Mercury Flow in the Wastes Stream of China

Qingru WU
Tsinghua University

Oct 15, 2020
Atmospheric Hg emissions have shown a downward trend in China.

Improved air Hg emission control led to the increase of Hg burden in the waste.
How much of Hg in solid wastes is re-emitted?

Hg would be reemitted to air or released to water/soil during the disposal of those waste/byproduct from air pollution control devices.

Wu et al., ES&T, 2015
Research scope of this study

- To examine the Hg sources and fate in China
- To examine the flow of mercury within and among 8 sectors (31 subsectors)

<table>
<thead>
<tr>
<th>Fuel consumption</th>
<th>Incineration and interment</th>
<th>Municipal solid wastes incineration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal-fired power plants</td>
<td>Coal-fired industrial boilers</td>
<td>Biomass combustion</td>
</tr>
<tr>
<td>Residential coal combustion</td>
<td>Other coal combustion</td>
<td>Interment</td>
</tr>
<tr>
<td>Natural gas combustion</td>
<td>Oil refining</td>
<td>Mercuric chloride catalyst production</td>
</tr>
<tr>
<td>Oil combustion</td>
<td>Production activities using Hg</td>
<td>Vinyl chloride monomer (VCM) production</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Building materials production</th>
<th>Thermometer production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron and steel smelting</td>
<td>Sphygmomanometer production</td>
</tr>
<tr>
<td>Cement production</td>
<td>Fluorescent lamp production</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nonferrous metal smelting</th>
<th>Battery production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper smelting</td>
<td>Dental amalgam production</td>
</tr>
<tr>
<td>Lead smelting</td>
<td>Use of thermometer</td>
</tr>
<tr>
<td>Zinc smelting</td>
<td>Use of sphygmomanometer</td>
</tr>
<tr>
<td>Industrial gold smelting</td>
<td>Use of fluorescent lamp</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hg recovery</th>
<th>Use of Hg-added products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg production from recyclable resources</td>
<td>Use of battery</td>
</tr>
<tr>
<td>Primary Hg ore mining</td>
<td>Primary Hg ore mining</td>
</tr>
<tr>
<td>Aluminum smelting</td>
<td></td>
</tr>
</tbody>
</table>
Conceptual framework of mercury flow analysis

Hui et al., ES&T, 2017

Hg concentration in raw materials → Hg needed to produce unitary product → Consumption of fuels/raw materials → Yield of products

Hg input factors → Activity levels

Tier 1 → Hg input

Tier 2

Air → Water → Land → Stabilization → Liquid wastes/byproducts → Solid wastes/byproducts

Tier 3

Air → Water → Land → Stabilization → Stocks → Exports → Recycling
Mercury is inputted embedded in raw materials or as pure Hg.

Hg input (Tier 1) and distribution (Tier 2)

Hg input \( \times \) Activity level \( \times \) Hg input factor

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Sample number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw coal</td>
<td>494</td>
</tr>
<tr>
<td>Zinc concentrate</td>
<td>381</td>
</tr>
<tr>
<td>Lead concentrate</td>
<td>198</td>
</tr>
<tr>
<td>Copper concentrate</td>
<td>207</td>
</tr>
<tr>
<td>Gold concentrate</td>
<td>26</td>
</tr>
<tr>
<td>Limestone</td>
<td>167</td>
</tr>
<tr>
<td>Iron concentrate</td>
<td>73</td>
</tr>
</tbody>
</table>

Hg distribution factor are determined by the Hg removal efficiency of air pollution control devices, which are obtained from field measurements.

\[
\begin{align*}
df_{\text{bottom ash}} &= 1 - R \\
\text{df}_{\text{fly ash}} &= R \times (1 - \eta_{\text{SCR+ESP}}) \\
\text{df}_{\text{waste water}} &= R \times (1 - \eta_{\text{SCR+ESP}}) \times \eta_{\text{FGD}} \times a \\
\text{df}_{\text{gypsum}} &= R \times (1 - \eta_{\text{SCR+ESP}}) \times \eta_{\text{FGD}} \times (1 - a) \\
\text{df}_{\text{flue gas}} &= R \times (1 - \eta_{\text{SCR+ESP}}) \times (1 - \eta_{\text{FGD}})
\end{align*}
\]

\( R \) released rate of PC boiler; \( \eta_{\text{SCR+ESP}} \) mercury removal efficiency of SCR and ESP; \( \eta_{\text{FGD}} \) mercury removal efficiency of FGD; \( a \) the proportion of mercury to waste water

National concentrates sampling sites

Number of samples
Tier 3: Wastes & byproducts

- How wastes were disposed?
- How was Hg re-distributed during different types of waste disposal processes?
Wastes disposal

Over half industrial wastes are re-used or land-filled.

Disposal of industry wastes

- Metallurgical industry
- Energy industry
- Petrochemical industry
- Mining industry
- Light industry
- Other industry

Hazardous wastes

National List of Hazardous Wastes

Municipal wastes

- Land
- Cement clinker
- Fly ash bricks
- Commodity concrete
- Building roads
- Mineral substances
- Used in agriculture

Wastes
Wastes disposal

Wastes
- Municipal wastes
- Industrial wastes
- Hazardous wastes

Hazardous wastes

National List of Hazardous Wastes

Disposal of hazardous wastes

Unit: 10kt

- Stock
- Disposal
- Reuse
- Production

2010 2011 2012 2013 2014

Stock
Disposal
Reuse
Production

2010 2011 2012 2013 2014

Metallurgical industry
Energy industry
Petrochemical industry
Mining industry
Light industry
Other industry
Wastes disposal

Industrial wastes
- Metallurgical industry
- Energy industry
- Petrochemical industry
- Mining industry
- Light industry
- Other industry

Wastes
- Municipal wastes
- Hazardous wastes

Hazardous wastes
- National List of Hazardous Wastes

Wastes disposal

1) Poor landfill site: Significant environmental pollution
2) Controlled landfill site: Problems on seepage, leachate treatment, daily cover
3) Advanced landfill site: Standard landfill site, accounting for more than 20%.

Graphical representation:
- Landfill
- Compost
- Incineration


Data:
- 2006: 81.8% Landfill, 3.7% Compost, 14.5% Incineration
- 2007: 81.9% Landfill, 2.7% Compost, 15.4% Incineration
- 2008: 82.9% Landfill, 1.7% Compost, 15.4% Incineration
- 2009: 80.2% Landfill, 1.6% Compost, 18.2% Incineration
- 2010: 79.4% Landfill, 1.5% Compost, 19.2% Incineration
- 2011: 76.9% Landfill, 3.3% Compost, 19.9% Incineration
- 2012: 72.6% Landfill, 2.7% Compost, 24.7% Incineration
Final fates of Hg consist of six categories:

- **Hg emissions to air, releases to water, and releases to land**
  Hg emissions releases in this study do not consider Hg transportation across different environmental media through biogeochemical cycling.

- **Hg exports**
  The term “export” indicates Hg exported abroad by embedding in Hg-containing products

- **Hg stabilization**
  The term “stabilization” means that Hg is properly treated in an environmental sound manner.

- **Hg stocks**
  The term “stock” implies that Hg is stored in wastes and byproducts due to the delay of sales or disposal (more than 1 year). Wastes and products containing Hg are generally sealed-stored. Thus, they are regarded to have few environmental impacts during the storage period. However, once these wastes and products are reused, the embedded Hg will re-enter production activities and cause potential environmental impacts.

Hg re-distribution factors are calculated by identifying the utilization/disposal method of wastes/byproducts and Hg distribution during different utilization/disposal process.

\[
r - RE_{l,q} = \sum_h RM_l \times \alpha_l \times \beta_h \times \theta_{q\times1,l,h}
\]

- The notation \( r - RE_{l,q} \) indicates Hg re-distribution from waste/byproduct \( l \) to fate \( q \).
- \( RM_l \) stands for Hg embedded in byproduct \( l \).
- \( \alpha_l \) is the utilization rate of waste/byproduct \( l \).
- \( \beta_h \) is the application proportion of treatment process \( h \).
- \( \theta_{q\times1,l,h} \) is a column vector, whose element \( \theta_{q\times1,l,h} \) represents the distribution factor from waste/byproduct \( l \) to fate \( q \) during the treatment process \( h \).
Re-distribution of Hg in fly ash disposal processes for example

Hg re-distribution during utilization of fly ash

1) Producing cement clinker  5% stabilized; 95% emitted to air
2) Producing fly ash bricks  7%-40% emitted to air; the rest stabilized
3) Producing commodity concrete  100% stabilized
4) Building roads  100% stabilized
5) Producing mineral substances  5% released to water;  the rest released to land as wastewater treatment residues
6) Used in agriculture  100% released to land

Hg re-distribution factors for fly ash utilization/disposal

<table>
<thead>
<tr>
<th>Fate</th>
<th>Air</th>
<th>Water</th>
<th>Land</th>
<th>Stabilization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg re-distribution factor, %</td>
<td>30.0</td>
<td>0.1</td>
<td>38.0</td>
<td>31.9</td>
</tr>
</tbody>
</table>
**Hg flows in China**

- **Hg input**: overall situation of motive Hg in China’s anthropogenic activities. Clean energy or scrap metals substitution; use of recycled Hg; reducing the production and use of Hg-added products.

- **Emission and Release**: Direct environmental impact; 51.8% end-of-pipe Hg control; increasing controlled landfills and strengthening solid waste recycling.

- **Safely disposed**: 15.8%

- **Stock**: Potential environmental impact, depending on the disposal/utilization methods.
Atmospheric Hg emissions

- Fuel consumption: 35.7%
- Building materials production: 16.11%
- Nonferrous metal smelting: 4.42%
- Secondary emissions: 1.58%
- Incineration and interment: 1.58%
- Production activities using Hg: 0.32%
- Primary Hg mining: 0.32%
About 102 t of Hg is emitted due to the use of wastes/byproducts. Recovery of zinc oxide in zinc smelters and wastes disposal in cement plants contribute to 26% and 25% of total secondary atmospheric Hg emissions.

If solid wastes containing Hg are treated through high temperature, we should either remove Hg from solid wastes before the treatment or strengthen Hg reduction of APCDs for treatment procedures. This is especially important for solid wastes disposal in zinc smelting and cement plants.
Hg release to water and land

- **Water**
  - Nonferrous metal smelting: 49.40%
  - Use of Hg-added products: 31.33%
  - Fuel consumption: 13.25%
  - Production activities using Hg: 13.6%
  - Primary Hg mining: 1.20%

- **Land**
  - Nonferrous metal smelting: 34.31%
  - Fuel consumption: 17.93%
  - Production activities using Hg: 14.68%
  - Primary Hg mining: 12.83%
  - Use of Hg-added products: 5.41%
  - Incineration and interment: 1.08%
  - Hg recovery: 0.15%
<table>
<thead>
<tr>
<th>Subsectors</th>
<th>Hg stocks (t)</th>
<th>Waste/product types</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg recovery</td>
<td>374</td>
<td>Hg-containing catalysts, waste activated carbon</td>
</tr>
<tr>
<td>Zinc smelting</td>
<td>310</td>
<td>Waste acid sludge, waste water treatment sludge, calomel</td>
</tr>
<tr>
<td>Lead smelting</td>
<td>40</td>
<td>Waste acid sludge, waste water treatment sludge</td>
</tr>
<tr>
<td>Fluorescent lamp production</td>
<td>40</td>
<td>Fluorescent lamp</td>
</tr>
<tr>
<td>Copper smelting</td>
<td>18</td>
<td>Waste acid sludge, arsenic slag, waste water treatment sludge</td>
</tr>
<tr>
<td>Dental amalgam production</td>
<td>7</td>
<td>Dental amalgam</td>
</tr>
<tr>
<td>LGSP</td>
<td>7</td>
<td>Waste acid sludge, waste water treatment sludge, arsenic slag</td>
</tr>
</tbody>
</table>

- Wastes stored in the Hg recovery companies and zinc smelters can be used as Hg recovery materials.
- Utilization/disposal of these wastes in a environmental sound manner will reduce potential emissions/releases.
Challenges for Hg waste management

Around 651 t Hg released to land, which proposes environmental risks. Around 795 t Hg stored in the wastes, which proposes big challenge for waste treatment/disposal.

- Information gaps: No information system on the production, transfer, recycle, and disposal of Hg-containing waste.
- The system of waste sorting, collection and recycling is still in its infancy.
- Current comprehensive utilization of solid wastes can reduce Hg releases to land, but lead to Hg re-emissions to air.
- Limit values for mercury containing waste are not set. Technical guidelines on mercury waste management in environmentally sound manners not set.
References


Thank you for your attention!

qrwu@tsinghua.edu.cn