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A BRIEF INTRODUCTION TO REMEDIATION OF HG CONTAMINATED SEDIMENTS

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MERCURY IN SOILS

Mercury is regarded as one of the “priority hazardous substances” by the Agency for Toxic Substances and Disease Registry (ATSDR) because of its toxicity, mobility, and long residence time in the atmosphere;

Mercury in soil generally originates from three major pathways:

- natural processes;
- anthropogenic activities;
- deposition of mercury from the atmosphere.

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Natural processes

- weathering of rocks;
- volcanic events
- geothermal activity

The average background concentration of mercury in soil ranges from 0.03 to 0.1 mg kg^{-1} with an average value of 0.06 mg kg^{-1}

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Anthropogenic activities

- Mining activities;
- chlor-alkali production;
- metal smelters;
- acetaldehyde producing plants;
- wood/forestry impregnation sites;
- coal combustion;
- waste incineration;
- municipal solid waste landfills.

Recent estimation of global mercury emissions ranges from 5000 to 8000 metric tons per year

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Mercury speciation in soil

the determination of a total mercury concentration is insufficient for:

- understanding the biogeochemical cycle of the metal;
- evaluating the reactivity (transformation/conversion), bioavailability and toxicity of mercury in soil;
- establishing an appropriate remediation method.

The study of mercury speciation can be used to predicate and explain the behavior of mercury in soil.

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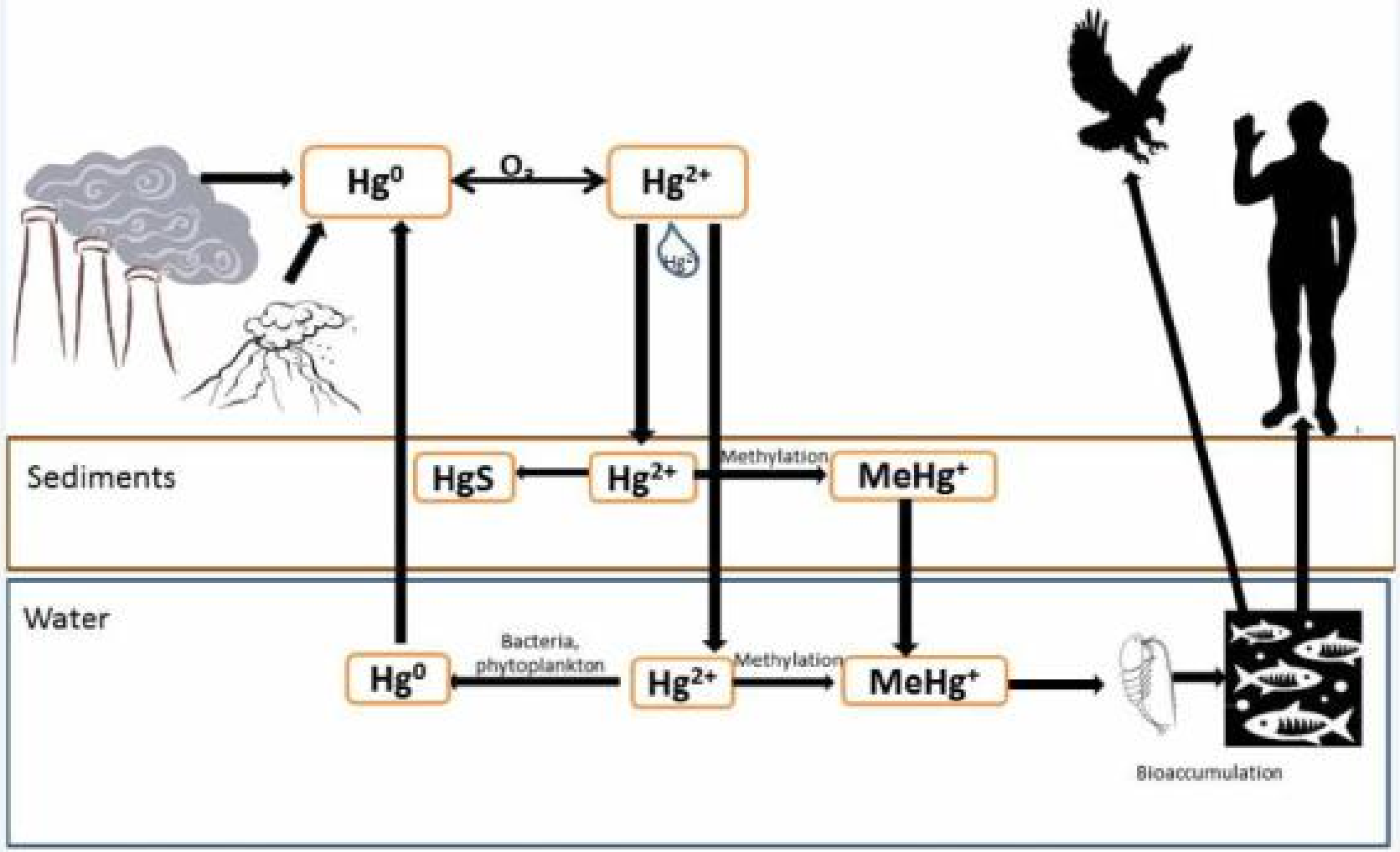
Mercury cycling through air, sediments, water, and organisms



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Th emical properties of mercury and its compounds

hemical Name	Elemental Mercury[a]	Mercuric Chloride	Mercurous Chloride (Calomelan)	Mercury Oxide	Mercury Sulphide (cinnabar)	Methylmercuric Chloride[c]	Dimethylmercu
Molecular ormula	Hg^0	$HgCl_2$	Hg_2Cl_2	HgO	HgS	CH_3HgCl	C_2H_6Hg
Molecular veight	200.59	271.52	472.09	500 (decom. position)	584 (sublimatio n)	251.1	230.66
olubility	5.6×10^{-5} g/L at 25°C	69 g/L at 20°C	2.0×10^{-3} g/L at 25°C	0.053 g/L at 25 °C	2×10^{-24} at 25 °C	0.100 g/L at 21°C	1 g/L at 21°C
Density	13.534 g/cm3 at 25°C	5.4g/cm3 at 25°C	7.15g/cm3 at 19°C	11.14g/cm3	8.10 g/cm^3	4.06 g/cm3 at 20°C	3.1874 g/cm3 at 20°C
Oxidation tate	+1, +2	+2	+1	+2	+2	+2	+2

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Applied speciation methods

sequential extraction procedures (SEP);

Pyrolysis;

X-ray absorption fine spectroscopy (XAFS);

nuclear magnetic resonance (NMR)

electron paramagnetic resonance (EPR)

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ation by SEP and pyrolysis

Samples	Operating conditions	Compounds released	Percentage of total mercury released	Reference
Soils (military site)	<180 °C	Hg^0, Hg_2Cl_2	10–30%	Liu et al., 2006
Soils (Mining)	25–350 °C 453 °C	Fe-oxyhydroxides/clay Minerals bound Hg Cinnabar	20–50% 50–80%	Biester et al., 1999
Sediments and soils (Mining)	<100 °C 150–250 °C 250–350 °C	Hg^0 Non cinnabar Hg Red Cinnabar	–5% –40% 5–30%	Biester et al., 2000
Soils	200–250 °C 250–350 °C	Non cinnabar Hg Cinnabar	–79% 18%	Gosar et al. (2006)
Soils (Chlor-alkali plant)	<100 °C 150–250 °C 350 °C	Metallic Hg Matrix-bound Hg Cinnabar	20% 80% –	Biester and Scholz, 2006
Soils (Hg mining)	<100 °C 150–250 °C 350 °C	Metallic Hg Matrix-bound Hg Cinnabar	– 11% 89%	Wang et al., 2012

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Contaminated Sediments remediation alternatives

- Sediment removal and ex-situ containment
- Sediment removal and ex-situ treatment (as a waste).

- In-situ containment
- In situ treatment (chemical, physical, biological or combinations)

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Containment technologies

- Capping
- Containment Barrier
- Confined Disposal Facility (CDF)
- Contained aquatic disposal (CAD)

Many of these technologies require sediment removal (dredging, dewatering and handling).

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Contained aquatic disposal and in-situ capping

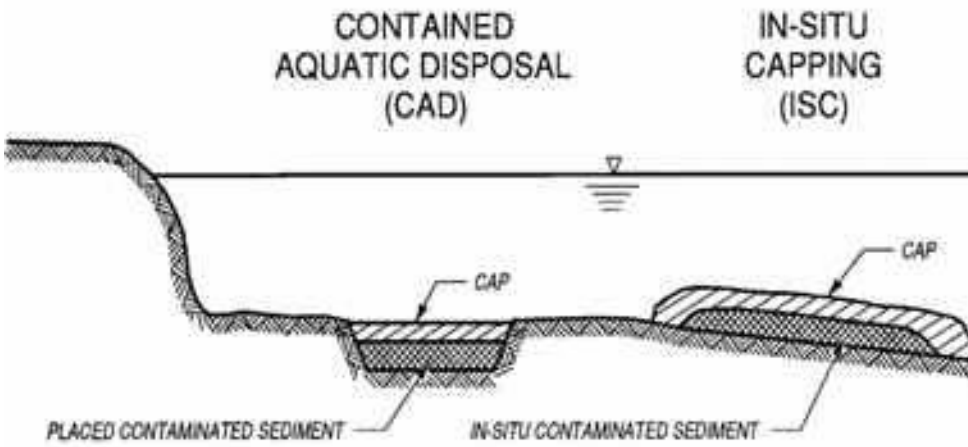
The cap can be made up of many different materials such as:

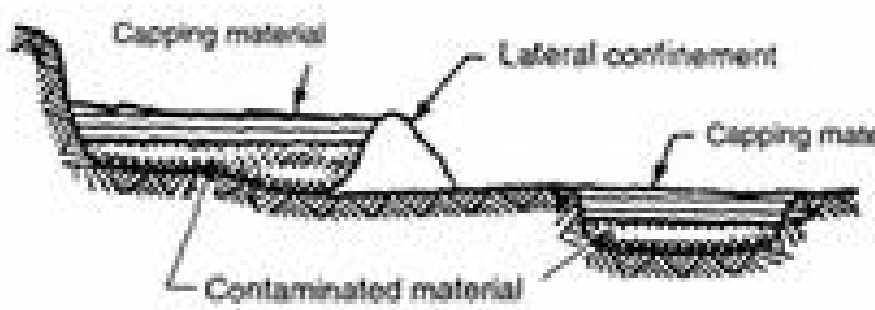
sand,

gravel,

geotextiles,

Adsorbent layer





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Sediment capping

- Capping materials can sorb 99.9% of the Hg from sediment, which contained Hg between 200 and 500 micrograms per liter (mg/L)(Moo-Young et al. (2001).
- A cap, approximately 35 cm thick and composed mostly of sand, after one year of field study, showed low Hg concentrations (<5 ug/kg) in
- the capping layer, while the concentration of Hg in the original
- sediment ranged between 0.43 g/kg and 0.96 g/kg (Azcue et al.,
- 1998).

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Remediation Technologies

ON-SITE/OFF-SITE

Thermal desorption

Stabilization/Solidification

Soil washing

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Application of thermal desorption to Hg contaminates soils/sediments

mercury thermal desorption experiments have demonstrated the feasibility of mercury removal at temperatures ranging between 127 and 700 °C with greater efficiency of mercury removal at relatively high temperature (460–700 °C).

Treatment time varies between 20min and 3 hours,

The desorbed contaminants are treated in the offgas treatment system to control air emissions

The negative effect of high temperature on the physical properties of the thermally treated soil should be taken into the consideration.

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Application of S/S to Hg contaminates soils/sediments

Experiences in ex situ treatment of mercury in waste:

S/S with **PAC and cement**:Hg up to 1000 mg kg^{-1} treated to pass the US TCLP test – 0,2 mgHg/L;

S/S with powdered **sulfur polymer cement (SPC) and sulfide**;

S/S with **thiol-functionalized zeolite and Portland cement**;

S/S with **sulfur polymer cement (SPC)**, made with 95 wt% elemental sulfur reacted with 5 wt% of an organic modifier.

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Application of soil washing to Hg contaminates soils/sediments

Soil washing (SW) is an *ex situ* treatment method for separating Hg from soil *by* chemical leaching, physical separation or physicochemical procedures.

The specific application of soil washing depends on the form of Hg in the sediment being remediated.

Iodide, EDTA, and thiosulfate have been found effective in the removal of mercury from soil with an efficiency variable between 30% and 99%

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Remediation Technologies

N SITU

Adsorption

Electro-remediation

Stabilization/Solidification

Phytoextraction