International Summer Water Resources Research School
Dept. of Water Resources Engineering, Lund University

Study of Mercury Wet and Dry Deposition in Xiamen Area

By

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Abstract
Mercury (Hg) continues to be of special concern because of its multitude of controllable sources, its volatility, mobility and strong tendency to bioaccumulate. Our project will study the wet and dry deposition in Xiamen area from June 18 to July 13. For the dry deposition, we will measure two kinds of mercury. One is total particulate mercury (TPM), and the other is gaseous elemental mercury (GEM). The TPM will be trapped in a glass fibre filter and released by being heated at 900°C for 5 minutes. The GEM will be trapped in two gold sand tubes. Both of the samples will be analysed in a cold vapour atomic fluorescence spectrometer (CVAFS). For wet deposition, we will measure the rainwater collected in bottles according to EPA method 1631. Then we will compare the differences for dry deposition between day and night. As for wet deposition, we will compare the differences in different sites and time.

Keywords: Wet and dry deposition, gaseous elemental mercury (GEM), total particulate mercury (TPM), rain water samples, total mercury (THg), dissolved mercury (DHg), CVFAS, EPA method 1631 and backward trajectory.
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1. Introduction
Mercury is considered as one of the most toxic environmental pollutants. The compound’s ability to bioaccumulate affects both the environment and living organisms. Emissions of mercury are a global environmental issue as the substance can be transported very long distances. Therefore, the determination of mercury levels in the environment is required in order to identify the sources of emission and develop policies to control them.

In this project, mercury species in wet and dry deposition are detected in order to obtain information about the mercury content in the atmosphere. In the air, two different types of atmospheric mercury are measured, gaseous elemental mercury (GEM) and total particulate mercury (TPM). The analysis of wet deposition is accomplished by analyzing rainwater samples from four different sampling sites in Xiamen area, as well as samples from four locations close by the University of Xiamen. Two different mercury species are measured in the water samples, total mercury (THg) and dissolved mercury (DHg).

The information from the analysis is utilized to estimate the transportation and distribution of mercury in the atmosphere with the NOAA HYSPLIT model. The model uses the data of dry deposition and meteorological parameters to generate backward trajectories of the sources of mercury emissions.

1.1. Aim
This project is conducted during one month, from the 18th of June to the 13th of July, to study the wet and dry deposition of mercury in Xiamen Area. The purpose of the project is to detect the wet and dry deposition of mercury species in order to estimate the distribution of mercury in the atmosphere.
2. Background

The toxic effects of mercury have been observed during the recent decades and several studies of the environmental impact of the compound have been executed. The first known incident concerning mercury poisoning through contaminated fish occurred 1956 in Minamata, Japan.¹

Mercury differs from other heavy metals as it has a high volatility and mobility, further the element have the ability to bioaccumulate.² In the environment pollutions of inorganic mercury can be transformed to methylmercury (MeHg), an organic form which can bioaccumulate in the food chain. The bioaccumulation of mercury is the biggest concern of the toxic element. When methylmercury enters the body it can cross the blood-brain barrier and cause neurotoxic effects.³

There are natural sources of mercury emissions, the compound can be released to the environment through geological materials and volcanoes. The anthropogenic sources of mercury contribute to the mercury emissions through combustion, burning of fossil fuels, non-ferrous metal production and waste incineration.⁴

In China a study of the anthropogenic sources was conducted in 1999. The results showed that non-ferrous metal smelting accounted for around 45% of the mercury emissions, coal combustion 38% and 17% from other activities mainly from production of battery, fluorescent lamp and cement.⁵

The atmosphere is the most important pathway for dispersion and transport of mercury, through wet and dry deposition mercury can enter the aquatic system. In the atmosphere mercury can occur in three different forms:

- Gaseous elemental mercury (GEM), Hg⁰, which is the most common form. It is relatively unreactive and has a residence time of one year.
- Gaseous ionic mercury fraction, Hg²⁺, which also is known as reactive gaseous Hg (RGM). The form is highly surface reactive and therefore more water-soluble than elemental mercury.
- Particulate-bound Hg, Hg-P, which is derived from high-combustion sources.⁶

Once mercury is released to the atmosphere the compound can be transported a long distance before being deposited through either dry or wet deposition.⁷ The concentration of gaseous elemental mercury is usually around 1-2 ng/m³, but in industrialized and urban areas the concentration can be higher and at around 10ng/m³.⁸ While the background concentration of

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¹ Landis Matthew S.
⁴ Sumner Ann L.
⁵ Streets David G. (2005)
⁶ Mason Robert P.
⁷ Pirrone Nicola
total particulate mercury can range from 3 to 91 pg/m$^3$ according to a study conducted in Toronto.$^9$

The most important contributor to wet deposition is particulate mercury, Hg-P. Dry deposition of elemental mercury does not occur normally. In the atmosphere elemental mercury, Hg$^0$, can be oxidised to reactive gaseous mercury, RGM, by the reactants H$_2$O$_2$, NO$_3$, O$_3$ and OH. Normally the reaction rate of elemental mercury is very slow but in the presence of radicals the reaction rate increases.$^{10}$

RGM have a high deposition velocity and in some regions the deposition of RGM can be higher than the wet deposition. From experiments it has been estimated that this can occur when the concentration of RGM exceeds 20 pg/m$^3$.$^{11}$

The deposition of mercury to the marine system is driven by particle dry deposition and wet deposition through precipitation. The wet deposition is the major contributor and accounts for about two-thirds of the mercury load. Due to the low water solubility of elemental mercury, the aqueous mercury mainly consists of inorganic ionic mercury Hg$^{2+}$, and organic methylmercury.$^{12}$

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$^9$ Lu Julia Y. et al. (1998)
$^{10}$ Mason Robert P.
$^{11}$ Mason Robert P.
$^{12}$ Pirrone Nicola
3. Material and method

The project includes analysis of mercury species in wet and dry deposition. In order to determine the dry deposition of mercury the amount of gaseous elemental mercury (GEM) and total particulate mercury (TPM) is measured. The analysis method is based on a pyrolysis method called the Method of Amalgamation – Cold Vapor Atomic Fluorescence Spectrometry.\(^\text{13}\)

For quantifying the wet deposition of mercury two mercury species is measured, total mercury (THg) and dissolved mercury (DHg). The method used for the analysis is called Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap.\(^\text{14}\)

The first step of the analysis is to collect samples in an efficient way. This is done in different ways for dry and wet deposition of mercury.

3.1. Dry deposition of mercury

For the dry deposition two different types of atmospheric mercury is measured, total particulate mercury (TPM) and gaseous elemental mercury (GEM). Therefore two different equipments are utilised for the sampling, one for the total particulate mercury (TPM) and one for the gaseous elemental mercury (GEM).

The sampling device for total particulate mercury (TPM) consists of a glass fibre filter (figure 1), which is connected to a pump at the sampling site on top of the Ocean building. Only the particulate mercury is trapped in the membrane, as other groups of mercury will pass through. The flow rate of air is determined by a controller and is set to approximately 1\(\text{m}^3/\text{h}\). As the amount of particles in the air is low the sample of TPM requires a high flow rate.

![Figure 1. Sampling device of total particulate mercury (TPM) consisting of a glass fibre filter connected to a pump and a flow controller which determines the flow rate of the air.](image)

The device to measure the amount of gaseous elemental mercury (GEM) consists of two gold sand tubes connected in series and with a filter at the inlet to get rid of the particles in the air (figure 2). The device is placed on the top of the Ocean building and connected to a pump, the flow rate is determined by a controller and the flow rate of the air is kept to approximately 0.5\(\text{mL/min}\).

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\(^{13}\) Julia Y. Lu et al. (1998)

\(^{14}\) EPA (2002)
The sampling is divided into day- and night-time sampling. The day-time sampling is conducted between 9.00 am and 5.00 pm, while the night-time sampling is carried out during the remaining hours of the day e.g. from 5.00 pm to 9.00 am.

Prior to the sampling the equipment needs to be purified in order to get rid of residual mercury. This is done by heating glass fibre filters to 450°C for an hour and cleaning the other equipment in a bath of 50% HNO$_3$ for 48 hours. The gold sand tubes are purified in the VM-10 Gas Mercury advice by heating them to 600°C in 30 seconds.

### 3.1.1. Analysis of dry deposition

The samples of dry deposition are analysed directly after the sampling. To quantify the total particulate mercury and the gaseous elemental mercury in dry deposition a VM-10 Gas Mercury Device is utilised together with a Cold Vapor Atomic Fluorescence Spectrometry (CVAFS or AFS) see figure 3.

The data of the GEM is obtained by analysing the two gold sand tubes utilising the AFS. The Gas Mercury Device heats the samples of GEM to 600°C in 30 seconds in order to release the mercury from the gold sand tubes. The gaseous elemental mercury is then transported to the CVAFS using argon as carrier gas with a flow of 80mL/min. The amount of mercury is analysed in the AFS and will be read as IF, the impact of the sample which can be seen as the peak or the maximum amount of GEM in the sample. The two IF-values of the tubes are then added to get the resulting value for the determination of the GEM-concentration.

![Figure 3. Experimental setup including VM-10 Gas Mercury Device and AFS utilised in the analysis of GEM.](image)

The procedure to analyse TPM includes two steps, the first step is to transform TPM to GEM. The glass fibre filter is cut in half and heated to 900°C during 5 minutes. At this temperature the total particulate mercury is naturally transformed to gaseous elemental mercury. By transforming the TPM to GEM the amount of mercury can be analysed utilising the AFS. The heating process is performed by a temperature control heating system, figure 4 and 5.
Figure 4. The temperature control heating system utilised to transform TPM to GEM.

The total particulate mercury on the glass fibre filter is transformed to gaseous elemental mercury and transported to the gold sand tubes of the carrier gas. The carrier gas consists of argon and has a flow of 80mL/min.

Figure 5. The temperature control heating system, the membrane containing particular mercury is heated to 900°C in order to transform the TPM to GEM.

After the heating process the gold sand tubes are analysed utilising the same procedure as for GEM. The total IF-value of the two filters is then used in order to determine the mass and concentration of total particulate mercury in the samples. Meteorological data will be received later to estimate the transportation and distribution of mercury in the atmosphere.

3.1.2. Standard curve

Samples of dry deposition are analysed by utilising an Atomic fluorescence spectrometer (AFS). In order to analyse the result provided by the AFS a standard curve for gaseous elemental mercury (GEM) is produced. This is done by analysing samples of GEM with different volume and temperature.

Before analysing the samples the tubes are purified in the VM-10 Gas Mercury device by heating them to 600°C in 30 seconds. The samples are injected through the injection point (figure 6) and collected in a gold sand tube trap by utilising argon as a carrier gas with a flow of 80mL/min. The gas is first purified in a gold tube to get rid of any kind of contamination.
Then the sample is analysed in the VM-10 Gas Mercury advice by first heating it to 600˚C in order to release the mercury from the gold sand tube trap. The result is analysed in the AFS and will be read as IF, the impact of the sample which can be seen as the peak or the maximum amount of GEM in the sample.

The results are used to calculate the corresponding mass in each sample. The correlation between the mass and the IF are then utilised in order to obtain the standard curve, with mass on the x-axis and IF on the y-axis (figure 7). The curve will be used during the project when analysing samples of dry deposition, by knowing the IF the mass can be obtained from the standard curve and thence the volume and concentration can be determined.

The standard curve can be utilised when analysing both GEM and TPM as the samples always are transformed to GEM in order to conduct the analysis with the AFS.
3.2. Wet deposition of mercury
The wet deposition is analysed with a method called EPA method 1631. Rain water and water samples from four locations around the University of Xiamen are collected and examined. The rain water is collected with an automatic device on top of the Ocean building at Xiamen University. The water samples are then divided into two parts in order to analyse both total mercury and dissolved mercury.

Samples of wet deposition from four locations around the campus of Xiamen University are collected. From each site two samples are collected, one for the analysis of total mercury and one for dissolved mercury. The external conditions including temperature, relative humidity, wind rate and solar radiation should be recorded at each site.

The first sampling site is located at the reservoir of the school campus, the second at Fulong Lake at the campus, the third at a sewage pool and finally a sample with sea water from the beach. The samples should be collected from a depth of 1 meter, accept at Fulong Lake and the beach as the water there is too shallow.

Rainwater samples from four sampling sites in Xiamen Area was also collected and analysed. The position of the sampling sites, Xiao Ping, Bantou, Hongwen and Gulang Island is presented in figure 8 below.

Figure 8. Location of the sampling sites of rainwater samples.
The water samples collected at the sampling sites are prepared for analysis and stored in a fridge. For the samples of dissolved mercury (DHg) each water sample is filtrated three times through a 0.45μm filter to get rid of the particles. The samples of total particular mercury (THg) do not need to be filtrated; instead they are poured straight into the bottles. All samples are then heated in the oven at 60°C during 24 h. After that the samples can be analysed otherwise they are stored in the fridge. It is recommended that the samples should not be kept in the fridge for longer than a month before it is analysed or the accuracy of the result might drop.

3.2.1. Analysis of water samples

The samples are prepared for analysis by adding chemicals in form of stannous chloride (SnCl₂), bromine monochloride (BrCl) and hydroxylamine hydrochloride (NH₂OH∙HCl). To preserve the samples BrCl are added to the samples in order to prevent evaporation of mercury, 0.5 mL BrCl solution is added to every 100 mL of sample.

Before the analysis hydroxylamine hydrochloride (NH₂OH∙HCl) is added to remove residual of bromine and chlorine, this step makes the mercury available to be released. The sample is then processed through a bubbler and stannous chloride (SnCl₂) is added to transform the ionic mercury, Hg²⁺, to elemental mercury, Hg⁰. To transport the mercury a carrier gas of nitrogen is used with a flow of 0.4mL/min and the gaseous elemental mercury is collected in gold sand tubes (figure 9).

![Figure 9. Equipment utilised for the analysis of wet deposition.](image)

The gold sand tubes are then analysed by the AFS, utilising the same method as for the dry deposition (figure 10).
Figure 10. The figure to the left displays the experimental setup for the analysis of wet deposition, with three bubblers in the middle and the gold sand tubes to the far left. The tubes are then analysed in the AFS, figure to the right, in order to obtain the amount of mercury in the water samples.

The analysis with the AFS will follow the same procedure as the analysis of dry deposition. After the three samples have been analysed in the AFS, a mean value of the IF will be calculated which is utilised to determine the mass and concentration of mercury in the sample.

3.2.2. Standard curve for wet deposition
In order to determine the mass and concentration of mercury in the water samples, a standard curve for wet deposition is required. The standard curve is generated by analysing solutions with known concentration of mercury. The correlation between the mass of mercury in the solution and the resulting IF-value can then be determined.

The same setup as in the figure 8 is used to execute the standard curve for wet deposition. The solution in the bubblers is though different, instead of rainwater the three bubblers will now be filled with 50 mL MQ-water each. The experiment will then be done for several different concentrations of standard mercury solution, starting with one blank where there is no concentration of mercury.

3.3. Meteorological data
In order to analyse the result of the dry deposition meteorological data and data from the dry deposition is combined. Four different meteorological factors are utilised including wind velocity, temperature, solar radiation and relative humidity. The parameters are used to estimate a model of the backward trajectory of mercury emissions utilising a NOAA HYSLPIT model.
4. Results
The results of dry and wet deposition of mercury in Xiamen area will be presented below. Also presented are NOAA HYSLPIT models of the backward trajectory of mercury emissions.

4.1. Dry deposition
The measured results of dry deposition, in form of gaseous elemental mercury and total particulate mercury are presented in the section below.

4.1.1. Standard curve for dry deposition
The results from the measurements of mercury for the standard curve can be seen in table 1.

Table 1. Data utilised to create the standard curve for dry deposition.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Volume (μL)</th>
<th>Mass (μg)</th>
<th>IF</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.5</td>
<td>10</td>
<td>0.224</td>
<td>9.7</td>
</tr>
<tr>
<td>26.5</td>
<td>20</td>
<td>0.447</td>
<td>25.7</td>
</tr>
<tr>
<td>26.1</td>
<td>40</td>
<td>0.867</td>
<td>49.8</td>
</tr>
<tr>
<td>26.5</td>
<td>80</td>
<td>1.790</td>
<td>121.5</td>
</tr>
<tr>
<td>26.7</td>
<td>100</td>
<td>2.273</td>
<td>197.2</td>
</tr>
<tr>
<td>26.6</td>
<td>200</td>
<td>4.510</td>
<td>387.9</td>
</tr>
<tr>
<td>26.1</td>
<td>300</td>
<td>6.501</td>
<td>518.2</td>
</tr>
<tr>
<td>25.6</td>
<td>400</td>
<td>8.327</td>
<td>642.2</td>
</tr>
</tbody>
</table>

To create the standard curve the mass and resulting IF-value is utilised, figure 10. The curve is then used to compare samples taken in field with samples of pure mercury with known mass.

Figure 11. Standard curve of dry deposition, with the IF-value depending on the mass of mercury.
Linear regression of the measured points is utilised in order to create the standard curve and resulting equation presented below.

\[ IF = 80.268m - 6.2014 \]

Where IF is the y-value in figure 10, i.e. the IF-values of the samples measured with the AFS. \( m \) is the mass of mercury, seen as x in the figure. The equation can be rewritten in order to calculate the mass of mercury, \( m \), for a specific IF-value.

\[ m = \frac{IF + 6.2014}{80.268} \]

Then the corresponding concentration of mercury in the sample can be calculated, utilising the following equation:

\[ c = \frac{m}{V} \]

Where \( c \) is the concentration of mercury in the air, \( m \) is the calculated mass of mercury in the sample and \( V \) is the volume of air that was used for the sampling.

4.1.2. Experimental data

In table 2 the experimental data of dry deposition is displayed and an entire table can be found in appendix 1.

Table 2. Experimental data of dry deposition including the concentration of the mercury species GEM and TPM.

<table>
<thead>
<tr>
<th>Date</th>
<th>Day or night</th>
<th>Hg species:</th>
<th>Volume (L):</th>
<th>IF-value:</th>
<th>Mass of Hg (ng):</th>
<th>Conc. of Hg (ng/L):</th>
</tr>
</thead>
<tbody>
<tr>
<td>2012-06-26</td>
<td>Day</td>
<td>GEM</td>
<td>0.224</td>
<td>874,7</td>
<td>10,97</td>
<td>49,03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TPM</td>
<td>7927,4</td>
<td>1001,5</td>
<td>12,55</td>
<td>0,00158</td>
</tr>
<tr>
<td></td>
<td>Night</td>
<td>GEM</td>
<td>0,390</td>
<td>158,9</td>
<td>2,06</td>
<td>5,28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TPM</td>
<td>16233,3</td>
<td>4352,1</td>
<td>54,30</td>
<td>0,00334</td>
</tr>
<tr>
<td>2012-06-29</td>
<td>Day</td>
<td>GEM</td>
<td>0,210</td>
<td>178,8</td>
<td>2,30</td>
<td>10,97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TPM</td>
<td>8265,4</td>
<td>1861,7</td>
<td>23,27</td>
<td>0,00282</td>
</tr>
<tr>
<td></td>
<td>Night</td>
<td>GEM</td>
<td>0,427</td>
<td>209,6</td>
<td>2,69</td>
<td>6,29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TPM</td>
<td>15825</td>
<td>2564,2</td>
<td>32,02</td>
<td>0,00202</td>
</tr>
<tr>
<td>2012-07-02</td>
<td>Day</td>
<td>GEM</td>
<td>0,218</td>
<td>240,7</td>
<td>3,08</td>
<td>14,09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TPM</td>
<td>7279,4</td>
<td>2053,5</td>
<td>25,66</td>
<td>0,00353</td>
</tr>
<tr>
<td></td>
<td>Night</td>
<td>GEM</td>
<td>0,403</td>
<td>179,4</td>
<td>2,31</td>
<td>5,74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TPM</td>
<td>16781,7</td>
<td>1596,1</td>
<td>19,96</td>
<td>0,00119</td>
</tr>
<tr>
<td>2012-07-05</td>
<td>Day</td>
<td>GEM</td>
<td>0,493</td>
<td>67,4</td>
<td>0,92</td>
<td>1,86</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TPM</td>
<td>7733,9</td>
<td>4447,4</td>
<td>55,48</td>
<td>0,00717</td>
</tr>
<tr>
<td></td>
<td>Night</td>
<td>GEM</td>
<td>0,514</td>
<td>837,2</td>
<td>10,50</td>
<td>20,42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TPM</td>
<td>15589,2</td>
<td>637,2</td>
<td>8,02</td>
<td>0,00051</td>
</tr>
</tbody>
</table>
As can be seen in table 2 the concentration of gaseous elemental mercury (GEM) varies between 1.86 and 49.03 ng/L. The measured concentration of total particulate mercury (TPM) has a range from 0.00051 to 0.00717 ng/L.

In table 3 the day-time concentration of GEM and TPM is presented for each sampling date.

Table 3. Day-time concentration of GEM and TPM.

<table>
<thead>
<tr>
<th>Sampling date</th>
<th>Concentration of GEM (ng/L)</th>
<th>Concentration of TPM (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2012-06-26</td>
<td>49.0298</td>
<td>0.00158</td>
</tr>
<tr>
<td>2012-06-29</td>
<td>10.9732</td>
<td>0.00282</td>
</tr>
<tr>
<td>2012-07-02</td>
<td>14.0852</td>
<td>0.00353</td>
</tr>
<tr>
<td>2012-07-05</td>
<td>1.8598</td>
<td>0.00717</td>
</tr>
</tbody>
</table>

The highest value of GEM was measured on the 26th of June and the highest concentration of TPM was recorded on the 5th of July.

In figure 11 the day-time concentration of GEM and TPM is presented. It should be noted that the concentration differs between the two mercury species as the concentration of GEM is in ng/L while the concentration of TPM is in pg/L.

![Day-time concentration of GEM and TPM](image.png)

Figure 12. Day-time concentration of GEM and TPM during the sampling period.

The difference in concentration of GEM during day and night is presented in table 4 and figure 12.
Table 4. Concentration of GEM in the air samples during day and night.

<table>
<thead>
<tr>
<th>Sampling date</th>
<th>Concentration of GEM during day (ng/L)</th>
<th>Concentration of GEM during night (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2012-06-26</td>
<td>49,0298</td>
<td>5,2795</td>
</tr>
<tr>
<td>2012-06-29</td>
<td>10,9732</td>
<td>6,2922</td>
</tr>
<tr>
<td>2012-07-02</td>
<td>14,0852</td>
<td>5,7411</td>
</tr>
<tr>
<td>2012-07-05</td>
<td>1,8598</td>
<td>20,4247</td>
</tr>
</tbody>
</table>

The concentration of gaseous elemental mercury is higher during the day-time than the night, except for the samples recorded on the 5th of July. The value is very high and might be out of range. The highest concentration of GEM is detected in the sample from the 26th of June, the concentration is almost 50ng/L which is much higher than the average.

The difference between the concentration of total particulate mercury, TPM, during day and night is presented in table 5 and figure 13 below.

Table 5. Concentration of TPM in the air samples during day and night.

<table>
<thead>
<tr>
<th>Sampling date</th>
<th>Concentration of TPM during day (pg/L)</th>
<th>Concentration of TPM during night (pg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2012-06-26</td>
<td>1.58</td>
<td>3.34</td>
</tr>
<tr>
<td>2012-06-29</td>
<td>2.82</td>
<td>2.02</td>
</tr>
<tr>
<td>2012-07-02</td>
<td>3.53</td>
<td>1.19</td>
</tr>
<tr>
<td>2012-07-05</td>
<td>7.17</td>
<td>0.51</td>
</tr>
</tbody>
</table>
The highest concentration of the day-time sampling was recorded on the 5\textsuperscript{th} of July, while the highest night-time sample was recorded on the 26\textsuperscript{th} of June. Out of the four sampling dates the concentration of TPM was higher during the day-time, accept for the samples recorded on the 26\textsuperscript{th} of June.

4.2. Backward trajectory of mercury emissions
According to the result of the dry deposition there was a peak in the gaseous elemental mercury at the 26\textsuperscript{th} of July and a peak of total particulate mercury on the 5\textsuperscript{th} of July. In order to estimate the source of the mercury emission a NOAA HYSPLIT model is generated. The model uses the data of dry deposition and metrological parameters to generate backward trajectories of the sources of mercury emissions.

In figure 15 a backward trajectory of the mercury emission which was detected as an increase in the concentration of gaseous elemental mercury in Xiamen on the 26\textsuperscript{th} of June. The lines indicates the most likely path of the pollutant, the colours red, blue and green represents the flow of air at 500, 1000 and 2000 meters above ground level.
Figure 15. Backward trajectory of mercury emission on the 26th of June.

According to the model the source of emission is located in Cambodia.

In figure 16 a backward trajectory of the mercury emission which was detected as an increase in the total particulate mercury in Xiamen on the 5th of June. The lines indicates the most likely path of the pollutant, the colours red, blue and green represents the flow of air at 500, 1000 and 2000 meters above ground level.
4.3. Analysis of wet deposition

In the section below the results of the analysis of wet deposition is presented, including the mercury species total mercury (THg) and dissolved mercury (DHg).

4.3.1. Standard curve for wet deposition

The standard curve of wet deposition is created by utilising the experimental setup in figure 8. The IF-values of the three tubes are recorded and an average IF-value is calculated for each mass of mercury. The results from the measurements of the standard curve from the 28th of June can be seen in table 6 below. The numbers in brackets differs from the average value and are not included in the calculations of the standard curve.

Table 6. Measurements utilised to create the standard curve of wet deposition, recorded on the 28th of June.

<table>
<thead>
<tr>
<th>Mass</th>
<th>Blanks</th>
<th>0.25</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>IF1</td>
<td>7.4</td>
<td>52.5</td>
<td>74.6</td>
<td>129.6</td>
<td>229.7</td>
<td>468.1</td>
</tr>
<tr>
<td>IF2</td>
<td>12.4</td>
<td>55.5</td>
<td>95.2</td>
<td>158.6</td>
<td>193.5</td>
<td>407.1</td>
</tr>
<tr>
<td>IF3</td>
<td>7.0</td>
<td>34.8</td>
<td>(142.0)</td>
<td>146.1</td>
<td>193.6</td>
<td>(250.7)</td>
</tr>
<tr>
<td>Average</td>
<td>8.9</td>
<td>47.6</td>
<td>84.9</td>
<td>144.8</td>
<td>205.6</td>
<td>437.6</td>
</tr>
</tbody>
</table>
The standard curve of wet deposition is presented in figure 14.

![Standard curve for wet deposition](image)

Figure 17. Standard curve for wet deposition, created on the 28th of June.

### 4.3.2. Analysis of water samples from sampling sites around Xiamen University

The water samples collected on sampling sites around the campus of Xiamen University was analysed on the 28th of June. The analysis included measurements of dissolved mercury (DHg) and total mercury (THg), the results is presented in table 7 and 8.

#### Table 7. Concentration of dissolved mercury (DHg) in water samples collected from four sampling sites around Xiamen University.

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Average IF-value</th>
<th>Mass (ng)</th>
<th>Concentration of DHg (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furong Lake</td>
<td>91.8</td>
<td>0.677</td>
<td>13.5</td>
</tr>
<tr>
<td>White Beach</td>
<td>80.0</td>
<td>0.562</td>
<td>11.2</td>
</tr>
<tr>
<td>Reservoir</td>
<td>130.6</td>
<td>1.055</td>
<td>21.1</td>
</tr>
<tr>
<td>Sewage pool</td>
<td>71.1</td>
<td>0.475</td>
<td>9.5</td>
</tr>
</tbody>
</table>

#### Table 8. Concentration of total mercury (THg) in water samples collected from four sampling sites around Xiamen University.

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Average IF-value</th>
<th>Mass (ng)</th>
<th>Concentration of THg (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furong Lake</td>
<td>93.8</td>
<td>0.697</td>
<td>13.9</td>
</tr>
<tr>
<td>White Beach</td>
<td>101.8</td>
<td>0.774</td>
<td>15.5</td>
</tr>
<tr>
<td>Reservoir</td>
<td>96.8</td>
<td>0.726</td>
<td>14.5</td>
</tr>
<tr>
<td>Sewage pool</td>
<td>326.1</td>
<td>2.959</td>
<td>59.2</td>
</tr>
</tbody>
</table>
The concentration of total and dissolved mercury is compared in order to determine the amount of particulate mercury in the water samples (figure 15).

![Figure 15. Concentration of total mercury (THg) and dissolved mercury (DHg) in water samples collected from four sampling sites around Xiamen University.](image)

The water at the sampling sites at Furong Lake, White Beach and the reservoir contain almost no particulate mercury as the concentration of total mercury and dissolved mercury is similar. The water sample from the sewage pool contains a large amount of total particulate mercury, as the concentration of dissolved mercury only is 10 ng/L while the concentration of total mercury is around 60 ng/L.

**4.3.3. Analysis of rainwater samples**

Rainwater samples from four different sampling sites in Xiamen Area is analysed and the results is presented in table 9.

![Table 9. Concentration of total mercury (THg) and dissolved mercury (DHg) in rainwater samples collected from four sampling sites in Xiamen Area.](image)
The highest concentration of total and dissolved mercury, 78.1 ng/L resp. 46.9 ng/L, was recorded on Gulang Island the 20th of May. The value of the lowest concentration of both total and dissolved mercury was measured at the sampling site in Xiao Ping on the 16th of May, the concentration of total mercury was 5.3 ng/L while the concentration of dissolved mercury was 10.1 ng/L.

There should be noted that some of the measured concentrations might be inaccurate as the concentration of dissolved mercury is higher than the concentration of total mercury.

The concentration of total mercury is compared between each sampling date, the result is displayed in figure 17.

![Concentration of Total mercury](image)

Figure 19. The concentration of total mercury in the rainwater samples.
The highest concentrations of total mercury are measured from rainwater samples collected at Gulang Island. On the 28th of May there is also high concentration in the sample from Hongwen. The lowest concentrations are measured in the samples from Xiao Ping.

The concentration of dissolved mercury is also compared for the different rainwater samples; the result is presented in figure 18.

![Concentration of Dissolved Mercury](image)

**Figure 20. The concentration of dissolved mercury in the rainwater samples.**

The highest concentration of dissolved mercury is above 45ng/L and was recorded at Gulang Island on the 20th of May. The lowest concentration is approximately 10ng/L and was measured in the samples from Xiao Ping on the 16th of May.

The measured results of each sampling site is presented below in order to estimate if there is a trend in the mercury concentration during the sampling period.

The concentrations of total and dissolved mercury in the three water samples collected at Xiao Ping is presented in figure 21.
Figure 21. Concentration of total and dissolved mercury in rainwater samples from Xiao Ping.

The concentration of total mercury was around 5ng/L at the beginning of the sampling period, while it increased during the two later sampling dates. The measured concentration of dissolved mercury is higher than the concentration of total mercury during the entire period, the result might indicate inaccuracy in the analysis.

The concentration of mercury species in the three rainwater samples from Bantou sampling site is presented in figure 22.

Figure 22. Concentration of total and dissolved mercury in rainwater samples from Bantou.
The concentration of total mercury in the rainwater samples at Bantou is quite stable over the sampling period, the concentration is around 30 ng/L. Whilst the concentration of dissolved mercury vary between 15 and 35 ng/L.

The concentration of total mercury and dissolved mercury for the five rainwater samples collected at the sampling site at Gulang Island is presented in figure 23.

![Concentration of mercury in rainwater at Gulang Island](image)

**Figure 23.** Concentration of total and dissolved mercury in rainwater samples from Gulang Island.

The concentration of both total and dissolved mercury varies over the period, the lowest notation is around 10 ng/L while the highest is almost 80 ng/L. The amount of particulate mercury in the rainwater samples is higher than at the other sampling sites, as the total mercury is higher than the dissolved mercury at every date except for the samples collected the 18th of May.

The concentration of total and dissolved mercury in the samples from Hongwen sampling site is presented in figure 24. There should be noted that the measurements only includes two sampling dates.
Figure 24. Concentration of total and dissolved mercury in rainwater samples from Hongwen.

The concentrations at the first sampling date, the 18th of May, seems to be inaccurate as the concentration of total mercury is lower than that of dissolved mercury. The concentration of dissolved mercury is just below 30 ng/L at both sampling dates. The concentration of total mercury varies between 20 ng/L at the first sampling date to almost 60ng/L for the second.
5. Discussion

The analysis of both wet and dry deposition is based on a standard curve of mercury. The procedure to complete a standard curve is both difficult and time consuming. For dry deposition the process of completing a standard curve included many crucial steps. The hardest part was to inject the right amount of mercury into the injection point, the injection must be done very carefully. Another crucial step was the withdrawal of mercury from the jar, for example if the procedure was done too quickly the concentration in the needle could get lower than the real concentration in the jar. For wet deposition there were some difficulties to achieve a blank sample at the beginning of the analysis, this might have affected the succeeding analysis.

According to the analysis of dry deposition the concentration of gaseous elemental mercury varies between 2 and 15 ng/L. There was a peak in the concentration at the 26th of June, where the measured concentration was 49 ng/L. One explanation might be that the sampling was conducted after a rainfall. The rain will transport mercury to the ground and it will later be released as the soil is dried. There are also dry bubbles of air in the soil that contain mercury. During a rainfall the holes is filled with water and the mercury from the air bubble is released. The rainfall will also affect the concentration of total particulate mercury in the air. The concentration is usually much lower as the water will carry the particle bound mercury to the ground. There is also a peak in the concentration of GEM during the night of the 5th of July. The source of the high value might be contamination in the sample.

The amount of total particulate mercury ranged between 1 and 3pg/L during the period of time. A peak with a concentration of 7 pg/L was detected on the 5th of July.

When comparing the concentration during the day- and night-time, the concentration was higher during the day for both gaseous elemental mercury and total particulate mercury. These results do not agree with the literature, which states that the concentration of mercury should be higher in night-time rather than day-time. One explanation to the result might be that there was some rainfall during three occasions of the night-time sampling. That might have an impact of the concentration of total particulate mercury as the rain will carry particular bound mercury to the ground. Another reason to the high concentrations of mercury might be emissions of mercury from the Ocean building were the sampling are conducted. The research at the laboratories might include mercury and the experiments are often conducted during day-time.

Considering the analysis of dry deposition the measurements was limited to only four samples and therefore the data is not sufficient to detect any trends.

The analysis of wet deposition of mercury illustrated that the concentration of both total mercury and dissolved mercury differed between the sampling sites. The highest concentrations was detected in the samples from Gulang Island and the lowest from Xiao Ping. According to the information about the sampling sites Xiao Ping is a back ground sampling site for other pollutants, while Gulang Island is exposed to mercury emissions from power plants. The highest level of total mercury was measured the 20th of May on Gulang Island.
Island and the concentration was almost 80 ng/L, 15 times higher than the lowest concentration at Xiao Ping.

The analysis of the water samples collected near the campus of Xiamen University showed that there was a high amount of particulate mercury in the samples from the sewage pool. The other sites did not contain any high amounts of particulate mercury. The concentration of total and dissolved mercury ranged between 10 and 20 ng/L at the sites, except for the sewage pool where the concentration of total mercury was 60 ng/L with only 10 ng/L of dissolved mercury.

From the results of the analysis of wet deposition it is hard to draw any conclusion about the trend of the concentration of mercury.

5.1. Limitations
The time of the project is limited to one month, therefore the data available for analysis is limited. If the project was conducted during a longer period of time more data would be available for analysis, which would give more reliable results.

It should be taken into consideration that some of the rain water samples had been stored for more than a month. Hence the accuracy in the detection will be lower and the results can not be considered totally reliable.

It is difficult to draw any certain conclusions of the analysis of dry deposition as the data is limited, a suggestion is to install other measurement points in order to obtain more information.

5.2. Sources of error
A source of error might be contamination of the samples and equipment, since the procedure of analysis is very sensitive even small sources of contamination makes a difference. As mentioned before were some of the rainwater samples detected more than a month after sampling, therefore the accuracy of the results might be lower.
6. Conclusion

From the results of this project it can be seen that the concentration of mercury species in dry deposition differed. The concentration of gaseous elemental mercury was much higher than the concentration of total particulate mercury. The concentrations of both GEM and TPM are too high to be considered as only background concentrations.

During the sampling date when a peak in the concentration was detected there might have been the result of a mercury emission. It is hard to tell if the concentration is high because there has been something wrong with the sampling and measuring or if it caused by mercury pollution.

Due to the limited time it is hard to draw any conclusion about the results of wet deposition.
7. Acknowledgement

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## Appendix 1. Data of dry deposition

<table>
<thead>
<tr>
<th>Date:</th>
<th>Day or night:</th>
<th>Hg species:</th>
<th>Flow rate (mL/min for GEM and m³/h for TPM):</th>
<th>Time (min):</th>
<th>Volume (L):</th>
<th>IF-value:</th>
<th>Mass of Hg (ng):</th>
<th>Conc. of Hg (ng/L):</th>
</tr>
</thead>
<tbody>
<tr>
<td>2012-06-26</td>
<td>Day</td>
<td>GEM 0,5</td>
<td>447,666667</td>
<td>874,7</td>
<td>10,97450292</td>
<td>49,02979709</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TPM 1,0625</td>
<td>447,666667</td>
<td>1001,5</td>
<td>12,55421089</td>
<td>0,001583642</td>
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</tr>
<tr>
<td></td>
<td>Night</td>
<td>GEM 0,4</td>
<td>974</td>
<td>158,9</td>
<td>2,056876962</td>
<td>5,279458322</td>
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