Lecture 7

TOXIC HEAVY METALS

http://www.theoldschoolhenstead.co.uk/Pupils/Mercurymetal/Mercury.htm

http://www.webelements.com
Heavy Metals

- Metallic elements that are denser than other common metals
- Mercury, lead, cadmium and arsenic (a semimetal) present the greatest environmental hazard - WHY?
  - Extensively used
  - Toxic
  - Widely distributed
- Ultimate sink for heavy metals are soils and sediments

### Heavy Metals - Densities

<table>
<thead>
<tr>
<th>Substance</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>13.5</td>
</tr>
<tr>
<td>Pb</td>
<td>11.3</td>
</tr>
<tr>
<td>Cu</td>
<td>9.0</td>
</tr>
<tr>
<td>Cd</td>
<td>8.7</td>
</tr>
<tr>
<td>Cr</td>
<td>7.2</td>
</tr>
<tr>
<td>Sn</td>
<td>5.8 – 7.3</td>
</tr>
<tr>
<td>As</td>
<td>5.8</td>
</tr>
<tr>
<td>Al</td>
<td>2.7</td>
</tr>
<tr>
<td>Mg</td>
<td>1.7</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.0</td>
</tr>
</tbody>
</table>

**Light metals**
Toxic Heavy Metals: Hg, Pb, Cd and As

Toxicity of the heavy metals:
- Of the four, Hg is highly toxic in the *elemental* form
  - Exposure through inhalation of Hg vapor from liquid Hg
- All four are *dangerous* in the following *form*:
  - Cations (e.g. from soluble compounds)
  - Organometallic (i.e. bonded to organic molecules)

Q. Why are they toxic?

Mechanism of heavy metal toxicity
- Due to strong affinity of metal cations \( (M^{n+}) \) for sulfur
  - Found in proteins (e.g. enzymes)
    - *Sulphydryl groups*, -SH, in many enzymes, react with ingested \( M^{n+} \)
    - Can deactivate the enzyme
      - => stops or alters metabolic processes
Drill: Write the balanced chemical reactions that correspond to the reaction of an Hg$^{2+}$ ion (a) with H$_2$S and (b) with R-SH (where R is an organic group) to produce hydrogen ions and an organometallic product.

*Is this what you got?*

\[
\begin{align*}
\text{Hg}^{2+} + 2 \text{H}_2\text{S} & \rightarrow \text{HS}^- \text{Hg}^- \text{SH} + 2\text{H}^+ \\
\text{Hg}^{2+} + 2 \text{RSH} & \rightarrow \text{RS}^- \text{Hg}^- \text{SR} + 2\text{H}^+
\end{align*}
\]

**Chelation Therapy: Treatment of Heavy Metal Poisoning**

- Utilizes a **chelating agent** that binds strongly to the metal cation

Ex. EDTA

[Diagram of EDTA molecule binding Mn$^{2+}$]

6 binding sites (orange) = *hexadentate*

Gk. “chela” = claw

Medical treatment

➢ Administers a compound that binds to the metal more strongly than does the enzyme. Ex. BAL

\[ \text{CH}_2 - \text{CH} - \text{CH}_2 \]
\[ \text{OH} \quad \text{SH} \quad \text{SH} \]
British Anti-Lewisite

Toxic Heavy Metals

(1) Mercury

Toxic forms:

➢ Elemental (Hg liquid/vapor), and
➢ Compounds of mercury
  ❖ Inorganic salts – ex. mercuric nitrate, Hg(NO\(_3\))_2
  ❖ Organometallic – ex. methylmercury

Mode of entry:

➢ Elemental Hg through inhalation
➢ Ingestion
➢ Transdermal: Hg (e.g. organomercury) can also enter the body by absorption through the skin
➢ Systemic: Once in the body, it is carried by the bloodstream to the brain
Toxic Heavy Metals: Mercury – Cont.

Effects of exposure:

Severity of health effects from mercury exposure depends on:
- the chemical form of mercury;
- the dose;
- the age of the person exposed (the fetus is the most susceptible);
- the duration of exposure;
- the route of exposure (inhalation, ingestion, dermal contact), and
- the health of the person exposed.

Effects of exposure:

(1) Elemental mercury effects
- Tremors;
- Emotional changes (e.g., mood swings, irritability, nervousness, etc.);
- Insomnia;
- Neuromuscular changes (such as weakness, muscle atrophy, twitching);
- Headaches;
- Disturbances in sensations; changes in nerve responses; performance deficits on tests of cognitive function.

At higher exposures there may be:
- Kidney damage,
- Respiratory failure, and
- Death
Toxic Heavy Metals: Mercury – Cont.

(2) Organomercury effects – Ex. Methylmercury

➢ Exposure in the womb (which can result from a mother’s consumption of fish and shellfish that contain methylmercury), can adversely affect a baby’s growing brain and nervous system.

➢ Impacts on cognitive thinking, memory, attention, language, and fine motor and visual spatial skills have been seen in children exposed to methylmercury in the womb.

Toxic Heavy Metals: Mercury – Cont.

(3) Inorganic mercury effects

High exposures to inorganic mercury may result in damage to:

- Gastrointestinal tract,
- Nervous system, and
- Kidneys

Mercury is the only common metal liquid at ordinary temperatures. Mercury is sometimes called \textit{quicksilver}. It rarely occurs free in nature and is found mainly in \textit{cinnabar ore} (HgS) in Spain and Italy. It is a heavy, silvery-white liquid metal. It alloys easily with many metals, such as gold, silver, and tin. These alloys are called \textit{amalgams}. Its ease in amalgamating with gold is made use of in the recovery of gold from its ores.

Image available at http://www.webelements.com

\textbf{History: Mercury}

- The first emperor of unified China, Qin Shi Huang, reportedly died of ingesting mercury pills that were intended to give him eternal life. \cite{43}

- The phrase \textit{mad as a hatter} is likely a reference to mercury poisoning, as mercury-based compounds were once used in the manufacture of felt hats in the 18th and 19th century. (The Mad Hatter character of Alice in Wonderland was almost certainly inspired by an eccentric furniture dealer, not by a victim of mad hatter disease.) \cite{44}

- In 1810, two British ships salvaged a large load of elemental mercury from a wrecked Spanish vessel near Cadiz, Spain. The bladders containing the mercury soon ruptured. The element spread about the ships in liquid and vapor forms. The sailors presented with neurologic compromises: \textit{tremor}, \textit{paralysis}, and \textit{excessive salivation} as well as \textit{tooth loss}, \textit{skin problems}, and \textit{pulmonary complaints}.

- For years Abraham Lincoln took a common medicine of his time called "blue mass" which contained significant amounts of mercury.
History: Mercury – Cont.

- The term **Hunter-Russell syndrome** derives from a study of mercury poisoning among workers in a seed packing factory in Norwich, England in the late 1930s who breathed methylmercury used as a seed disinfectant and preservative.[48]

- Outbreaks of methylmercury poisoning occurred in Minamata, Japan during the 1950s due to industrial discharges of mercury into the Minamata bay. More than 600 people died due to what became known as Minamata disease. In 22 documented cases, pregnant women who consumed contaminated fish showed mild or no symptoms but gave birth to infants with severe developmental disabilities.[2]

- Widespread mercury poisoning occurred in rural Iraq in 1971-1972, when grain treated with a methylmercury-based fungicide intended for planting only was used by the rural population to make bread, causing at least 459 deaths (see Basra poison grain disaster). [49]

History: Mercury – Cont.

- On August 14, 1996, Karen Wetterhahn, a Dartmouth College chemistry professor, spilled a small amount of dimethylmercury on her latex glove. She began experiencing the symptoms of mercury poisoning five months later and, despite aggressive chelation therapy, died a few months later from brain malfunction due to mercury intoxication. [24][25]

- On March 19, 2008, Tony Winnett, 55, inhaled mercury vapors while trying to extract gold from computer parts (by using liquid mercury to separate gold from the rest of the alloy), and died ten days later. [51][52]

- In December 2008, actor Jeremy Piven was diagnosed with hydrargyria resulting from eating sushi twice a day for twenty years. [53]

Mercury (Cont.)

Uses:

- \( \text{Hg}(l) \) in thermometers, barometers and sphygmomanometer
- \( \text{Hg}(g) \) is used in fluorescent bulbs and advertising signs
- The basis of dental amalgams and preparations
  (~ 50% Hg by mass plus other metals such as Ag, Sn and Cu)


**Mercury Sphygmomanometer**


Dental amalgam: Image available at
http://www.fda.gov/MedicalDevices/ProductsandMedicalProcedures/DentalProducts/DentalAmalgam/ucm171094.htm

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Mercury (Cont.)

When lamp is on, current flows through the electrical circuit to the electrodes. There is a considerable voltage across the electrodes, so electrons will migrate through the inert gas from one end of the tube to the other. This energy changes cause some of the mercury in the tube to vaporize. As electrons and charged atoms collide with the gaseous mercury atoms, the Hg atoms undergo electronic excitation. When the electrons return to their ground state, they release energy in the form of light.

Mercury (Cont.)

Sources of Hg contamination of the environment:
NOTE: Mercury is a naturally-occurring element and exists mainly as cinnabar ore (HgS).

- Burning of coal and fuel oil (electric utilities; industries)
  - Contains low levels of Hg
- Incineration of municipal waste that contain Hg
- Hg spills, e.g. from broken thermometers

Sources of Metallic Mercury Spills, New York HSEES
(1/1/92 to 12/31/97)

http://acc6.its.brooklyn.cuny.edu/~scintech/mercury/alternatives_main.htm
**Mercury (Cont.)**

Q. Are you familiar with the origin of the expression “mad as a hatter”?

- Mercuric nitrate (source of $\text{Hg}^{2+}$) was used in hat-making in the old days
  - Made the fur fibers soaked in this solution rough and twisted
    - Easily mat together

- Workers in hat industry constantly exposed to $\text{Hg}$ developed nervous disorder:
  - Muscle tremors
  - Depression, memory loss, irritability


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**Mercury (Cont.)**

**Methylmercury toxicity**

- Methylmercury = more toxic than $\text{Hg}^{2+}$
  - Soluble in fatty tissues of animals
    - Bioaccumulates
    - Biomagnifies
Toxic Heavy Metals

2) Lead

- Elemental form is not an environmental problem until it dissolves into Pb$^{2+}$ (or the less stable Pb$^{4+}$)

Mode of entry:
- Pb$^{2+}$: Usually through ingestion of contaminated water and food

Effects:
- Pb$^{2+}$ can inhibit the synthesis of hemoglobin
- Adverse effect on the nervous systems (CNS and peripheral) and the kidneys
- Interferes with the normal development of children’s brains
  - Behavioral effects, including lack of attentiveness
  - Possibly low IQ

Lead (Cont.)

Lead is a bluish-white lustrous metal. It is very soft, highly malleable, ductile, and a relatively poor conductor of electricity. Alloys include pewter and solder. Tetraethyl lead (PbEt$_4$) is still used in some grades of petrol (gasoline) but is being phased out on environmental grounds.

http://www.espimetals.com/
**Lead** (Cont.)

**Uses:**

- Storage batteries, cable covering, plumbing, ammunition or lead shots (Pb\(_s\)) and PbO

- Paints (*yellow* PbCrO\(_4\), white PbCO\(_3\*))
  - Pre-1978 homes used lead-based paints

- Solder

Image available at http://www.machinedesign.com/ASP/viewSelectedArticle.asp?strArticleId=56764&strSite=MDSite&catId=0

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**Lead** (Cont.)

**Sources of Pb contamination in the environment:**

- Lead industries, mining and smelting
  - Air and dust emissions (processing or smelting of lead ores)

- Vehicle emissions (in many countries)
  - The U.S., Canada and Europe use unleaded gasoline

- Piping, fixtures and solder
  - Common source of Pb\(^{2+}\) in drinking water

- Leaching from landfills (discarded batteries and other Pb-containing products)
Cadmium is a soft, bluish-white metal and is easily cut with a knife. It is similar in many respects to zinc. Cadmium and its compounds are highly toxic.

**Cadmium** (Cont.)

**Mode of entry:**
- Mostly through ingestion of contaminated food (in the form $\text{Cd}^{2+}$)
  - Seafood, organ meats have the highest levels among food

**Effects:**
- Cd is acutely toxic (lethal dose ~ 1 g)
  - Fortunately, low levels of Cd (as $\text{Cd}^{2+}$) is complexed by a sulfur-rich protein and is eliminated by urination
- Kidney disease may result from chronic exposure to high levels of Cd
  - Excess Cd (not complexed by proteins) is stored in the liver and kidneys
Cadmium (Cont.)

Uses:

- Rechargeable batteries (Nicad)
- Compounds of Cd are used as pigment
  - CdS and CdSe color plastics
- Also used in paints
- Also used in TV screens

Sources of Cd contamination in the environment:

- Metal smelters (In nature Cd occurs with Zn, Pb and Cu)
- Coal burning
- Incineration of Cd-containing waste (plastics, batteries, etc.)

Van Gogh’s “Sunflower” was painted with CdS pigment (Baird, C. “Environmental Chemistry, 2nd ed.”)

Toxic Heavy Metals

4) Arsenic

Historical perspective:

- Arsenic compounds (e.g. As₂O₃) used for murder and suicide from Roman times to Middle Ages

Elemental arsenic occurs in two solid modifications: yellow, and grey or metallic. The element is a steel grey, very brittle, crystalline, semimetallic (metalloid) solid. It tarnishes in air, and when heated rapidly oxidises to arsenous oxide which has a garlic odour. Arsenic and its compounds are poisonous as any reader of “who-done-it” books knows. www.webelements.com
**Arsenic** (Cont.)

**Mode of entry:**
- Mostly through ingestion of *contaminated water*
- As$_2$O$_3$ can be absorbed through the lungs and intestines

**Effects:**
- A known *carcinogen*
- Acute dose can be lethal
  - Causes gastrointestinal damage – severe vomiting; diarrhea
- Coagulates proteins and complexes with coenzymes
- Inhibits production of ATP

Note: As (III) is more toxic than As (V) – presumably due to stronger binding with S-containing proteins

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**Arsenic** (Cont.)

**Uses:**
- Pesticides (compounds of As) – prior to use of organic pesticides
- Hardening and improving the sphericity of shots
- Doping agent in solid-state devices such as transistors

**Sources of environmental contamination:**
- From the continued use of its compounds as pesticide (e.g. in CCA-treated wood)
- Unintended release during mining and smelting of gold, copper, etc.
- Lead and steel production
- Burning of coal (As is a contaminant)
Speciation and Toxicity of Metals

**Speciation** = chemical form of an element

- Affects toxicity of heavy metals

**Relative toxicity and speciation**

- **Methylmercury** > Hg\(_{(s)}\) (metallic; elemental)
- **Pb\(^{2+}\)** (soluble; ionic) > Pb\(_{(s)}\) (metallic; elemental)
- **As (III)**, like in arsenic oxide, As\(_2\)O\(_3\) > As (V), as in arsenic acid, HAsO\(_4\)

Chromium

Common oxidation states: **+3 and +6**

- **Trivalent, Cr\(^{3+}\)** (insoluble)
- **Hexavalent, Cr\(^{6+}\)** (soluble)

**Relative toxicities**

- **Cr\(^{6+}\)** or Cr (VI) (soluble, ionic) > **Cr\(^{3+}\)** or Cr (III) (insoluble)
- Ex. chromate ion, CrO\(_4^{2-}\); A suspected **carcinogen**
- Much less toxic than Cr (VI); Acts as a **trace element**
Chromium – Cont.

Uses of Chromium

- Electroplating
- Corrosion protection
- Leather tanning
  - Increases resistance to water, heat and bacteria
- Doping agent in solid-state devices such as transistors

Sources of contamination

- Industrial emissions (metal plating)
- Leaching from hazardous waste sites
- Leaching from CCA-treated wood (also a source of As contamination)
- Unintended release during mining and smelting of gold, copper and other metals

Major Contamination Problems with Heavy Metals

Mercury

- At the fishing village of Minamata, Japan (1950s)

Source of contamination:

- Hg-containing waste (PVC production) discharged into the bay
  - Bioconversion of Hg to methylmercury (more toxic form)
  - Bioaccumulated (moved up the food chain) at levels as high as 100 ppm in fish [vs. 0.5 ppm recommended limit of total Hg in fish in No. America] => Up to 200x higher!!

Results of contamination:

- Death: Hundreds; Thousand more suffer from various symptoms of Hg poisoning (numbness in the arms/legs, blurring or loss of vision, irritability, etc)
Mercury (Cont.)

- Methylmercury could be passed on to the fetus (can cause severe brain damage)
- READ p. 527, bottom paragraph for more information on Hg contamination

Dartmouth College (1997) cancer researcher Karen Wetterhahn

- Died several months after 1-2 drops of dimethylmercury apparently seeped through her latex gloves (recommended protection at that time)

Major Contamination Problems … (Cont.)

Lead

- The 1845 Franklin Expedition to find a Northwest Passage across the Arctic is thought to have failed because all the members died from Pb poisoning. How?
  - Source of contamination = solder in the tin cans that held their food
  - Read “The Age of Lead” paragraph on page 681.
**Cadmium**

- Acute environmental problem in the Jintsu River Valley region, Japan

**Source** of contamination:
- Contaminated (with Cd$^{2+}$) irrigation water drawn from the river, used for rice cultivation
- Zinc mining/smelting plant upstream = source of Cd$^{2+}$

**Results** of contamination
- Degenerative bone disease called *itai-itai* (“ouch-ouch”) in 100s of people
  - Severe pain in the joints
  - Resulted from Cd$^{2+}$ replacing Ca$^{2+}$ in the bones
    - Porous bones; Easily fractured

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**Arsenic** (a metalloid)

- Arsenic’s lethal effect when consumed in acute dose is due to *gastrointestinal damage*
  - Causes severe vomiting and diarrhea
- Major problems from high levels of arsenic occur in the Bengal Delta
  - Up to 40 million people in Bangladesh and in the West Bengal region of India drink As-laced water
  - WHO called this the “largest mass poisoning of population in history.”
- Read p. 699 for more information
- LD$_{50}$ values for some common form of arsenic
Note that arsenous acid, an inorganic form of As, is the most toxic of the various forms of arsenic.