Mercury in a Swedish landscape over 30 years

A thesis on mercury concentrations in different water-catchments in Krycklan and Degerö stormyr

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Swedish University of Agricultural Sciences, SLU
Faculty of Forest Sciences
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Abstract

The purpose of this thesis is to examine trends in concentrations of total mercury (TotHg) and methylmercury (MeHg) in water streams around Vindeln, Sweden, located northwest of Umeå. The relationship between dissolved organic carbon (DOC) and TotHg were also examined in this thesis. Data gathered for 30 years from four different sample sites collected from Krycklan catchment study (KCS) and Degerö stormyr. All samples were compiled into excel files and sorted by location and date to later analyse the concentrations of TotHg, MeHg and DOC. To analyse the concentrations of TotHg and MeHg a Mann-Kendall test was conducted to identify monotonic trends, with a significance level of 0.05, using RStudio. The tests null hypothesis was that there were no monotonic trends in the data. The alternative hypothesis was that a significant trend could be observed. When testing the correlation between DOC and TotHg scatterplots were made with a trendline, with TotHg on the y-axis and DOC on the x-axis. A descriptive analysis was made to observe any trends present in the plots as the samples was dependent to each other a linear regression could not be conducted. The results presented no significant trend in the concentration of TotHg and MeHg on any of the sites. Most surprising, no positive trend could be observed in the correlation between TotHg and DOC. One emphasized importance of this thesis is that it's furthered and the work of monitoring mercury in these streams are continued, to see how a longer timespan effects concentration.

Keywords: Atmospheric deposition, concentrations, dissolved organic carbon, mercury, methylmercury, peatlands, water-catchments

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Abbreviations

C*x*	Catchment *x*
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
Hg	Mercury
IRB	Iron-reducing bacteria
KCS	Krycklan catchment study
L*x*	Sample location *x*
MeHg	Methylmercury
RGM	Reactive Gaseous Mercury
SRB	Iron-reducing bacteria
TotHg	Total Mercury

1. Introduction and background

1.1 Introduction

Anthropogenic activities have caused an increase of mercury emitted into the atmosphere since the industrialism initiated. This has further caused a global spread of mercury and an increase of mercury concentration in all living organisms (Bergman et al. 2012). The ionic form of mercury (Hg (II)) can transform into the potent neurotoxin methylmercury (MeHg). This neurotoxin can further bioaccumulate into food chains and get biomagnified within tissues of fish and could cause problems for us humans (Gerson & Driscoll 2016).

1.2 Problem background

Reports and models show a decline in atmospheric concentrations of gaseous elemental mercury over Europe, due to a reduction of anthropogenic emissions released. This is a direct effect of implemented conventions against emission made by humans, in order to protect human health and the environment (Osterwalder et al. 2017). Although there has been a decline of mercury (Hg) deposition in Sweden for last 40 years, there are still substantial amounts of stored Hg in the aquatic and terrestrial ecosystems. The Hg will remain affecting the ecosystem and keep cycling for decades or even centuries to come. This will especially be more extreme in locations where disturbances are abundant, such as locations where land use are frequently exposed or where resources from the nature is extracted and climate change is also a disturbance able to affect this (Lam et al. 2022).

1.3 Mercury & Methylmercury

Mercury is a metal that exists in most living things among the landscape. There are multiple ways mercury enters the ecosystem, primarily from the atmosphere where it mainly enters the ecosystem through bodies of water (precipitation). Other

sources are anthropogenic activities such as mining and industrial emissions which can directly introduce Hg into the terrestrial environment (Bishop et al. 2020).

The gas elemental form of mercury (Hg^0) has a long lifetime span (approximate 0,5 years) in the atmosphere, which makes it possible for the mercury to spread over long ranges from the original emission site. Although the forms of mercury that is oxidized have a shorter lifespan in the atmosphere, these mercury forms are: Hg (II), particulate mercury (HgP) and reactive gaseous mercury (RGM). A short lifespan refers to the fact that these forms will deposit close to the origin of the emission (Gerson & Driscoll 2016).

Mercury is highly toxic. After being emitted into the atmosphere it falls as wet or dry deposition. Forest enhances deposition, and this can increase concentrations in bodies of water draining forested catchment (Gerson & Driscoll 2016). Through a process called methylation mercury ions Hg (II) can be transformed into a very potent and bioaccumulated neurotoxin called methyl mercury (MeHg). When deposited into watersheds the ionized mercury is methylated mostly by sulphate or iron-reducing bacteria (SRB, IRB). To make this process happen a reducing environment are required. Examples of such environments are wetlands or in sediments (Wang et al. 2021). For methylation to occur some parameters must be met. The reaction is very dependent on the bioavailability of Hg, and the presence of methylating microorganisms. Until recently it was thought that an insoluble form of mercury often found in soils called HgS (cinnabar) had an unsignificant effect on the methylation of mercury. Later studies have shown that SRB in some circumstances can methylate HgS and therefore contribute to the amount of MeHg in water and soils (O'Connor et al. 2019).

There are studies made that shows an increase in fish Hg concentrations in Sweden and Finland (also Canada), although only some species and regions are known to follow this trend. Although recent studies show samples taken from lakes in Sweden that indicate a decline in Hg concentrations in fish over a five-decade period. These observations seem more plausible considering the decline of mercury deposition into the atmosphere in Europe since 1990 (Braaten et al. 2019).

1.3.1 Dissolved organic matter and dissolved organic carbon

Dissolved organic matter (DOM) is a compound that helps transport mercury through watersheds. The DOM contains of dissolved organic carbon (DOC) that has thiol groups that are effective in binding to the oxidized form of mercury Hg(II) (Jonsson et al. 2014). The transportation of Hg in waters in the terrestrial environment is almost all held responsible by organic matter (Bishop et al. 2020).

The correlation between MeHg and dissolved organic carbon varies between site to site. Some sites reach positive correlations between MeHg and DOC meanwhile some show negative correlations. However, TotHg shows less variability and has a steadier correlation with DOC (Bishop et al. 2020).

1.3.2 Conditions affecting the concentrations on mercury and methylmercury

There are multiple conditions that affects the concentration of mercury and methylmercury in the terrestrial ecosystem. These factors are for example organic matter levels, nutrient status, pH, temperature, and deposition of Hg from the atmosphere (Braaten et al. 2019). Deposition of other materials into the ground water can also influence the amount of Hg and MeHg. Research has been made to determine if sulfate (SO_4^{2-}) deposition has a significant effect on MeHg. There are multiple sources of MeHg, one of them is peatlands (e.g. wetlands) (Grigal 2003). Furthermore, sulfate has been identified as an important control of peatlands strengths as MeHg sources. An increase of sulfate concentration in peatlands results in higher concentrations of MeHg, see figure 1 (Bergman et al. 2012).

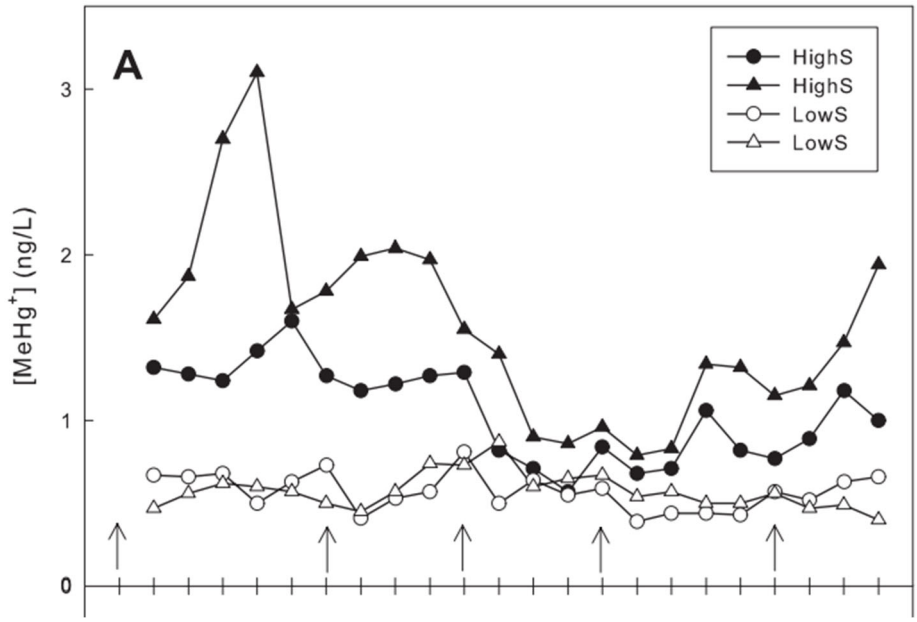

Figure 1. MeHg concentrations in peatlands with different concentrations of sulfate (Bergman et al. 2012).

Seasonality tends to be a large factor in the variation of Hg and MeHg concentrations during the year. But also, location of streams or watersheds can have a large impact on the flux of Hg. The MeHg concentrations sometimes increase from spring to summer (Grigal 2003). Studies show that during summer flow conditions

the DOC and Hg total peaked in some sites. But in other sites the peak were observed much later in the year during autumn stormflow events, although these sites tend to be forested sites and not wetlands (Eklöf et al. 2015).

Re-emission of Hg from the terrestrial ecosystem, both soils and vegetation, is a part of the global Hg cycle. This can occur from both soils and vegetation, through biotic and abiotic mechanisms. The difficulty of quantifying this re-emission means that landscape Hg mass balances still have considerable uncertainty. This makes long-term runoff observations of particular value in trying to see how this output from the landscape is varying, as this is an indirect indication of the soil pool status (Bishop et al. 2020).

1.4 Sample site description

Krycklan catchment study (KCS) is a 6790 hectares large region where broad research has been conducted the last 35 years. Since 1992 water samples has been collected there where data on everything from mercury concentrations to streamflow has been gathered (Laudon et al. 2021). Figure 1 shows a small proportion of the water catchment area where water sampling is performed for location 2, 4, 5, 6 and 7. As also shown in figure 1 location 7 is a downstream sample location of location 2 and 4.

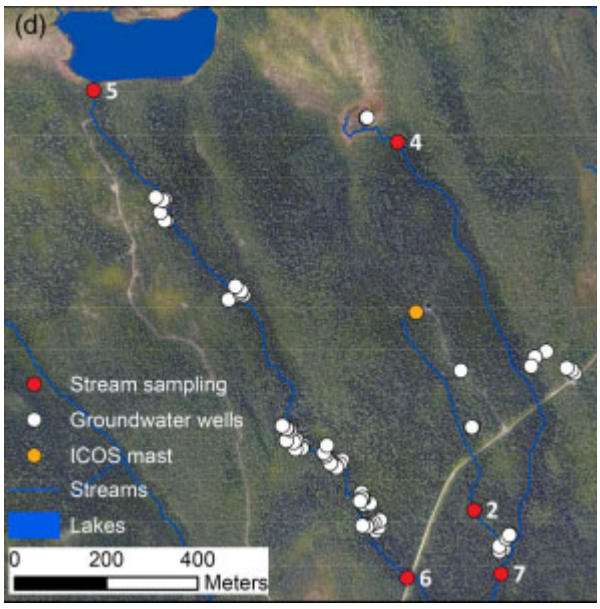

Figure 2. Water-streams and sample location at KCS (Laudon et al. 2021).

Degerö stormyr (Lat. 64°11'N, Long. 19°33'E, altitude 270 m a s 1) is in addition to KCS another location that is correlated to Vindeln Research Forests done by SLU. Degerö stormyr is shown in *figure 3* and where location 18 is sampled.

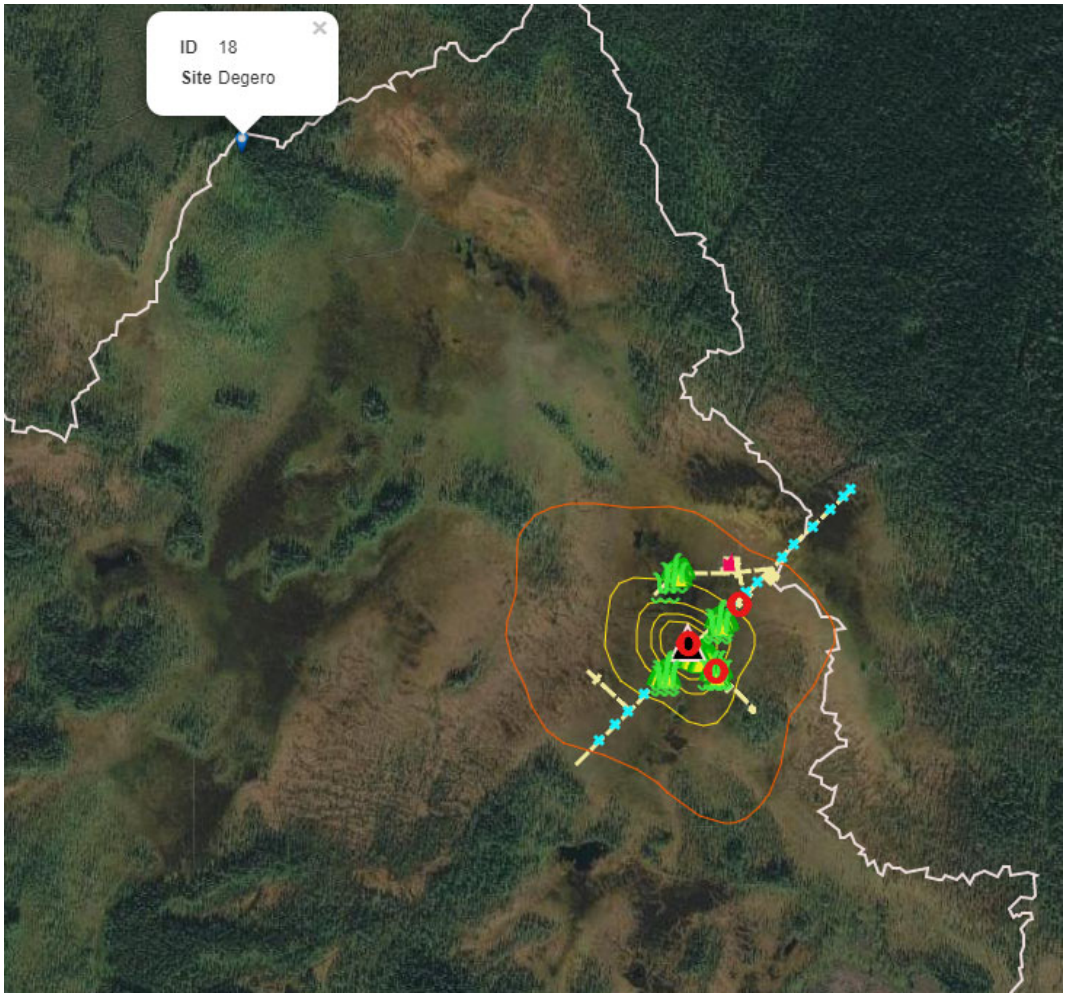

Figure 3. Sample location 18 on Degerö stormyr (Noumonvi 2021).

Each water-catchments and its characteristics is presented In *Table 1*. Each catchment is the same as sample location (C2 is sample location 2 etc). As shown in *table 1*, C2 mostly consists of forest, C4 is a large proportion of a peatland and majority of C7 is forest. In addition to these catchments sample location 18, from Degerö stormyr also consists mostly of peatland as seen shown in *figure 3* (Bergman et al. 2012; Laudon et al. 2021).

Table 1. Water-catchments and it's characteristics (Laudon et al. 2021).

Catchment	Area (ha)	Lakes[a] (%)	Forest[a] (%)	Open land[a] (%)	Arable land[a] (%)	Mire[a] (%)	Till[b] (%)	Thin soils[b] (%)	Rock outcrops[b] (%)	Sorted sediment[b] (%)	Tree volume[c] (m^3ha^{-1})	Birch[d] (%)	Spruce[d] (%)	Pine[d] (%)	Stand age[c] (years)
C1	48	0	98	0	0	2	92	8	0	0	187	2	63	35	87
C2	12	0	100	0	0	0	84	16	0	0	212	0	36	64	103
C3	4	0	59	0	0	40	43	0	0	4	133	1	5	93	77
C4	18	0	56	0	0	44	22	27	0	0	83	0	45	55	57
C5	65	6	54	0	0	39	40	6	0	0	64	12	26	62	50
C6	110	4	71	0	0	24	54	11	2	0	117	4	26	70	69
C7	47	0	82	0	0	18	65	15	0	0	167	1	35	64	86
C8	230	0	88	0	0	12	63	19	2	0	118	12	20	68	71
C9	288	2	84	0	0	14	69	7	2	4	150	6	29	65	78
C10	336	0	74	0	0	26	60	12	0	1	93	12	21	68	60
C12	544	0	83	0	0	17	67	8	0	6	129	8	34	57	72
C13	700	1	88	0	1	10	61	9	1	16	145	8	25	68	78
C14	1410	1	90	1	3	5	45	8	2	38	106	10	23	67	62
C15	1913	2	82	1	0	14	65	8	1	10	85	10	26	64	54
C16	6790	1	87	1	2	9	51	7	1	30	106	10	26	63	62
C20	145	0	88	0	3	10	45	20	2	21	59	16	16	68	42
C21	26	0	99	0	0	1	53	3	0	44	138	8	10	82	74
C22	491	3	68	0	0	29	61	7	1	0	78	10	22	67	54

1.5 Purpose

The purpose for this thesis is to sort gathered Hg and MeHg measurement data from four streams in Krycklan and Degerö. This data has been gathered in the space of the last 30 years, but much of it has never been examined on this timescale. The purpose is therefore to organize all the data gathered during the last 30 years. Then we will search for patterns or trends in the measurements to see how the concentration of Hg and MeHg have fluctuated over these years in relation to each other (TotHg and MeHg), between catchment times (peatlands versus forest, upstream versus downstream) in relation to streamflow rates, in relation to dissolved organic carbon and in relation to time (long term trend).

1.6 Research question

How has the mercury and methylmercury concentrations changed in a Swedish landscape (KCS and Degerö stormyr) over the last 30 years?

1.7 Theory

There are several relationships that have been observed between mercury concentrations and export at different places and different times. But it is rarely that these

relationships can be tested over long periods. Key drivers that have been hypothesized and will be tested for are: Atmospheric deposition (which has declined over the last 30 years), organic carbon dissolved in water, streamflow rate and catchment soils (peatlands, forest).

2. Material & Methods

The data that's been utilized in this thesis are all gathered at numerous sample sites around Vindeln. One major region where the data has been gathered are at Krycklan catchment study (KCS). In addition to the data gathered at KCS there's more data applied to this thesis from Degerö stormyr. This stream sample location in this thesis is mentioned as location 18.

The data collected from the numerous sample sites was initially provided through existing excel files and were fixed into similar formats. All the data work was handled with excel. The different datafiles were then added into a main file to gather all the data in one spot. Furthermore, a lot of duplicates arose in the main file and were deleted using excel functions. When all the data was added and fixed in the main file, a major sorting was initiated, firstly by location (from which water stream the sample was collected from, listing from 1-66) to then be sorted by date to create a timeline. To further investigate the water streams and proceed the data work the locations 2, 4, 7 and 18 were chosen.

All the data from the samples were provided as concentrations of MeHg and TotHg (ng/L). To add dissolved organic carbon (DOC) into the rows of mercury data, additional excel files were provided. These files had DOC for almost all dates from 1993 to 2021, where DOC weren't present, total organic carbon (TOC) data were used instead. Then the excel function "VLOOKUP" were used to add DOC into the rows of mercury data. This function is based on searching for a value in a range and then adding it into the corresponding cell. In this case the search values were the mercury sample date and the range the DOC excel files, this gave a DOC concentration (mg/L) on the same date as the mercury sample date (on the same excel row).

When all the variables were added and the major sorting were done, means for respective variable was calculated. This were done through the excel function "AVERAGEIF", which calculates the average of a range which meets a given criteria. The criteria in this case were years, meaning which year the specific sample were taken. Hence to get means on the variables for each year. Means were calculated on each separate location (2,4,7 and 18) for all the variables (MeHg, TotHg and DOC)

To see how the total Hg concentration correlates with DOC all the samples gathered were used. These were put on the y-axis while the corresponding DOC value sampled the same day were placed on the x-axis. This was made to a scatterplot and when a trendline was inserted the trend between the two values could be observed. Since the observations of the samples are dependent a linear regression analysis could not be applied, therefore a descriptive analysis on the trendline was made.

To analyse if MeHg or TotHg has positive/negative trends over the timeline. The Mann Kendall test was used to identify monotonic average trends (in y-values). The y-values in this case are the means for TotHg and MeHg, meanwhile the x-axis values are the years. The Significance level used is 0,05. The null hypothesis used in the test contains no monotonic trend in the time series and the alternative hypothesis is that there's an existing trend in the timeseries. This statistical analysis was made using RStudio.

3. Results

All the results from all four sites including both MeHg and TotHg got similar results as illustrated in *figure 4-11*. With a significance level of 0.05 no stream showed a statistically significant trend. Although some graphs showed a smaller p-value indicating a start to a significant trend (location 4 & 18 for MeHg).

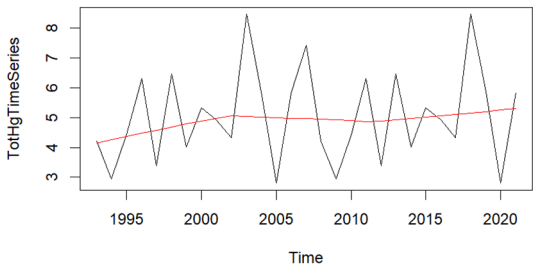

Figure 4. Graph of total mercury (TotHg) concentrations (ng/L) *on location 2 with trendline.*

TotHg2 tau = 0.0852, 2-sided pvalue =0.5349

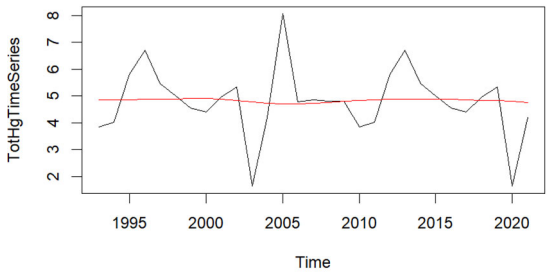

Figure 5. Graph of total mercury (TotHg) concentrations (ng/L) *on location 4 with trendline.*

TotHg 4 tau = -0.0676, 2-sided pvalue =0.62496

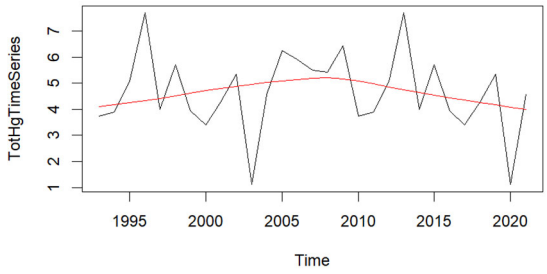

Figure 6. Graph of total mercury (TotHg) concentrations (ng/L) *on location 7 with trendline.*

TotHg 7 tau = -0.005, 2-sided pvalue =0.985

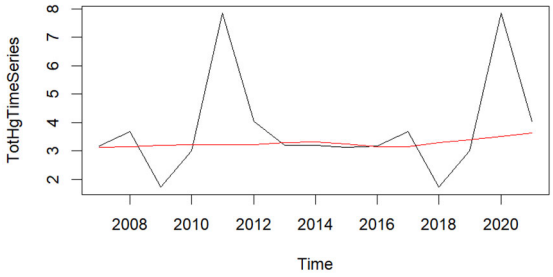

Figure 7. Graph of total mercury (TotHg) concentrations (ng/L) *on location 18 with trendline.*

TotHg 18 tau = 0.0883, 2-sided pvalue =0.69001*

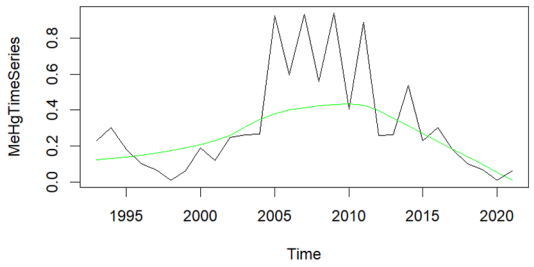

Figure 8. Graph of methylmercury (MeHg) concentrations (ng/L) *on location 2 with trendline.*

MeHg 2 tau = -0.00248, 2-sided pvalue =1

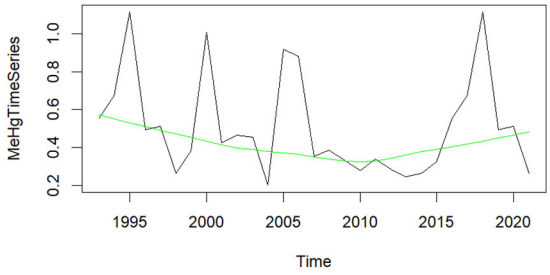

Figure 9. Graph of methylmercury (MeHg) concentrations (ng/L) *on location 4 with trendline.*

MeHg 4 tau = -0.199, 2-sided pvalue =0.13795

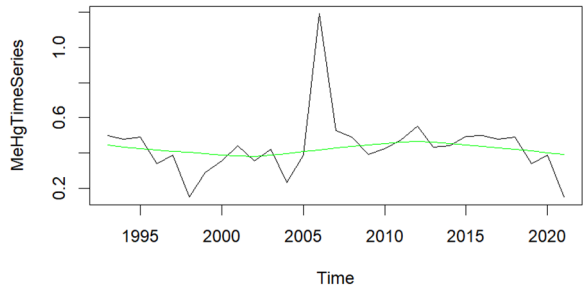

Figure 10. Graph of methylmercury (MeHg) concentrations (ng/L) *on location 7 with trendline.*

MeHg 7 tau = 0.0893, 2-sided pvalue =0.51104

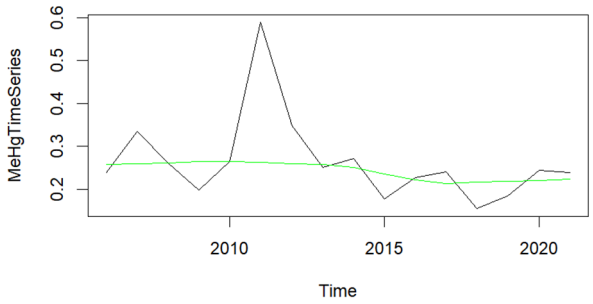

Figure 11. Graph of methylmercury (MeHg) concentrations (ng/L) *on location 18 with trendline.*

MeHg 18 tau = -0.293, 2-sided pvalue =0.12544

As visible in *figure 12* these scatterplots show the relationship between TotHg which is on the y-axis and DOC which is on the x-axis. As what can be observed the datapoints seem to be scattered randomly across the graph. There is no apparent positive trend between TotHg and DOC as was to be expected. No significant relationship can be observed.

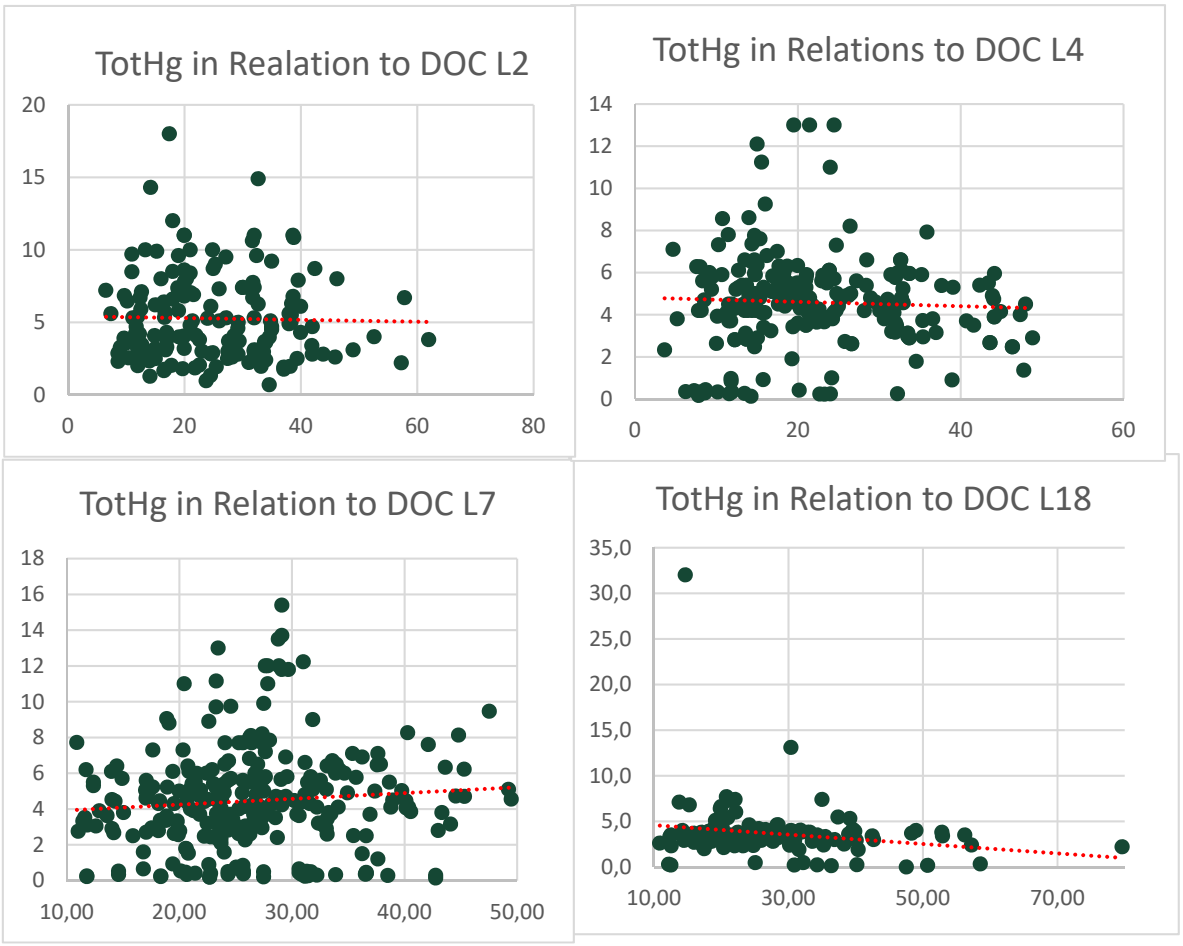

Figure 12. Concentrations of total mercury (TotHg) (ng/L) in relation to concentrations of dissolved organic carbon (DOC) (mg/L), on all sites with trendline.

In *figure 13* there's a visual representation of average TotHg concentrations per year. And *figure 14* is the average MeHg concentrations per year.

As shown in *figure 13* the average TotHg concentration in the four different locations follows each other for the most part until splitting up in recent years. The graph shows two big fluctuations, one in 2009 with a large decrease in concentration and one large increase in concentration in the year 2016.

In *figure 14* there is higher fluctuation between locations. MeHg concentration seems more unstable in contrary to TotHg. The different locations concentrations seem to correlate very little with each other until there is one unanimous peak in 2011 before they later again start to differ more in recent years.

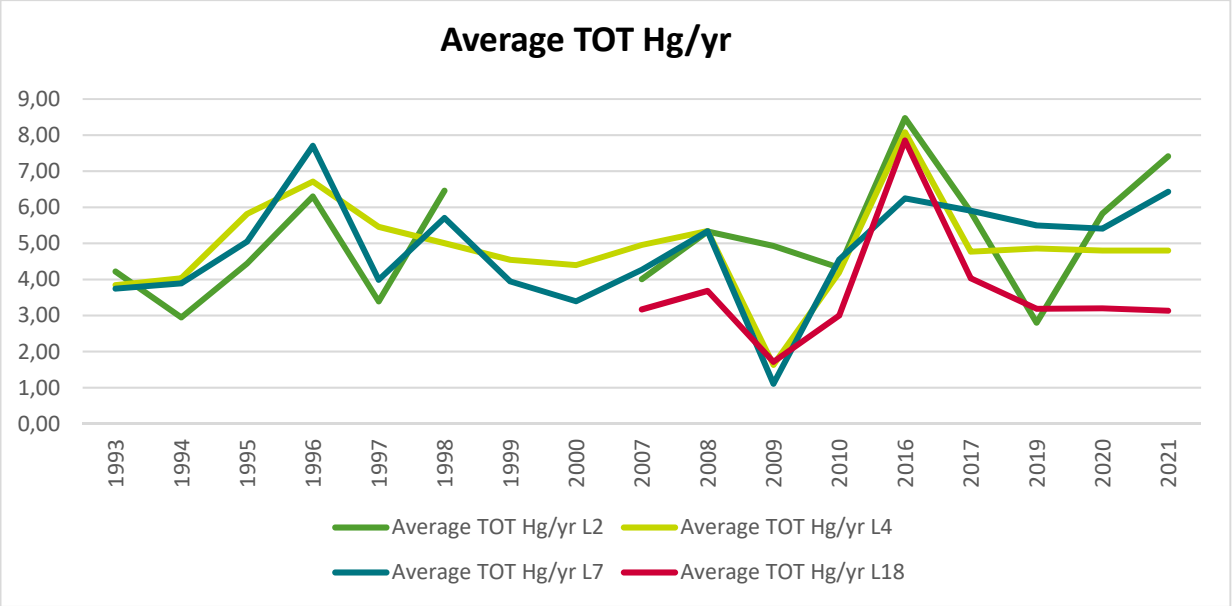

Figure 13. Average total mercury (TotHg) concentration (ng/L) for each year.

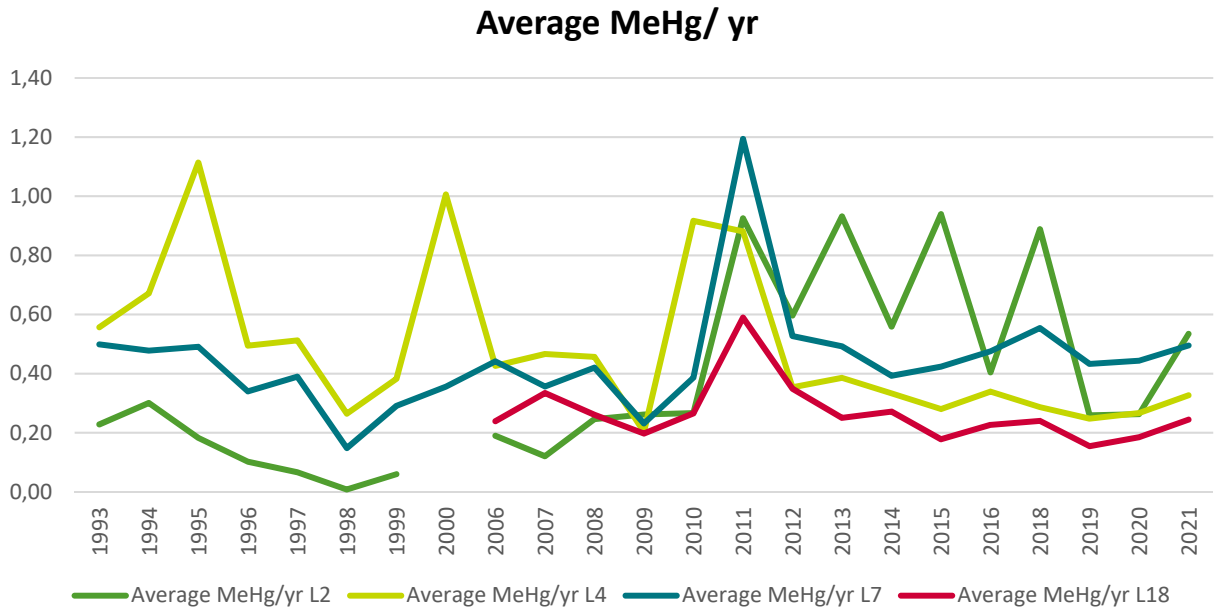

Figure 14. Average methylmercury (MeHg) concentration (ng/L) for each year.

Table 2 and Table 3 illustrates the results from using the excel function "AVERAGEIF" and these averages were further implemented to create *figure 12 & 13. Table 4* shows the average carbon concentration in all the locations, sampled on the same days as both TotHg and MeHg were sampled.

Table 2. Average methylmercury (MeHg) concentrations (ng/L)/ year.

Average MeHg/year				
Year	L2	L4	L7	L18
1993	0.23	0.56	0.50	-
1994	0.30	0.67	0.48	-
1995	0.18	1.11	0.49	-
1996	0.10	0.49	0.34	-
1997	0.07	0.51	0.39	-
1998	0.01	0.26	0.15	-
1999	0.06	0.38	0.29	-
2000	-	1.01	0.36	-
2006	0.19	0.43	0.44	0.24
2007	0.12	0.47	0.36	0.33
2008	0.25	0.46	0.42	0.26
2009	0.26	0.20	0.23	0.20
2010	0.27	0.92	0.39	0.27
2011	0.93	0.88	1.19	0.59
2012	0.60	0.35	0.53	0.35
2013	0.93	0.39	0.49	0.25
2014	0.56	0.33	0.39	0.27
2015	0.94	0.28	0.42	0.18
2016	0.40	0.34	0.48	0.23
2018	0.89	0.29	0.55	0.24
2019	0.26	0.25	0.43	0.15
2020	0.26	0.27	0.44	0.18
2021	0.53	0.33	0.50	0.24

Table 3. Average total mercury (TotHg) concentrations (ng/L)/ year.

Average TotHg/year				
Year	L2	L4	L7	L18
1993	4.22	3.84	3.74	-
1994	2.95	4.03	3.89	-
1995	4.44	5.82	5.05	-
1996	6.30	6.71	7.71	-
1997	3.39	5.46	3.99	-
1998	6.46	5.01	5.70	-
1999	-	4.54	3.94	-
2000	-	4.40	3.39	-
2007	4.01	4.96	4.27	3.17
2008	5.33	5.34	5.34	3.68
2009	4.93	1.63	1.11	1.72
2010	4.33	4.20	4.55	3.00
2016	8.47	8.08	6.25	7.85
2017	5.87	4.77	5.90	4.03
2019	2.80	4.86	5.50	3.19
2020	5.83	4.80	5.41	3.20
2021	7.42	4.80	6.43	3.13

Table 4. Average dissolved organic carbon (DOC) concentrations (mg/L)/ year.

Average Dissolved Organic Carbon/year				
Year	L2	L4	L7	L18
1993	18.20	27.13	21.28	-
1994	23.77	33.16	20.49	-
1995	27.00	20.55	24.57	-
1996	22.89	15.55	28.16	-
1997	35.95	15.57	24.21	-
1998	10.20	16.72	32.15	-
1999	8.59	26.86	29.55	-
2000	-	28.40	24.12	-
2006	20.36	16.98	27.41	28.70
2007	19.11	20.74	21.30	24.57
2008	36.49	16.00	31.21	36.98
2009	29.61	16.70	26.58	32.62
2010	30.41	29.89	26.10	31.71
2011	34.55	23.23	17.77	21.34
2012	21.72	20.43	24.59	24.26
2013	18.67	25.12	33.38	32.35
2014	23.50	15.50	24.19	24.34
2015	20.73	20.71	20.30	22.24
2016	18.65	22.26	25.24	19.79
2017	19.65	18.64	33.66	31.12
2018	25.78	23.19	20.82	35.05
2019	25.71	25.61	27.59	23.85
2020	26.50	17.52	28.12	20.67
2021	22.00	25.59	24.15	28.10

4. Discussion

The results from the Mann Kendall test shows no significance in negative / positive trends of TotHg and MeHg since no test resulted in a p-value under 0.05, this is illustrated in *figure 4-11*. With a deposition decline of gaseous elemental mercury over Sweden the last 40 years you could believe that there should be a negative trend of both TotHg and MeHg. However, there are still large amounts of stored mercury in the terrestrial and aquatic ecosystems and will remain in the ecosystems for decades or centuries to come. To be able to observe a significant trend the test would have to be conducted on an even longer timespan to see a decline in Hg in this particular area.

As stated previously, L4 and L18 are sample sites in or catchment areas to peatlands. L4's area is covered up to 44% peatland and L18 is directly taken on a peatland. Peatlands in Sweden acts as net sources of methylmercury and should therefore theoretically contain high concentrations of MeHg. In *figure 14,* location 4 initially have higher concentrations compared to the other sample location which proves the theory. However, from 2011 to 2021 there is decline of the MeHg concentrations especially on location 4. An explanatory reason to these results can be caused by variation in sulphate (SO_4^{2-}) in the peatlands throughout the years. Sulphate is a major factor regulating the peatlands strength as MeHg sources. It is also claimed that peatlands with higher level of sulphate also results in higher concentrations of MeHg. A cause to this increase is also strengthened by sulphates ability to methylate mercury ions to methylmercury. To further strengthen that sulphate variations is the cause to the decline of MeHg in our results, trends for sulphate and ratios between sulphate and MeHg must be measured for corresponding sample site.

The averages for TotHg and MeHg have some peaks in its values throughout the timeline as seen in *figure 13 & 14.* For MeHg there's a peak at 2011-2012 for all the sample location. It is hard to draw any exact conclusions on why this occurred and what caused it. One certain conclusion that can be drawn is that one or many of the factors that affects the concentration of MeHg is involved in the average MeHg peaks. For example, the year 2011-2012 could have been a wet year where high precipitation have been present. Since water sheds and water availability makes it possible for mercury to methylate into methylmercury, a year with high

precipitation will lead to higher concentrations of MeHg. To test if the high precipitation is the cause of this peak, the streamflow in the water streams would need to be investigated, to see whether it's higher than regular. In addition, the ratio between MeHg and streamflow must be plotted to see if there's a positive trendline between them.

The relation between TotHg and DOC showed minimal results as in a positive trendline which was surprising. As seen in *figure 12,* if there is a trend it is unconvincing. Although there should be an increasement in TotHg with higher DOC values, due to the thiol groups binding to the mercury and transporting it downstream resulting in a higher value of Hg concentration. There is a marginal positive trend on L7 which is rather far downstream. Although L2 is also located far downstream but does not display a positive correlation trend. This theory is thereby unconvincing.

The data set had some issues. Due to many people inserting their data in different ways into the master file, the data sorting took far longer than anticipated. Because of the long timespan of the study some data is presumed to be lost for the time this study was conducted. Other reasons for the data gaps could have been accidentally losing sample data during the sorting process, but due to lack of time only minor control investigations could be made. However, these investigations showed no misplacements or lost data from the data sorting. Nonetheless the gaps in the data still creates uncertainty in both TotHg and MeHg samples. So, at this moment only rough estimates could be calculated. Although there's thousands of samples contributing to the results. For example, in *table 2* and *table 3* obvious gaps in the data can be observed. In *table 4* there's similar missing DOC data, although those gaps only mimic the missing mercury data. There was more complete data in that set but since the lack of mercury data in certain places the DOC data for these certain periods was rendered useless and was left out of the study.

When the Mann-Kendall tests was conducted, means for every year was used to easier see how the concentrations fluctuated and see trends on the timeline. But this method presents a problem. As described in the paragraph above there were gaps in the data set. Not only were there years unaccounted for but also different frequencies in the number of samples each year had. This can make the means uncertain and could even be misleading. Due to fluctuations of Hg because of different weather patterns caused by seasonality it is important that every year and location has the same number of samples. It is also of great importance that samples are collected during the same time of year. Since the data had flaws in these aspects there could be a large error in the means of some the locations. Which further can have caused misleading results.

As a conclusion there is still a lot that can further improve this thesis. The most important is the gaps in the data. To get values that are trustworthy, the missing data, if it still exists, must be found and put into the study. More correlating parameters such as streamflow, sulphate concentrations, temperature and seasonality could be used to explain the fluctuations of mercury in the streams. Since no declining trend of concentration for both mercury variations could be observed, a continuation of gathering samples is important to see if there is a decline in the future.

References

Bergman, I., Bishop, K., Tu, Q., Frech, W., Åkerblom, S. & Nilsson, M. (2012). The Influence of Sulphate Deposition on the Seasonal Variation of Peat Pore Water Methyl Hg in a Boreal Mire. de Oliveira Azevedo, S.M.F. (red.) (de Oliveira Azevedo, S. M. F., red.) *PLoS ONE*, 7 (9), e45547. https://doi.org/10.1371/journal.pone.0045547

Bishop, K., Shanley, J.B., Riscassi, A., de Wit, H.A., Eklöf, K., Meng, B., Mitchell, C., Osterwalder, S., Schuster, P.F., Webster, J. & Zhu, W. (2020). Recent advances in understanding and measurement of mercury in the environment: Terrestrial Hg cycling. *Science of The Total Environment*, 721, 137647. https://doi.org/10.1016/j.scitotenv.2020.137647

Braaten, H.F.V., Åkerblom, S., Kahilainen, K.K., Rask, M., Vuorenmaa, J., Mannio, J., Malinen, T., Lydersen, E., Poste, A.E., Amundsen, P.-A., Kashulin, N., Kashulina, T., Terentyev, P., Christensen, G. & de Wit, H.A. (2019). Improved Environmental Status: 50 Years of Declining Fish Mercury Levels in Boreal and Subarctic Fennoscandia. *Environmental Science & Technology*, 53 (4), 1834–1843. https://doi.org/10.1021/acs.est.8b06399

Eklöf, K., Kraus, A., Futter, M., Schelker, J., Meili, M., Boyer, E.W. & Bishop, K. (2015). Parsimonious Model for Simulating Total Mercury and Methylmercury in Boreal Streams Based on Riparian Flow Paths and Seasonality. *Environmental Science & Technology*, 49 (13), 7851–7859. https://doi.org/10.1021/acs.est.5b00852

Gerson, J.R. & Driscoll, C.T. (2016). Is Mercury in a Remote Forested Watershed of the Adirondack Mountains Responding to Recent Decreases in Emissions? *Environmental Science & Technology*, 50 (20), 10943–10950. https://doi.org/10.1021/acs.est.6b02127

Grigal, D.F. (2003). Mercury Sequestration in Forests and Peatlands: A Review. *Journal of Environmental Quality*, 32 (2), 393–405. https://doi.org/10.2134/jeq2003.3930

Jonsson, S., Skyllberg, U., Nilsson, M.B., Lundberg, E., Andersson, A. & Björn, E. (2014). Differentiated availability of geochemical mercury pools controls methylmercury levels in estuarine sediment and biota. *Nature Communications*, 5 (1), 4624. https://doi.org/10.1038/ncomms5624

Lam, W.Y., Mackereth, R.W. & Mitchell, C.P.J. (2022). Landscape controls on total mercury and methylmercury export from small boreal forest catchments. *Biogeochemistry*, 160 (1), 89–104. https://doi.org/10.1007/s10533-022-00941-9

Laudon, H., Hasselquist, E.M., Peichl, M., Lindgren, K., Sponseller, R., Lidman, F., Kuglerová, L., Hasselquist, N.J., Bishop, K., Nilsson, M.B. & Ågren, A.M. (2021). Northern landscapes in transition: Evidence, approach and ways forward using the Krycklan Catchment Study. *Hydrological Processes*, 35 (4). https://doi.org/10.1002/hyp.14170

Noumonvi, K.D. (2021). Google satellite basemap, Koffi Dodji Noumonvi. https://slughg.github.io/Kulbacksliden-Instrumentation

O'Connor, D., Hou, D., Ok, Y.S., Mulder, J., Duan, L., Wu, Q., Wang, S., Tack, F.M.G. & Rinklebe, J. (2019). Mercury speciation, transformation, and transportation in soils, atmospheric flux, and implications for risk management: A critical review. *Environment International*, 126, 747–761. https://doi.org/10.1016/j.envint.2019.03.019

Osterwalder, S., Bishop, K., Alewell, C., Fritsche, J., Laudon, H., Åkerblom, S. & Nilsson, M.B. (2017). Mercury evasion from a boreal peatland shortens the timeline for recovery from legacy pollution. *Scientific Reports*, 7 (1), 16022. https://doi.org/10.1038/s41598-017-16141-7

Wang, B., Zhong, S., Bishop, K., Nilsson, M.B., Hu, H., Eklöf, K., Bravo, A.G., Åkerblom, S., Bertilsson, S., Björn, E. & Skyllberg, U. (2021). Biogeochemical influences on net methylmercury formation proxies along a peatland chronosequence. *Geochimica et Cosmochimica Acta*, 308, 188–203. https://doi.org/10.1016/j.gca.2021.06.010

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