13. Mercury, Hg (Atomic no. 80)
- Hg is in the same periodic table group as Zn and Cd; it is the only liquid metal at STP.
- Hg has 3 oxidation states, Hg(0) (metallic), Hg(I) (mercurous), and Hg(II) (mercuric), the monovalent form is rare owing to its instability.
- Hg in water, soil, and sediment is predominantly as the inorganic Hg(II) form; methyl mercury (MeHg\(^+\)) is dominant in biota, and Hg(0) is the primary species in the atmosphere.
- All forms of Hg are toxic, but particularly poisonous are the organic forms such as methyl-mercury (MeHg), a neurotoxin.
- Two notorious poisoning episodes associated with MeHg exposures occurred in Minamata, Japan (contaminated fish), and Iraq (grain treated with MeHg as a fungicide).
Gaseous elemental Hg is the predominant form (>99%) of Hg from natural emissions, including geologic activities (volcanic and geothermal), volatilization of Hg in marine environments, and emission of Hg from land (e.g. soils).

Figure 1.1 shows global emissions of Hg.

Anthropogenic emissions of mercury can be from point sources (e.g., incinerators and coal-fired power plants) and diffuse sources (landfills, sewage sludge, and mine waste).

Point sources, including combustion, and manufacturing, are thought to be the main anthropogenic sources of mercury (95%).
Figure 1.1 Annual global mercury emission (tons) from major anthropogenic sources.
- The drinking water guideline for the World Health Organization (WHO) for (total) Hg is 1,000 ng/L (0.001 mg/L, 1.0 μg/L, 1 ppb).
- The USEPA Hg MCL is 2,000 ng/L (2 ppb).
- The USEPA has a reference dose for MeHg in drinking water of 0.1 μg/kg bw/day (or 100 ng/kg body-weight/day).

- Although MeHg may constitute a minor fraction of total mercury present in aquatic and soil environments (less than 10% in water and and 3% in soil/sediment), MeHg can bio-accumulate along the food web and reach high concentrations, particularly in aquatic organisms and in wildlife that prey on fish.
Aqueous Forms of Hg

- Elemental mercury (Hg$^0$) is quite soluble in water (60 μg/L at 25°C), can be oxidized to the metastable dimer Hg$_2^{2+}$, Hg(I), and to more stable Hg(II) forms.
- The redox potential and pH of the system determine the stable forms of Hg that will be present in aqueous environments. Mercurous (Hg$_2^{2+}$), and mercuric (Hg$^{2+}$) mercury are more stable under oxidizing conditions.
- The Hg(II) compounds (including inorganic and organic) are present in a variety of physical and chemical forms through complexation with various inorganic (e.g., chloride and sulfide) and organic (e.g., organic matter) ligands, making it very soluble in oxidized aquatic systems.
Aqueous Forms of Hg

- For example, both laboratory experimental studies and modeling results have suggested that more than **90%** of inorganic Hg(II) and from **70%** to **97%** of MeHg in water may be associated with Dissolved Organic Matter (primarily humic substances) in some lakes.

- The complexation of Hg species with Natural Organic Matter may be decreased in seawater because of competition with chloride ions.
When mildly reducing conditions exist, organic or inorganic Hg may be reduced to elemental Hg, which may then be converted to alkylated forms (e.g. MeHg) by biotic (sulfur reducing bacteria) or abiotic processes.

- Acidic conditions (pH < 4) also favor the formation of methyl mercury, whereas higher pH values favor precipitation of HgS(s).

- During the methylation process, inorganic Hg(II) is transformed to the MeHg molecule by the action of mainly iron (III) and sulfate reducing bacteria.
pE-pH diagram for Hg: (a) solid phases; (b) aqueous phases, both with $10^{-3}$ M $\text{Cl}^-$ and $\text{SO}_4^{2-}$; and $10^{-1}$ M $\text{Cl}^-$ (dotted line)

F&C
Hg Adsorption

- The biogeochemistry of Hg in soils and sediments is dominated by inorganic and organic mercury(II) complexes.
- In general, adsorption of Hg is pH dependent and increases as pH increases.
- The total concentration of Hg(II) in the aqueous phase of soils and sediments is normally in the range 5–100 pM, and solid phase concentrations are often in the range 50–500 ng/g (250–2500 pmol/g).
- Hg concentrations in contaminated sediments may be 50 times higher in the aqueous phase and up to 1000 times higher in the solid phase.
- Concentrations of MeHg are up to 10% of the total Hg (Hg and MeHg) in solid phases and 5–80% of total Hg in aqueous phases of soil and sediment.
Mercury Speciation and Mobilization in a Wastewater-Contaminated Groundwater Plume (Lamborg, 2013)
- The importance of redox conditions in Hg mobility was examined in recent research at the USGS research site located near the MMR on Cape Cod, specifically in the sewage plume.
- Background concentrations of Hg in the oxic uncontaminated groundwater were about 0.2 ng/L (1pM).
- The study examined Hg fate and transport within the plume and found that Hg(0) constituted >50% of the Hg present in the iron reduction zone near the sewage beds, where Hg concentrations ranged up to about 200 ng/L (1,000 pM); and that Hg levels rapidly diminished down-gradient from the beds.
Upgradient, Background
Uncontaminated Groundwater:
Oxic, Zero Fe,
Total Hg = ~1-10 pM

Near-Source Contaminated Groundwater:
low DO, Detectable Fe, Total Hg = 10-1000 pM
- Figure 4 (below) shows the correlation of Hg° with dissolved Fe for those wells and depths where both values were available and Fe was detectable.
- This correlation was evident for those samples where Hg° was greater than 10% of total Hg.
- For some samples collected under the beds, the absolute amount of Hg° was high, but a low percent of total Hg, suggesting little in-situ production (i.e. a sewage source for Hg).
- Dissolved Fe concentrations are supported by large concentrations of sorbed Fe²⁺, but the correlation also suggests progressive release of Hg from Fe reduction.
Figure 4. The correlation between dissolved Hg° and dissolved Fe(II) in the northern end of the plume.
Hg in Far-Field Contaminated Groundwater

- About 1-2 km downgradient from the source (Ashumet Valley), the anoxic zone had essentially no dissolved iron, but concentrations of both ammonium ($\text{NH}_4^+$) and nitrate ($\text{NO}_3^-$) were high. MeHg comprised up to 100% of the dissolved Hg in some samples from this region of the plume.

- In addition, the distribution of dissolved Hg suggests that down-gradient from the source, dissolved Hg has been mainly mobilized from the non-calcareous, quartz-rich aquifer sediments rather than being transported long distances in the wastewater stream.
Far field concentrations of total dissolved Hg, N species, and O$_2$, as well as the percent of total Hg as CH$_3$Hg$^+$ in the Ashumet Valley plume; CH$_3$Hg$^+$ represented $>10\%$ of total dissolved Hg at depths within the low-oxygen region of the plume.
- The studies of Hg-contaminated groundwater in New Jersey and Cape Cod have provided conceptual models for Hg mobilization in groundwater, shown in figure 2.

- Mercury, either naturally occurring and/or from anthropogenic origin, is released to the water table as Hg(II) from surface soils and subsoils by weathering or by inputs of anthropogenic chemicals such as road salt or fertilizers, or by other subsurface inputs (e.g. septic-system effluent).
Figure 2. Mobilization of mercury from land surface to groundwater and biogeochemical transformations along flow paths in an unconsolidated, sandy, acidic aquifer.
- Under oxidizing conditions, dissolved Hg is mobile as a complex with DOM, and sorbed Hg(II) is mobile on Fe hydroxide particles.
- Effluent discharges provide electron donors and sorbed Hg(II) is released as Fe hydroxides reductively dissolve in a saturated, reducing environment, and Hg(II) may be reduced either by DOM or by Fe(II) to Hg(0).
- Where anoxic conditions are present, sulfate reduction is an important terminal electron accepting process, and MeHg may be produced. Additionally, sulfides may precipitate, removing Hg from the aqueous phase.
- Hg(0) may be re-oxidized to Hg(II) should groundwater become more enriched in oxygen farther down a flowpath.
"It is noteworthy that there is still not a single study in which the absolute concentration of Hg in the pore water of a soil or sediment has been satisfactorily explained by thermodynamic models, covering molecular species pertaining to aqueous and solid phases."

- ULF SKYLLBERG, *Environmental Chemistry and Toxicology of Mercury*, 2013
Summary

- The dominant form of Hg in water, soil, and sediment is the inorganic Hg(II) form, while methyl mercury (MeHg+) is dominant in biota, and Hg(0) the primary species in the atmosphere.
- All forms of Hg are toxic, but particularly poisonous are the organic forms such as methyl-mercury (MeHg), a neurotoxin.
- Adsorption of Hg is pH dependent and increases as pH increases.
- The biogeochemistry of Hg in soils and sediments is dominated by inorganic and organic mercury(II) complexes.
- The fate and transport of Hg in the pore water of soils or groundwater is poorly understood, and has not been satisfactorily explained by the use of thermodynamic (i.e. quantitative chemical) models.
Next:
As in Contaminant Plumes