samples were collected in three different weeks and also that the concentrations of mercury do not show to be higher closer to the road or the urban zone. This means that the measurements do not differ from each other and that none of the samples actually have an anomalous concentration. With this result, I can conclude that the process of collection of samples and analysis in the laboratory has been carried out correctly and that none of the results are out of the expected value range. I can also infer that atmospheric deposition of mercury spread throughout the area in a largely uniform manner and that there is not a precise local source of contamination. That is the reason why I can discard the road (E12) and the vehicles which run through it near the forest as an important and abundant source of emissions of mercury. We know from a number of studies (Anicic, 2009, Cheng, 2013; Keith, 2008) that the urban atmosphere is subjected to large inputs of anthropogenic contaminants produced by power plants, industries and residential heating and mobile sources related to traffic. All these processes emit mercury into the atmosphere, but based on these results I suggest that these emissions cannot be considered especially pernicious for the environment and cannot be considered a real source of contamination in Umeå, because moss samples that are located directly close to these potential emitters (road: plots 4, 6 and 8; urban area: plots 1, 3 and 5) are not particularly affected and do not show elevated values of mercury.

My results indicate that there are small differences in the concentration of mercury depending on the sampling week (week 1, average: 23.1 ng/g; week 2, average: 27.3 ng/g; week 3, average: 26.0 ng/g). Therefore, the time has some influence on the variability of the study, causing that concentration of mercury shows higher or lower, despite having been collected at the same plot. This may be due to a large number of factors that may influence the conclusions of the study. One of these factors that have a strong influence in temporal trends is always the changing weather during the different sampling weeks. Precipitation, temperature, snowmelt, fluctuations in wind currents are factors that can show really different parameters in a short period and may have an important effect on the absorption efficiency of moss and the concentration of mercury present in the atmosphere (Chakraborty and Paratkar, 2006). Interaction of precipitation with the forest canopy can greatly alter the chemical composition of the water (usually termed throughfall or crown drop) which falls on to the mosses (Ross, 1990). There are studies about mercury concentrations across different forest sites that show the highest concentrations in litter layers, and some of them show that deposition was greater in the coniferous stand due to larger throughfall mercury (Blackwell et al., 2014; Orbist et al., 2011). In my study as recommended in Swedish and ICP protocols, I tried to avoid throughfall and litterfall by collecting samples in forest clearings where there are fewer trees to influence my results, but this factor can contribute to the difference in spatial variability. It is demonstrated that forest cover clearly influences Hg deposition processes, but also there has been some research on

variability of atmospheric Hg deposition across different forested landscapes. Evidence suggests that the structure of hardwood or conifer forest stands impacts Hg deposition processes (Demers et al. 2007; Sheehan et al. 2006; Obrist et al. 2012; Witt et al. 2009) being the coniferous forest again the most susceptible to mercury deposition. The problem in monitoring process using moss in urban environments is the added difficulty of finding green areas in the city where it is possible to collect the right species and avoid the previously mentioned risks related to throughfall and litterfall. Green areas in cities tend to have few clearings between trees due to the lack of space and fewer mosses populations. This is a factor that greatly limits the achievement of specifically comparable biomonitoring results in urban environments.

To compare my results of mercury concentration in 2016 with the data of 2015 (IVL.se) first I have to take into account that samples that I collected in 2016 have not been caught in the same place where samples in 2015. These samples were collected in forests distant to Umeå that do not have urban environmental conditions. Despite this, there is a small difference of concentration between years. In Blackwell's et al., (2014) study is said that annual variability in meteorological conditions was substantial between 2009 and 2010, and changes in Hg deposition over this period appear to be related to variation in temperature and precipitation quantity. In my study, the differences in mercury concentrations between years also can be related to meteorology factors, throughfall and in a small scale by the influence of anthropogenic pollutants.

#### **4.2 Plot-scale factors influencing moss mercury concentrations**

As is said in Chakraborty and Paratkar (2006) study, the concentration of metals in mosses is affected by many "natural" factors associated with the site where the mosses are growing and their immediate environment. In my variability study depending on the growth environment condition, results suggest that values are higher as expected when mosses are collected under young and old spruce/pines trees (in some cases reaching 60.0 ng/g) than the values of mosses collected close to a pathway (average of 35.4 ng/g) or under a dead tree (average: 36.2 ng/g) (Table 2). Again, throughfall and litterfall seem to be responsible for this result. Coniferous forest includes plants like junipers, pines, redwoods, spruces, and yews. As I said before, coniferous forests are the most susceptible for mercury depositions. Again, as Obrist et al (2012), Witt et al (2009) and Demers (2007) indicated in their studies, evidence suggests that the structure like conifer forest stands impacts mercury deposition processes and facilitate the throughfall. The concentration of mercury is noticeably lower in mosses near to the pathway (average of 35.4 ng/g), because there are fewer trees nearby. The same situation occurs with the mercury values of the moss collected under the dead tree (average: 36.2 ng/g). It covers and protects the moss from mercury deposition of throughfall and litterfall.

Results of mercury concentration depending on moss growth section show that the brown section, as expected, associated with the oldest part of mosses have a concentration of this element much greater in two of the three cases that I have studied. Mosses collected in the plot 5 (green: 15.0 ng/g; brown: 42.9 ng/g) and plot 7 (green: 38.6 ng/g; brown: 53.8 ng/g) there is a huge difference of concentration between both parts of the moss, but in plot 1 (green: 28.1 ng/g; brown: 27.1 ng/g) there is not difference (Table 3). The green section of mosses is the new section that has grown recently and is useful for us to know the amount of mercury and other elements absorbed by the moss in the last year. This is the section that researchers should use when employing mosses as biomonitors (Ross, 1990). The amount of mercury present in the brown section is because the trend of this element to bioaccumulate in the organism. The loss of mass in this section due to cellular deterioration and the age of the moss are factors that reduce the accumulation and therefore the concentration of mercury and make this part useless. The conclusion is that the most representative part of the moss in order to determine mercury concentration is the green section, and it is the

section used and recommended in most of the research related to the use of moss as biomonitor.

### **4.3 City-scale variability in moss mercury concentrations and regional comparison**

For the next part I leave behind the study focused in only one forested area and I increase the scale that I cover in my study, obtaining a more general vision of the city comparing 12 green areas with urban environment (Fig. 4). Results obtained indicate that the concentrations of mercury of these 12 green areas close to the city of Umeå are different with average values ranging from 30,68 ng/g in site 8 and 30,38 ng/g in site 12 to 10,73 ng/g in site 2 (Table 5). These differences between sites can be related to the variation in the collecting process done by the students and changes in local deposition rates depending on air currents and weather. Another hypothesis to explain these results can be the existence of sources of mercury that operating only in specific areas, enabling a spatial variation of mercury. The first factor that I take into account is the facts that all the green areas of my study are located close or inside the city, but some finding sources of pollution are more developed. The urban atmosphere is subjected to large inputs of anthropogenic contaminants produced by both stationary sources (power plants, industries and residential heating) and mobile sources related to traffic (Anicic, 2009). But if I come back in my study focus only on the site 8 for small-scale variability, moss directly close to the road or urban area have not especially high concentrations of this element. The answer to this unknown can be that urban sources release mercury to the atmosphere in a moderate way, preventing them from being considered as real pernicious sources of mercury but allowing them to emit evenly this element. This should be the case of the sites 8 (30,68ng/g) and 12 (30,38 ng/g), where I find the highest concentrations of mercury. Site 8 is a coniferous forest that I described in the first part of the study. It is closely surrounded in the north by an important and transited road (E12) and in other directions for urban roads and housing areas. Site 12 is situated in the northern part of the city, where there are some industries and roads. In site 2 I found the lowest concentration of mercury in mosses. This site is located in the middle of the city, in a green area called Stadsliden. Despite being completely surrounding by residential areas there are no any important roads close to this site. This can be a proof of how traffic and other anthropogenic contaminants can possibly affect the results of biomonitoring research using mosses in urban environments and how different levels of urban development affect the absorption of pollutants in green areas.

The last result in my study was that there are differences in mercury concentrations from the Umeå region in the last two decades (IVL.se). It is important to clarify that the concentrations measured in my study for the 12 green areas in Umeå are not significantly different from the IVL data obtained in sites in the commune located outside of the city of Umeå, in the vicinity of other major communes in the region. This is a proof of the small differences that a study focused in an urban environment obtains with respect to a biomonitoring study conducted far from a city. Probably 1995 (the last year of the data) show the highest levels of mercury because in this year there are fewer restrictions with pollutions emission than in recent years and the fact that in this year the methodology of sampling and analyzing was different.

## **5. Conclusion**

Before concluding I recognize that my study has the usual limitations of the chosen design, highlighting the small sample size. The conclusion is that the use of mosses is a representative and valuable method of obtaining information in an urban environment. Results do not differ much respect the results obtained sampling mosses far from the city, but it is subject to many factors that can alter the quality of the study. Most of these factors are the anthropogenic emissions, commons in an urban environment, and the difficulty of

finding green zones close to cities with the suitable conditions to find mosses and perform a property sampling process avoiding throughfall and litterfall. In any case, the relative facility of sampling, the absence of any need for complicated and expensive equipment, the accumulative and time-integrative behavior of the moss biomonitor give biomonitoring of atmospheric trace elements methods advantages for their continued practice in the future, especially in larger-scaled surveys.

## Acknowledgment

The author is grateful to my supervisor and professor of the course “Field Methods” Richard Bindler and all students involved in the process of collecting samples. Also to Dr. Cesareo Fernandez Alonso and Dr. Manuel Fuentes Ferrer for his help in the statistical analysis.

## Bibliography

- Anicic, M., Tasic, M., Frontasyeva, M.V., Tomasevic M., Rajsic S., Mijic Z. and Popovic A. 2009. Active moss biomonitoring of trace elements with *Sphagnum girgensohnii* moss bags in relation to atmospheric bulk deposition in Belgrade, Serbia. *Environmental Pollution*. 157: 673–679.
- Berg, T. and Steinnes, E. 1997. Use of mosses (*Hylocomium splendens* and *Pleurozium schreberi*) as biomonitoring of heavy metal deposition: from relative to absolute deposition values. *Environmental Pollution*. Vol. 98. No. 1: 61-71.
- Blackwell, B. D., Driscoll, C. T., Maxwell, J. A. and Holsen, T. M. 2014. Changing climate alters inputs and pathways of mercury deposition to forested ecosystems. *Biogeochemistry*. 119: 215–228.
- Chakraborty S. and Paratkar G. T. (2006) Biomonitoring of Trace Element Air Pollution Using Mosses. *Aerosol and Air Quality Research*. Vol. 6. No.3. 247-258.
- Chakraborty, S. and Paratkar, G. T. 2006. Biomonitoring of Trace Element Air Pollution Using Mosses. *Aerosol and Air Quality Research*. Vol. 6. No.3: 247-258.
- Cheng, I., Zhang, L., Blanchard, P.; Dalziel, J., Tordon, R., Huang, J. and Holsen, T. M. 2013. Comparisons of mercury sources and atmospheric mercury processes between a coastal and inland site. *Journal of Geophysical Research: Atmospheres*, Vol.118(5): 2434-2443.
- Clarkson, T. W. and Magos, L. 2006. The toxicology of mercury and its chemical compounds. *Crit. Rev. Toxicol.* 36 (8): 609–662.
- Demers, J. D., Driscoll, C. T., Fahey, T. J. and Yavitt, J. B. 2007. Mercury cycling in litter and soil in different forest types in the Adirondack region, New York, USA. *Ecol Appl.* 17: 1341–1351.
- Environmental Protection Agency of Sweden. Available 16/03/2017. <http://www.ivl.se/>
- Fitzgerald, W. F., Engstrom, D. R., Mason, R. P., Nater, E. A. 1998. The case for atmospheric mercury contamination in remote areas. *Environ. Sci. Technol.* 32 (1): 1–7.
- Harmens, H., Norris, D.A., Koerber, G.R., Buse, A., Steinnes, E. and Ruhling, A. 2008. Temporal trends (1990–2000) in the concentration of cadmium, lead and mercury in mosses across Europe. *Environmental Pollution*. 151: 368–376.
- Homann, P. S., Darbyshire, R. L., Bormann, B. T. and Morrissette, B. A. 2015. Forest Structure Affects Soil Mercury Losses in the Presence and Absence of Wildfire. *Environ. Sci. Technol.* 49: 12714–12722.
- Johansson, K., Aastrup, M., Andersson, A., Bringmark, L. and Iverfeldt, A. 1991. Mercury in Swedish forest soils and waters – Assessment of critical load. *Water Air & Soil Pollution*. Vol.56: 267-281.
- Johnson C. C. and Ander E. L. 2008. Urban geochemical mapping studies: how and why we do them. *Environ Geochem Health.* 30: 511–530

- Keith S. 2008. Fuel-mercury combustion emissions: an important heterogeneous mechanism and an overall review of its implications. *Environmental Science and Technology*. Vol.42(24): 9014–9030.
- Leticariu, L., Blum, J. D. and Gleason, J. D. 2011. Mercury isotopic evidence for multiple mercury sources in coal from the Illinois basin. *Environmental science & technology*. Vol.45: 1724-1729.
- Lindberg, S., Bullock R., Ebinghaus, R., Engstrom, D., Feng, X., Fitzgerald, W., Pirrone, N., Prestbo, E. and Seigneur, C. 2007. A Synthesis of Progress and Uncertainties in Attributing the Sources of Mercury in Deposition. *A Journal of the Human Environment*. 36: 19-33.
- Ljung, K., Otabbong, E. and Selinus, O. 2006. Natural and anthropogenic metal inputs to soils in urban Uppsala, Sweden. *Environmental Geochemistry and Health*. 28: 353–364
- Markert, B.A., Breure, A.M., and Zechmeister, H.G. 2003. Definitions, Strategies, and Principles for Bioindication/Biomonitoring of the Environment. Markert, B.A., Breure, A.M., and Zechmeister, H.G., (eds.) *Elsevier, Oxford*: 3-39.
- Obrist, D., Johnson, D. W. and Edmonds, R. L. (2012). Effects of vegetation type on mercury concentrations and pools in two adjacent coniferous and deciduous forests. *J Plant Nutr Soil Sci*. 175. 68–77.
- Orbist, D., Johnson, D. W., Lindberg, S. E., Luo, Y., Hararuk, O., Bracho, R., Battles, J. J., Dail, D. B., Edmonds, R. L., Monson, R. K., Ollinger, S. V., Pallardy, S. G., Pregitzer, K. S. and Todd, D. E. (2011). Mercury Distribution Across 14 U.S. Forests. Part I: Spatial Patterns of Concentrations in Biomass, Litter, and Soils. *Environ. Sci. Technol*. 45, 3974–3981.
- Rodríguez, J. A. and Nanos, N. 2016. Soil as an archive of coal-fired power plant mercury deposition. *Journal of Hazardous Materials*. Vol.308, 131-138.
- Ross H. B. 1990. On the use of mosses (*Hylocomium splendens* and *Pleurozium schreberi*) for estimating atmospheric trace metal deposition. *Water, Air, and Soil Pollution*. 50: 63-76.
- Ross, H. B. 1990. On the use of mosses (hylocomiums plendens and pleurozium schreberi) for estimating atmospheric trace metal deposition. *Water, Air, and Soil Pollution*. 50: 63-76.
- Rühiling, Å., and Tyler, G. 1968. An Ecological Approach to the Lead Problem. *Botaniska Notiser*.122: 248-342.
- Rühiling, Å. And Tyler, G. 1995. Changes in Atmospheric Deposition Rates of Heavy Metals in Sweden A Summary of Nationwide Swedish Surveys in 1968/70. *Water, Air and Soil Pollution: Focus* Vol.1(3): 311-323.
- Schroder, W., Pesch, R., Englert, C., Harmens, H., Suchara, I., Zechmeister, H.G., Tasic, M., Rajsic, S., Tomasevic, M., Mijic, Z., Anicic, M., Novakovic, V., Markovic, M.D., Markovic, A.D., Lazic, L., Radenkovic, M. and Joksic, J. 2008. Assessment of air quality in an urban area of Belgrade, Serbia. *Gungor, B.O (Ed.), Environmental Technologies, New Developments*. 209–245.
- Sheehan, K. D., Fernandez, I. J., Kahl, J. S. and Amirbahman, A. 2006. Litterfall mercury in two forested watersheds at Acadia National Park, Maine, USA. *Water Air Soil Pollut*. 170: 249–265.
- Swedish Environmental Protection Agency, ICP Manual. Beskrivning av delprogrammet (Metaller i mossa). Available 16/03/2017. <http://www.naturvardsverket.se/>
- Turetsky, M. R., Harden, J. W., Friedli, H. R., Flannigan M., Payne N., Crock J. and Radke L. 2006. Wildfires threaten mercury stocks in northern soils. *Geophysical Research Letters*. Vol. 33: 1-6.
- Tyler, G. 1990. Bryophyte and Heavy Metals: A Literature Review. *Bot. J. Linn. Soc*. 104: 231-253.
- Wiener, J. G., Krabbenhoft, D. P. and Heinz, G. H. 2003. Ecotoxicology of mercury. In: Hoffman DJ et al (eds) *Handbook of ecotoxicology*, 2nd edn. Lewis Publishers. Boca Raton: 409–464.

- Witt, E. L., Kolka, R. K., Nater, E. A. and Wickman, T.R. (2009). Influence of the forest canopy on total and methyl mercury deposition in the boreal forest. *Water Air Soil Pollut.* 199: 3–11.
- Woodruff, L. G. and Cannon W. F. 2010. Immediate and Long-Term Fire Effects on Total Mercury in Forests Soils of Northeastern Minnesota. *Environ. Sci. Technol.* 44: 5371–5376.







Dept. of Ecology and Environmental Science (EMG)  
S-901 87 Umeå, Sweden  
Telephone +46 90 786 50 00  
Text telephone +46 90 786 59 00  
[www.umu.se](http://www.umu.se)