

Distribution of Anthropogenic Mercury in a Forested Wetland

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Abstract

As global usage of mercury and methylmercury increases, climate change will impact its distribution and movement in unexpected ways. In wetlands, elemental mercury (Hg) is methylated into its more environmentally toxic form, methylmercury ($[\text{CH}_3\text{Hg}^+]$). The two main sources for anthropogenic mercury are atmospheric deposition and legacy soil mercury. Methylmercury bio-accumulates and causes neurological damage to terrestrial and aquatic organisms. Our research demonstrated that there was mercury within the forested wetland watershed. Also, the analysis suggested that although organic carbon was an indicator for the presence of Hg. However, the best predictor was when horizon mid-point, % C, and $\delta^{13}\text{C}$ parameters were all considered together. Studying the dynamics and distribution of mercury within wetlands can inform environmental and resource managers on best practices to mitigate these ecological health issues.

1. Introduction

The organometallic form of mercury, methylmercury, causes neurological damage to organisms in terrestrial and aquatic ecosystems (Madenjian *et al.*, 2014). Methylmercury is known to bio-accumulate in tropic levels resulting in numerous neurological and birth effects becoming a major health threat to pregnant women and young children. The global mercury input is estimated to be between 6,000-11,000 tons per year. Anthropogenic sources have been estimated to contribute up to 70 percent of the mercury introduced into the environment (Engstrom *et al.*, 2014). In the Midwest environmental mercury has increased since the 1980s. It

has done so despite numerous legislative measures that restricted mercury emission, especially coal fired power plants.

Several studies agree the concentration of mercury in wetlands will continue to increase with due to land-use practices (Hurley et al., 1995). Research conducted by *J.B. Shanley et al.*(2008) indicated that low-land lakes and large watersheds have been the sources of mercury input to lakes. Further, increased total mercury input into aquatic systems appears to parallel increased organic carbon input. Watershed geometry and local geology play a significant role in mercury-laden Particulate Organic Carbon (POC) residential times (Kolka *et al.*, 1999; Driscoll et al., 1995). Research indicated that both Dissolved Organic Carbon (DOC) and POC have a role in the movement of mercury, but POC had a more critical role (Kolka *et al.*, 1999).

The two main sources for anthropogenic mercury are atmospheric deposition and legacy soil mercury. Current research estimates that atmospheric deposition accounts for 60~70 percent of the increased mercury balance. However, the extent to which soil mercury contributes to anthropogenic mercury deposition has not been thoroughly investigated. In this work, we assessed the following hypothesis: (i) Is there mercury in the Honeysuckle watershed? (ii) If there is Hg within the wetland, how is it distributed (vertically and horizontally)?, (iii) and what are the factors controlling mercury abundance in a local forested wetland? Answering these questions will be the first steps by informing resource management on how Hg behaves in soils. Especially since global climate change will have an impact on the distribution and movement of global mercury during a period in which the global mercury budget is increasing.

2. Site location



Figure 1. A map of Northern Michigan. Honeysuckle Creek watershed is a Located south of the University of Michigan research center and drains into Burk Lake.

Field work was conducted at the Honeysuckle Creek watershed, located at the University of Michigan Biological Research Station (UMBS), USA (4535N 8443W). It is within the dry region of an early ancient, Holocene-era lake, which existed until about 5000 years ago. The watershed is a 113 hectare topographic region, composed of 13 ecosystems (ES) in an array of xeric to mesic aspen, northern hardwoods, and mixed conifer-hardwood swamp. It is also composed of a number of landforms; such as outwash plains, moraine, lake plain, stream channel, and old dunes and shorelines. The parent materials are composed of calcareous till, gravelly or sandy glacio-fluvial or aeolian deposits, lake-bottom sands/silts and organic deposits.

3. Materials and methods

3.1 Soils

The lowlands are made up of hydric, spodosol soil, which is characteristic of this type of forest wetland. The soil is acidic and composed of organic O horizons. It is underlain by A, E, B horizons. These soils are representative of well-drained sandy soils. The area is glacial-till covered from the remnants of the last glacial period.

At least 25 survey points within ES 55, an anoxic, water-saturated lowland, were generated by the GPS/IPAD and numbered. During July 2015, soil samples were arbitrarily

selected from 20 of the 25 sites. In ES 55, at each profile location was probed until contact with the clay layer was reached or depth pressures prevented further penetration. A McCauley peat corer was used to bore to the predetermined depth in 35-50 cm increments to determine depth. The soil profiles ranged in depth to 1.6 meters deep and each profile had a 6 cm diameter. A meter stick was used to measure the depth of the probe in centimeters. This allowed for minimum compaction of the wetland soil. With each boring iteration, the type of horizon was to be identified and the thickness recorded. Composite samples were generated while processing the soil profiles. This was accomplished by identifying horizons of each profile in situ and subsamples were taken of each one. The composite sampled varied between 3-7 subsamples. The sub-sampled horizon was placed in a plastic bag and then labeled with the profile number and horizon for future identification. A total of 84 sub horizons were collected and transported to the Lakeside lab for processing.

3.1 Soil Processing

The samples were placed in standard plastic tray to air dry. All soils were allowed to dry at room temperature for 3-6 days. Daily temperature ranged from 55 ° F to 80 ° F. When the soils were sufficiently dried, they were placed back into their plastic bags.

During the actual processing, each bag was given a progressive sequential number (1-84). The material of each bag was placed on a plastic tray. Rocks, POM and roots over 2mm thick were physically removed from each sub-sampled horizon, separated, and weighed. The individual bags were marked with the profile number, type of horizon and sequential number. The remaining material was considered to be organic or mineral soil. It was weighed on a balanced scale, which was recorded onto XLS generated data sheets.

A scintillation (scint) vial without the cap and written with the same sequential number, was weighed and recorded on the data spread sheet. Soil from each sample was filled to the neck of the vial if there was sufficient amount. The weight of the vial with the material was performed. The weight was then recorded on the data sheet under air dry weight. This is done for all 84 subsamples.

Each subsample was balled milled in a mixture for five minutes. The entire contents of the scint vial was placed into a stainless steel chamber along with a large and small stainless steel pelt. Two chambers were used at the same time. After completion of the ball milling process, they were replaced into their respectively numbered sample vial. After the grinding of the samples, chemical analysis was conducted on the samples.

After Hg and carbon isotope value analysis, the samples were dried in a muffled furnace oven at 105C oven-dried for 24 hours. After cooling, the samples were removed from the oven ten samples at a time to prevent rehydration. The vial and material was weighed to obtain the 105c oven dry weight for each vial sample. This information was then recorded on the master data sheet.

Because this operation was supposed to be performed before the ball milling, scint vials which had remaining material, was oven dried at 500c. These samples were placed in a muffled furnace for 24 hours. After being given sufficient time to cool (4 hours), each sequential sample was removed from the oven; ten samples at a time to prevent rehydration. This information was then recorded on the master data sheet under scint vial and material at 500c.

3.2 $\delta^{13}\text{C}$ Values

$\delta^{13}\text{C}$ was measured to determine the isotopic abundances of the carbon in the soil. $\delta^{13}\text{C}$ value was measured using a Costech Analytical CHN analyzer (Costech The analysis provided $\delta^{13}\text{C}$, percent carbon and percent nitrogen for each subsample Analytical, Valencia, CA, USA) coupled to a Finnigan Delta Plus XL isotope ratio mass spectrometer (Thermo Scientific, West Palm Beach, FL USA) at UMBS Lakeside laboratory building. To prepare each subsample for testing, approximately 0.5 g of processed material from each sub-sampled horizon were combusted. Values on %N, %C and $\delta^{13}\text{C}$ were provided in digital format .

3.3 Mercury Analysis.

The mercury levels in each sample were determined by atomic absorption spectroscopy using a Direct Mercury Analyzer-80. For the area ES 55, approximately 0.5 g of processed sub-horizon material from each of the sequential number were weighed and placed in one the 40 positions of the DMA-80s auto-sampler. The material was then combusted in an oxygen-rich furnace, which determined the total mercury content via thermal decomposition, amalgamation and atomic absorption. Each subsample required 7 minutes to undergo the entire process. The results were provided via electronic display in milligrams/Kg and ng. A calibration standard was used after every tenth sample. Also random samples were performed to compare Hg results.

3.4 Data Analysis

Parametrical statistical tests (t test, ANOVA, simple linear regression) of the data were conducted using SigmaPlot (SYSTAT Software, San Jose, CA USA). Linear regression analysis was used to test the correlations between organic carbon and inorganic mercury. $P < .05$ was the standard employed to determine if the test results are significant.

4. Results

4.1 Correlation between Hg and Carbon stocks.

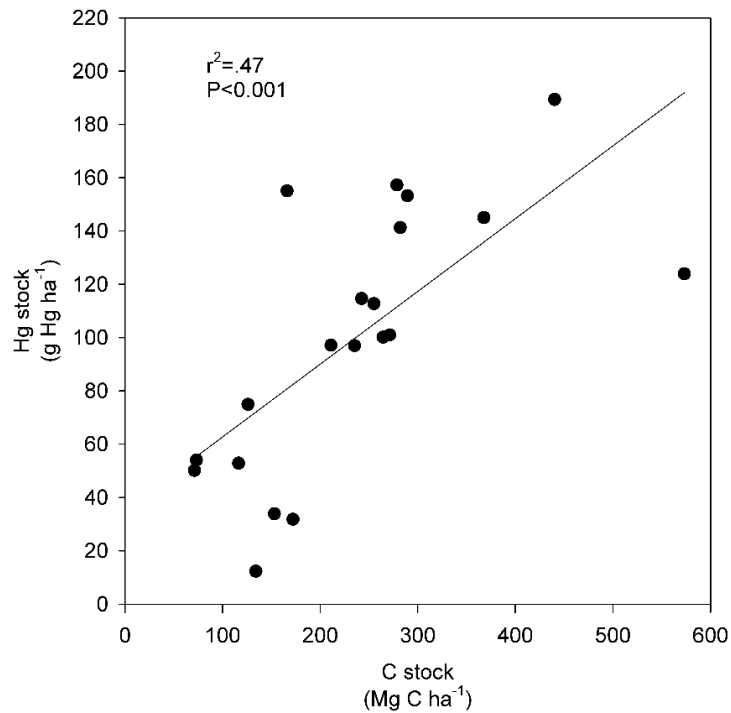


Figure 2. Comparison of Hg stock and Carbon stock. Graft demonstrates a positive correlation between the amount of the carbon present and the amount of the Hg present.

There was a positive correlation between measurement in carbon stock and measurement in Hg stock. As the amount of carbon stock increased, there was a corresponding increase in the amount of the Hg.

4.2 Vertical Hg profiles

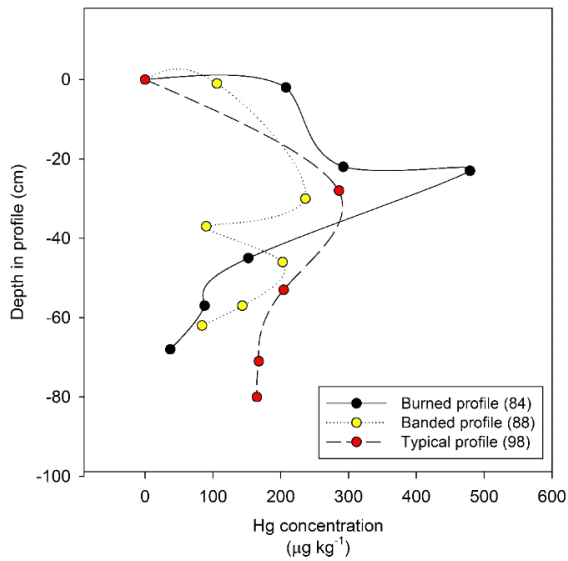


Figure 3. Three representative Hg vertical profiles for ES 55. Profile 88 is the typical profile. The Burned and Banded profile demonstrates that there are variables in the soil profiles controlling the vertical retention of Hg.

Another analysis associated with vertical profiles demonstrated that there were other variables in the soil which was controlling the vertical retention of the Hg. There were three discernable vertical profiles. The standard profile was represented by Hg obtaining a maximum Hg concentration around 20-30 cm and then decreased in its Hg concentration. The burned profile had a maximum concentration which occurred at depths between 20-30 cm. There was a steep reduction in Hg concentrations as the profile became more buried. In the banded profile, the Hg concentrations reached a maximum concentration around 20-30 cm. It then decreased in concentration, increased at the 50cm depth, and finally decreased in Hg concentration. This profile was noted to have striations or different bands of the soils as the vertical profile increased.

4.3 Horizon depth mid-point

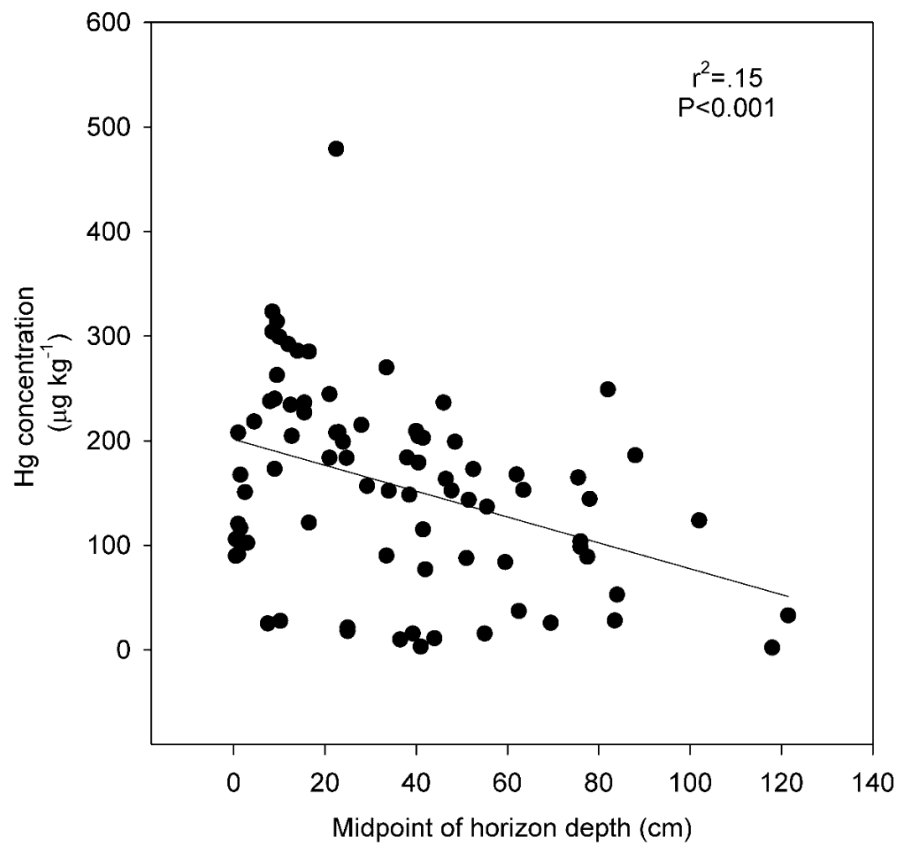


Figure 4. Chart demonstrating the relationship between Hg and depth. As depth increases, the Hg becomes more concentrated.

The mid-point of the all of the horizons were used as a means of calculating the amount of the mercury in a sample. As the depth increased, the Hg became more concentrated.

4.4 Best sub-set regression as an indicator of the Hg distribution

Table 1. A regression analysis indicates that all three variables; horizon mid-point, % C and $\delta^{13}\text{C}$, affect mercury abundance.

Model #	Variable	Cp	R ²	Adj R ²	MSerr	A [†]	B [§]	C [‡]
1	1	12.808	0.148	0.137	7531.172	*		
2	2	6.012	0.232	0.212	6873.370	*		*
3	3	4.000	0.270	0.242	6614.646	*	*	*

† Horizon mid-point

§ % Carbon

‡ $\delta^{13}\text{C}$

Figure 5. According to our statistical analysis, the best predictor using R-squared as a criterion was horizon depth alone, followed by horizon depth and delta C13 isotope. The use of all three had the least favorable results.

Statistical analysis also suggest that soil vertical depth profile is probably the most significant factor for determining the relationship between organic carbon and Hg. Derived data showed a positive relationship between increasing soil depth with a reference from the midpoint of the sub-horizon layer and increasing Hg concentrations. The sub-horizon layer depth, carbon enrichment and overall percent of carbon showed a collective correlation for increased Hg concentrations.

4.5 Carbon stock as a mechanism of Hg distribution

There are several mechanisms which control the distribution of the Hg within the watershed. The first is the spatial distribution of the carbon stock.

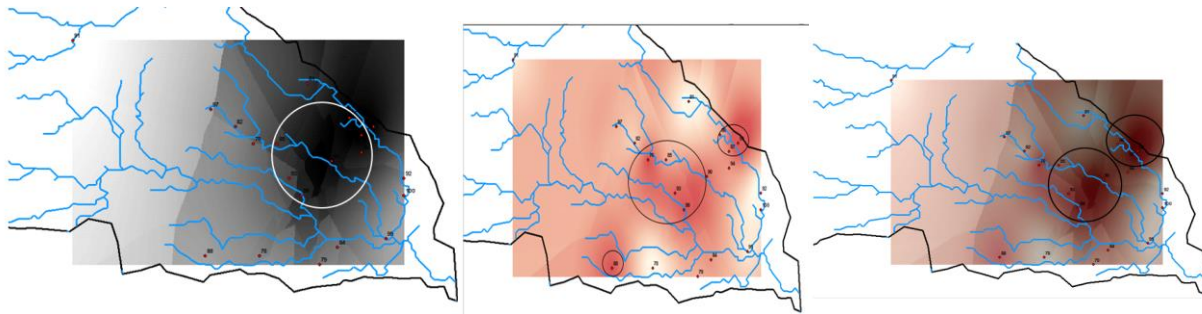


Figure 6a.

Figure 6b.

Figure 6c.

Figure 6. Comparison of Hg stock and Carbon stock in ES 55. Graft demonstrates a positive correlation between the amount of the carbon present and the amount of the Hg present. Figure 6a. is an interpolation of the C stock. Figure 6b is an interpolation of the Hg Stock. Figure 6c is an overlay of the C/Hg Stock.

4.5 Interpolation maps.

The values obtained from Hg analysis and carbon analysis and inputted into an ArcGIS mapping program. To produce maps of high resolution required a number of datum points generated from the soil profiles. The spatial interpolation of Carbon and Hg across the ES 55 area wetland used to predict the amount of the carbon and mercury concentrations with ES 55.

4.6 C/N ratio as a mechanism for Hg distribution

The C/N ratio was plotted against the Hg for the Oi soil layers. The carbon and nitrogen ratio could be used to determine relationship of Hg within the soil properties. The concentration of Hg decreased with the increase of C/N ratio, from 200 $\mu\text{g kg}^{-1}$ to C/N ratio of 30:1 to approximately 80 $\mu\text{g kg}^{-1}$ to a C/N ratio of 55:1 the . The C/N ratio were more significant in the thinner Oi layers than the thicker Oi layers. All of the points are from points representing the horizon on the wetland surface. The decreasing slope of Hg with C/N ratio suggested a quantitative change in Hg concentration demonstrating decreased Hg concentration with

increased C/N ratio. There is a r-squared value of .61. This

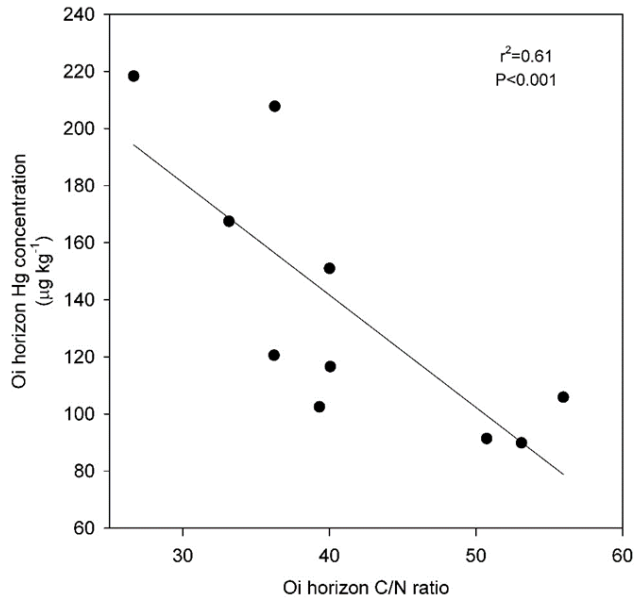


Figure 7. Comparison of C/N ratio and Hg concentrations for the ES 55 Oi layers. 61% of Hg concentration is able to be explained as a result of the organic material in the layers. The Y coordinate for each point represents the concentration of Hg for the corresponding X axis as Oi horizon C/N ratio.

means that 61 percent the of observed relationship can be explained in this manner. The p-value also supports that the results are significant.

5. Discussion

Our analysis demonstrated that ES 55 had a Hg present in the soil. Our sub-horizon samples from the mercury analysis demonstrated that there was Hg in each of the soil profiles. The sub-horizon profiles with the greatest amount of organic material had the most Hg. We are able to conclude that Hg has been retained in the lower wetland area of the watershed. However, we were unable to determine instrumentally the relative portions of anthropogenic and legacy mercury. Because we know that the age of the Holocene lake which once existed in the area, and

that anthropogenic Hg has been present for only about 200 yr, most of the Hg in the lower soil profiles would be legacy mercury from natural sources.

5.1 Correlation between Hg and Carbon stocks.

Mercury stock within the ES 55 represents a potential for release into the nearby aquatic environment, Burk Lake. Our subsamples from the mercury analysis demonstrated that there was Hg in each of the soil profiles. Organic carbon functions as an effective container for the retention of Hg. Our research suggests that mercury stock in the soil is proportional to the carbon stock. Mercury stock and carbon stock is defined as the sum of individual mercury and carbon within the different horizons. Each was calculated based on the respective mercury/carbon content within each horizon of the respective profiles. Wetland research has shown that the decomposition of organic matter is slow. This results in the gradual build-up of a robust wetland carbon stock. There were some disagreement with the relative concentrations between the Hg stock and Carbon stock concentrations. This disagreement can be explained by the relative few profiles collected within close proximity of each other.

We are able to conclude that Hg has been retained in the lower wetland area of the watershed. However, we were unable to determine the relative portions of anthropogenic and legacy mercury. We suspect that carbon stock may be related to the hydrological flow and past conditions within the ES 55 resulting in asymmetrical distribution of the Hg. Research suggests that anthropogenic sources Hg enhance the abundance of the Hg stock within a forested wetland (Friedli et al., 2007).

Because we know that the age of the former Holocene lake which once existed in the area and that anthropogenic Hg was a significant factor only about 200 years ago, most of the Hg

in the lower soil profiles would be legacy mercury from natural sources. Mercury stock within the ES 55 represents a potential for release into the near-by aquatic environment, Burk Lake.

5.2 Vertical Hg profiles

Historical records show that the region, which currently make up the University of Michigan, Biological Research Center, was logged for 30 years before being acquired by the University of Michigan. It is most probably that it was during this period of logging that a period of localized climate and hydrological change occurred in the watershed. This would place the age of these first turning points over a 30 year period from 1880 to 1909. The material on top of this turning point represents events which have occurred in the local region since 1909, to include successional vegetation and a new local climate regime.

The lowlands environment, which includes vegetation, anthropogenic activity and soil structure, may be able to explain the different types of the soil profiles as they relate to the enrichment of the $\delta^{13}\text{C}$. Some of the areas where profiles were taken were dominated by sphagnum. According to research, the slow decomposition of $\delta^{13}\text{C}$ depleted compounds, like those of sphagnum species, result in a small decrease in $\delta^{13}\text{C}$. In these microenvironments, the isotopic profile is dominated by the enrichment of the soil.

Our isotope profiles proceeded to a certain “turning point” which is defined by Atewell et al. (2011) as the point at a certain depth in which the $\delta^{13}\text{C}$ value of the profile decreases or increases. There is a positive or negative slope which develops in relationship with the turning point. As predicted, the anoxic soils of the lowlands started to display stable isotopic profiles due to little or no degradation. Also depth profiles values would become lighter because of the enrichment of the organic material caused by the depletion of C^{13} from anaerobic

mineralization. Wetlands are poorly drained soils and there was limited fractionation. The typical profile is representative of a microenvironment in which this is taking place.

5.3 Horizon depth mid-point

The results strongly suggest that those horizons with mid-point between 20-80 cm had a very strong affinity for mercury. These layers are also the organically enriched layers of the soil profiles. The lower layers were predominately sandy in texture and retained less mercury than the higher layers.

5.4 Best sub-set regression as an indicator of the Hg distribution

Research conclude that organic carbon was a good indicator of the Hg distribution. However, it was not as strong an indicator as soil depth. Best sub-set regression analysis was applied to a set of three variables. The results strongly suggest that all three variables, horizon mid-point, % C, and $\delta^{13}\text{C}$ parameters, were the best variables to explain Hg concentrations. Collectively, they predicted the horizontal abundance distribution and vertical concentration Hg within the lowland watershed.

5.5 Carbon stock as a mechanism of Hg distribution

Our research showed an overall correlation between the location of carbon and mercury. We then interpolated the carbon stock using kriging interpolation. The spatial interpolation of Carbon and Hg across the ES 55 area wetland used to predict the amount of the carbon and mercury concentrations with ES 55. An interpolation program was able to generate a carbon interpolated map and an Hg interpolated map. The maps showed varying concentrations of Hg and carbon from analytical derived values. The maps suggested that there are high and low

concentrations of carbon and Hg. When overlain, some of these high and low concentrations are in agreement. In other regions they are not in agreement.

5.5 Distribution of Hg stocks within soil profiles.

C/N ratio influences rate of organic matter decomposition by microorganisms. Low C/N ratio results in faster decomposition and less available organic C resulting in less Hg. High C/N ratio results in slow decomposition and more available organic C resulting in more Hg.

6. Conclusion

Both atmospheric and legacy Hg is known to be affected by watershed hydrology. Precipitation has increased in Northern Michigan, and this trend is expected to continue over the next two decades. The climate in the region is expected to be cool instead of warm, so any major changes from climate change in the region will most probably be associated with the change in Hydrology. By researching the vertical and horizontal distribution of mercury within soil profiles throughout the Honeysuckle Creek watershed, it was possible to estimate the total amount of the mercury entering aquatic systems. The mercury input into the nearby Burt Lake is probably from inputs from the Honeysuckle creek. There is a large percentage of wetlands in the Upper Michigan peninsula which are indicative of the type of climate and hydrological history associated with the Honeysuckle watershed. These wetlands appear to be a source of mercury input into the great lakes region. Also there has been varying concentrations of mercury discovered in the fish flesh of interior lakes within Michigan. Atmospheric deposition as well as legacy mercury must be considered significant inputs in these aquatic environments. Most people are exposed to mercury by eating fish from the great lakes. This includes small/large mouth bass,

walleye, northern pike and lake trout. The research is strongly supportive of the existence of the Hg within the Honeysuckle Watershed.

Our research supports other studies which predict that wetlands are a robust source of Hg. They possess both anthropogenic and legacy forms. It is likely that most of the anthropogenic input is located in the upper soil layers with the source of the lower layers mainly being natural. As such, it is reasonable to assume that the global concentrations will continue to increase making more mercury available for bioaccumulation in both aquatic and terrestrial food webs. We predict that the effects on wetlands from climate change will have a positive feedback on total mercury concentrations exacerbating ecological communities and human health.

To understand the distribution and movement of Hg within a watershed, it is recommended that it be studied in its entirety. We also recommended that at least twice as many data points be taken to conduct interpolation. C-14 should be a test of soil profiles to establish a baseline between anthropogenic and natural mercury. Research should be conducted to determine what percent of mercury methylation is from anthropogenic or legacy soil.

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