# MICHIGAN WHITE PINE SMELTER

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# INTRODUCTION

Trees has been known to absorb mercury (Hg) through its roots from the soil or injuries caused by insects. Trees also absorb atmospheric Hg through foliar stomata and its subsequent translocation. Michigan White Pine Smelter is known produce atmospheric Hg while it was in operation. White Pine trees are widely grown around that area. While this plantation operated, the annual amount of Hg released varied. In our research, we measured the amount of Hg in the trees surrounding the plantation and compared it to the trees around the trees in Cedar Creek Minnesota. Using the trees' rings, the samples were cut into different years. We want to test if the amount of Hg per year in the tree samples match up with the amount of Hg that is produced by the plantation that same year.

# HYPOTHESIS

- The amount of Hg concentration in the tree samples will follow the same trend as the amount of Hg released by the Michigan White Pine Smelter.

# METHOD

- The samples were taken from Cedar Creek Minnesota and near the Michigan White Pine Smelter.
- Field work was done in August 2010 through October 2010. Samples were collected using PVC gloves and were contained in plastic tubes that were cleaned by acid wash. The method of sample collection was with tree bores.
- The samples were stored in the refrigerator inside the acid wash plastic tubes, bagged, sealed and labeled.
- In lab, the samples were cut into section of 5 to 10 years by the tree rings. They were weighed and put into plastic bottles called bombs that has also been cleaned by acid wash. These samples were then digested with 10 ml of HNO3 for an hour and then 10 ml of H2SO4 and left in the oven overnight.
- After complete digestion, 3 ml of the sample was put into the purging and trapping system; which we call the bubbler, for mercury extraction using gold-coated sand traps and Nitrogen gas. The purging takes about 21 minutes to complete.
- After Diffusion, the gold-coated sand traps were transferred to the analytical system that will measure the amount of Hg in the sample. This system uses Argon gas to extract the amount of Hg in the sample by measuring the area of the signal received for 4.5 minutes. The signals are recorded and the Hg concentration was calculated.
- Traps and Bubblers were cycled to make sure that they are putting out the right numbers and before any sample is run, a regression line is made to check the accuracy of the system. All regression line had an R^2 of .9995 or higher. Also, SRM, Standard, Duplicates and Blanks were tested to ensure accuracy.

# METHOD SET-UP

- This picture is from Claas (35 – 39)

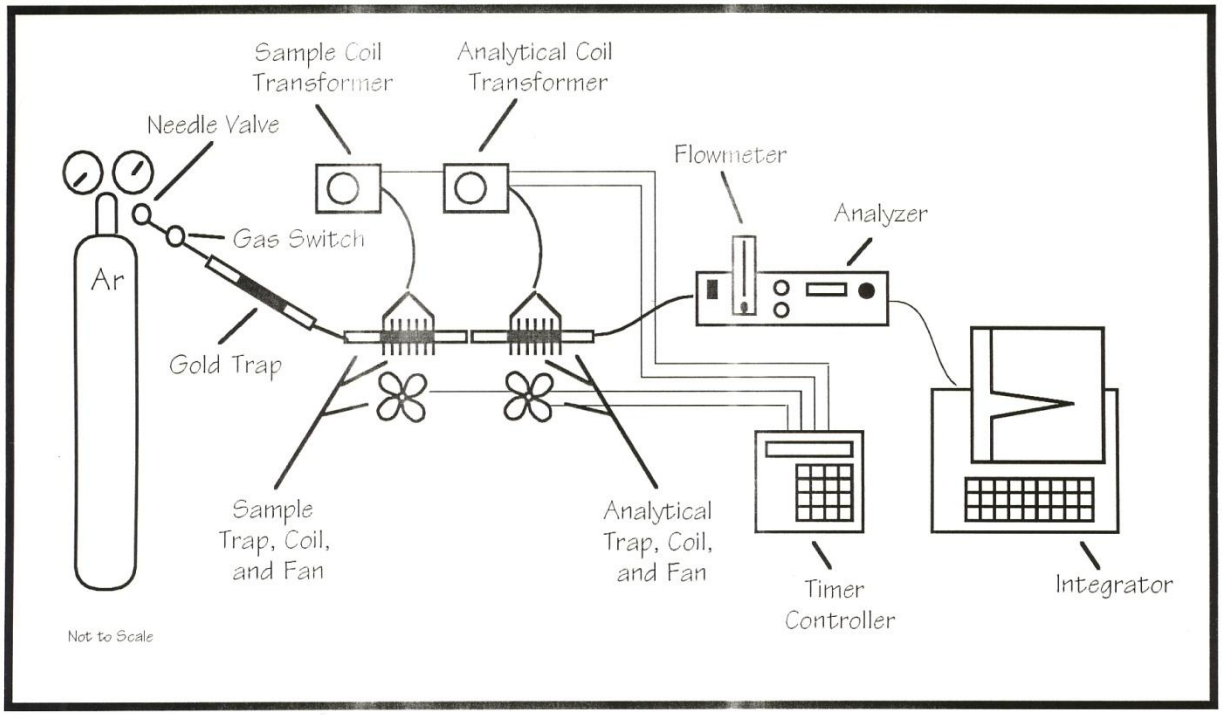



Figure 6-1. The Total-Mercury Analytical System

# METHOD SETUP

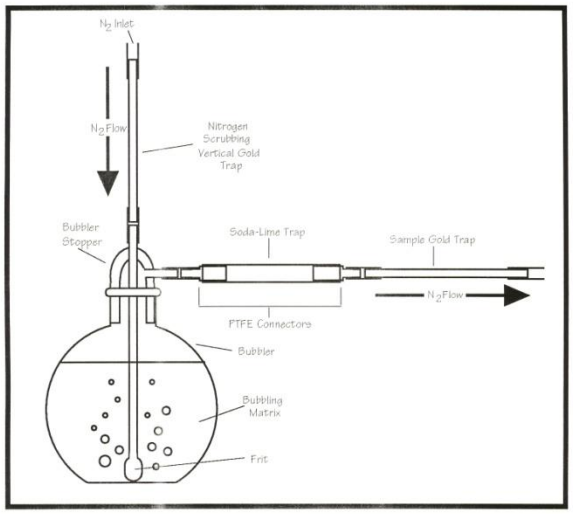



Figure 6-4. Total mercury purging and trapping system.

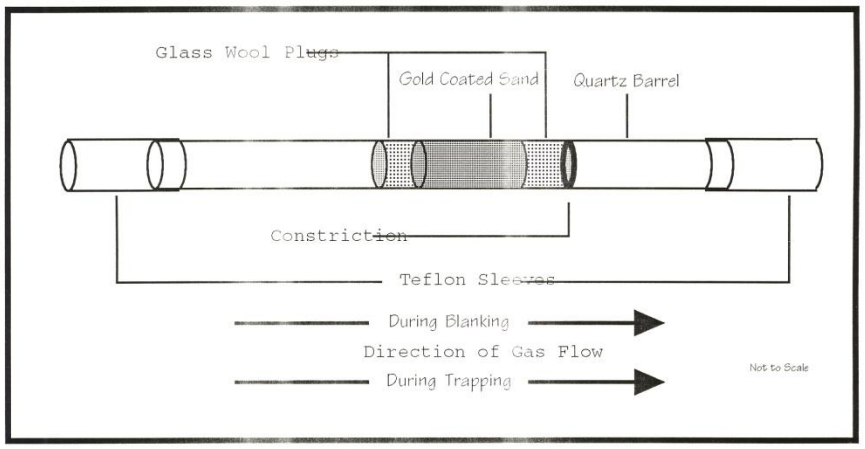



Figure 6-2. Gold-Coated Sand Trap

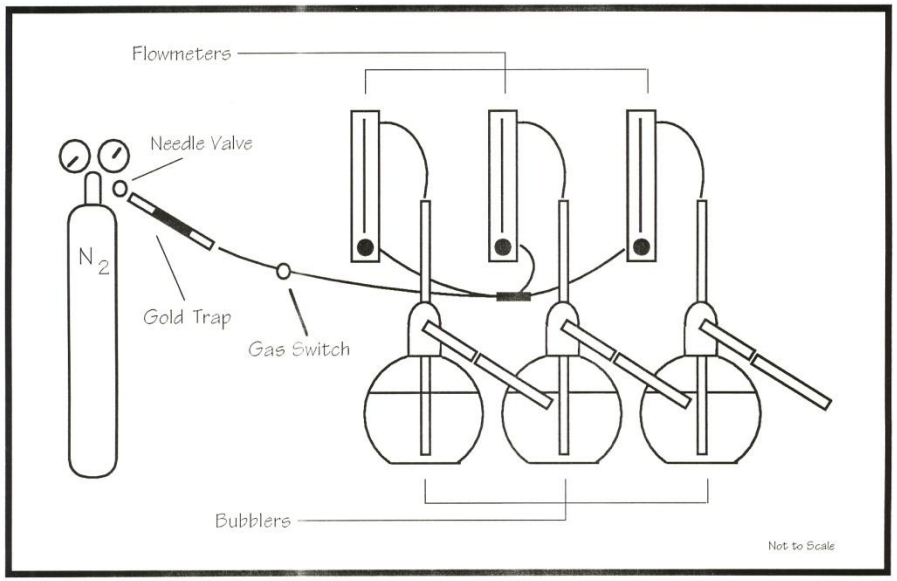


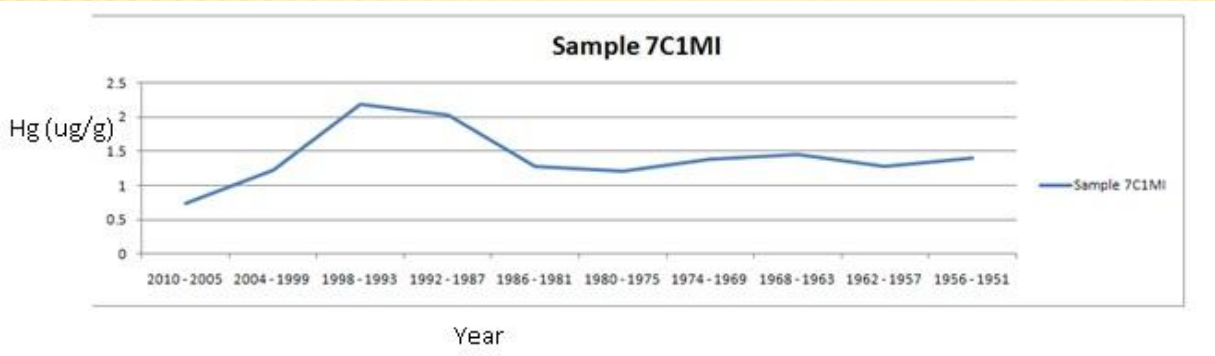

Figure 6-5. Total mercury purging and trapping system. Nitrogen, flowmeters, and bubblers.

These pictures are from Claas (35 - 39)

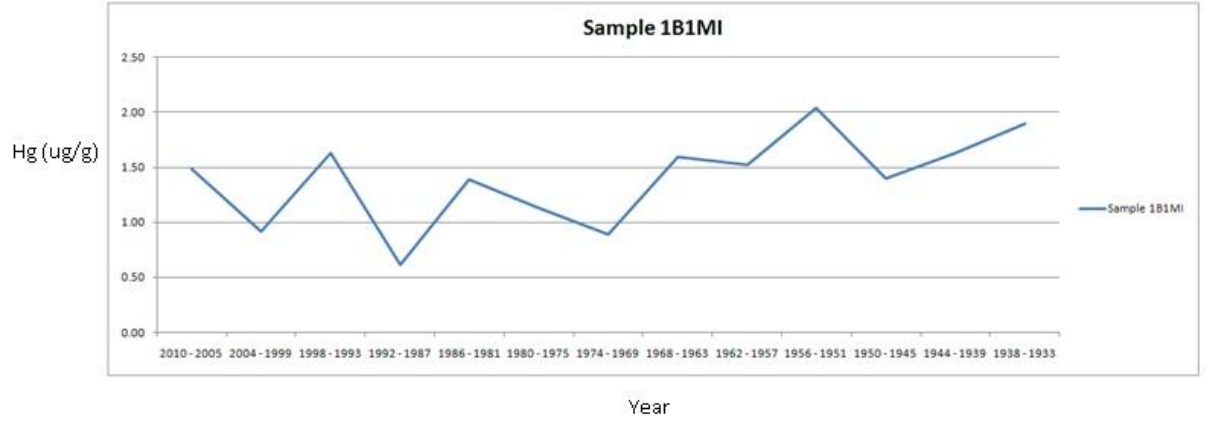
# RESULTS

- After sampling the white pines, the results indicate that there was no definite relation of mercury concentration in the tree tissues and the mercury concentration released by the White Pine Smelter. The mercury concentration in the trees samples was very low which made it hard to distinguish a pattern. Even the samples from the same years had different concentration. This may be due to the sensitivity of the instrument used to detect the levels of mercury.
- Also, there were duplicate samples that gave out different mercury concentration, which shows how low the mercury levels were. Trees from Cedar Creek Minnesota were also sampled as a reference and control sample.
- Theses Cedar Creek samples showed the same results as the White Pine samples. Although the mercury levels were low, it was still present in all of the samples. The samples had an average of about 1.4 ug/g of mercury in them.

# RESULTS OF SAMPLES FROM MICHIGAN




-This is the type of pattern we expected to find with increasing slope then a steady line showing the years of the smelters operation.




-This is an example of other graphs that we obtained. Notice the graph has an inconsistent pattern.

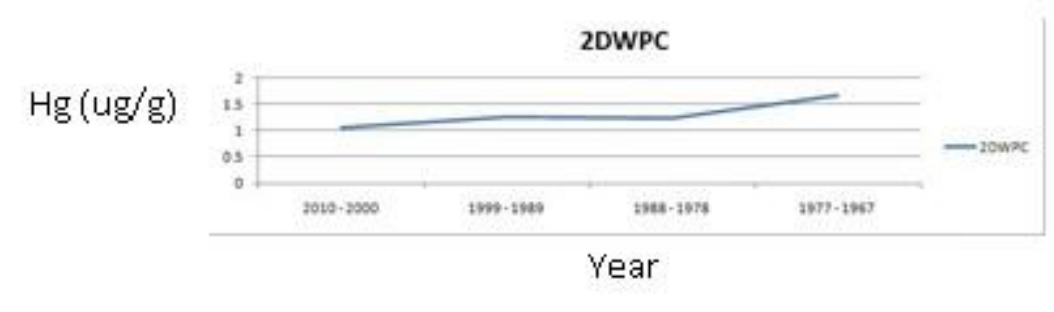
# RESULTS OF SAMPLES FROM MICHIGAN

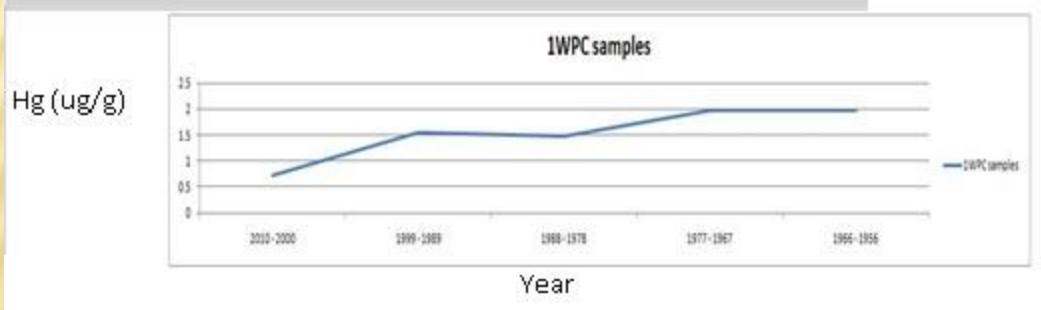
| Sample ID | ng/g | Year |
|---|---|---|
| 7C1MI-1 | 0.73 | 2010 - 2005 |
| 7C1MI-2 | 1.22 | 2004 - 1999 |
| 7C1MI-3 A.DUP | 2.19 | 1998 - 1993 |
| 7C1MI-3 A.DUP | 2.02 | 1992 - 1987 |
| 7C1MI-4 | 1.27 | 1986 - 1981 |
| 7C1MI-5 | 1.21 | 1980 - 1975 |
| 7C1MI-6 | 1.39 | 1974 - 1969 |
| 7C1MI-7 | 1.45 | 1968 - 1963 |
| 7C1MI-8 | 1.28 | 1962 - 1957 |
| 7C1MI-9 | 1.4 | 1956 - 1951 |
| | | |
| Avg | 1.416 | |
| Std | 0.415965 | |

| sample | ng/g | year |
|---|---|---|
| 1B2MI-1 | 2.18 | 2010 - 2000 |
| 1B2MI-2 | 1.08 | 1999 - 1989 |
| 1B2MI-3 | 1.95 | 1988 - 1978 |
| 1B2MI-4 | 2.05 | 1977 - 1967 |
| 1B2MI-5 | 1.51 | 1966 - 1956 |
| | | |
| | | |
| avg | 0.56 | |
| std | 0.4531335 | |

-This is the type of data that were obtained. Notice that some samples needed more than One duplicate in order to obtain consistent Hg concentration. These are the data highlighted in green.

# RESULTS OF SAMPLES FROM CEDAR CREEK




-These are graph obtained by the samples from Cedar Creek. These samples were suppose to have lower concentration levels since they are in a very secluded area, but these two graphs shows an increasing trend. Other Cedar Creek samples did not follow the same pattern though.

# RESULTS OF SAMPLES FROM CEDAR CREEK

| sample | ng/g | year |
|---|---|---|
| 2DWPC-05 | 1.05 | 2010 - 2000 |
| 2DWPC-06 | 1.25 | 1999 - 1989 |
| 2DWPC-07 | 1.24 | 1988 - 1978 |
| 2DWPC-08 | 1.67 | 1977 - 1967 |
| | | |
| avg | 1.3025 | |
| std | 0.2617 | |

| sample | ng/g | year |
|---|---|---|
| 1WPC-1 | 0.71 | 2010 - 2000 |
| 1WPC-2 | 1.55 | 1999 - 1989 |
| 1WPC-3 | 1.48 | 1988 - 1978 |
| 1WPC-4 | 1.98 | 1977 - 1967 |
| 1WPC-5 | 1.98 | 1966 - 1956 |
| | | |
| | | |
| avg | 1.54 | |
| std | 0.519567 | |

-These are the data obtained for the graphs above. Notice that the average amount of Hg in these samples are the same as those in the Michigan samples. Also that both locations had about the same standard deviations.
-The higher amount of Hg found in These samples may be due to the amount of samples analyzed.
-These samples were cut into sections Of 10 years at a time.

# DISCUSSION

- During the process of this research, we did run into problems with the instruments and had to buy new parts which put this research on hold for two weeks. Also, there were problems that we came across with our procedures so we had to change that as well.

- For example, during the Hg purging, the solution became very reactive and it formed foam all the way through the traps. This caused damage to both the soda lime traps and the Hg trap. Also, the coating on the gold beads for the Hg traps were old and needed recoating. This process took over 2 weeks to complete due to ordering and time spent coating the beads.

- Another factor that may influence the results were the conditions of the samples. While the samples were stored in a plastic tube, sealed in a plastic bag, and refrigerated, it had what looks like dew on it. The samples were moist and some even grew small amounts of mold on it. The samples that had mold were not tested. Would recommend drying the samples before digesting them.

- Due the instruments inability to reproduce consistent concentrations, this project could not be completed. In addition, the number of samples were not great enough to truly determine if there is a pattern. For further investigation, more samples in larger abundance would give better and more consistent results. Even though we could not find data to support our hypothesis; we found ways to improve our methods.

# SPECIAL THANKS…

- Thanks to Ed Nater, David Bell, and Jim Browzwoski in the Soil department of the University of Minnesota Twin Cities. Without them this project would not happened. It was a great pleasure working with them!

# REFERENCE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