### HEALTH & ENVIRONMENTAL EFFECTS OF TRACE ELEMENTS IN METAL-MINING WASTES

# ARSENIC

## Quick Facts:

- Description: Elemental Arsenic (As) occurs as a yellow, black, or silver-gray solid, and can be tin-white, shiny, brittle, crystalline and metallic-looking. Arsenic rarely occurs in elemental form, but usually is found as a compound or dissolved ion.
- Usage: inorganic compounds preserve wood; organic compounds as pesticides and insecticides; used as alloy (hardener of lead for leadshot, copper, and alloys)
- Drinking Water Standards: Current MCL: 0.05 mg/L; on January 23, 2006, 0.010 mg/L (EPA) (0.010 mg/L = 10 ppb)
- EPA Classification: Class A human carcinogen
- Chemistry: Symbol: As; CAS Number: 7440382; Class: metalloid (Group VA) naturally occurring inorganic element

**Hardrock Mining Facts:** Often found as a byproduct of both acid mine drainage and of neutral pH leaching of mining waste from many precious and base metal ore deposits. Once dissolved either by oxidation and/or acid leaching of sulfide minerals, or by dissolving non-sulfide As compounds in water, dissolved As does not readily precipitate from solution. Probably the most common method of removing As from water is by co-precipitation with iron (Fe). This process is moderately effective, but often expensive and is usually employed only when the volume of water to be treated is low. **Background:** Widely distributed in earth's crust; found in the metal sulfides, and as oxides, and arsenates. Geothermal water (e.g., Yellowstone Park) contains natural sources of As where there are naturally high As concentrations in groundwater. Arsenopyrite (FeAsS) is the most common arsenic mineral in ores and is also a byproduct associated with

copper, gold, silver, and lead/zinc mining. Arsenic trioxide ( $Fe_2As_3$ ) is present in flue gases from copper ore roasting; coal-fired power plants and incinerators also may release As into atmosphere. Organic compounds (*i.e.*, As in compounds combined with carbon and hydrogen) are less toxic than inorganic compounds (*i.e.*, As combined with oxygen, chlorine, and sulfur). As is a human carcinogen (see "Human Health Effects"). As (III) is more toxic than As (V) but As (V) easily converts to As (III) when ingested; thus, this difference in toxicity is no longer considered that important.

### Environmental Availability:

- Air: average concentrations range from less than 1 to 2,000 ng/m<sup>3</sup>; settles to the ground or is washed out of the air by rain.
- Surface Water: average concentration is 1 ppb, but can be > 1,000 ppb in mining areas; As(V) most prevalent; many compounds dissolve in water. More As is taken up as water temperature increases (this is probably a minimal aspect of bioavailability, which is much more dependent on the form, organism and oxidation state, etc.).
- Soil: most As ends up in soils/sediments with concentration ranging from 1-40 ppm (for non-contaminated values, much higher in contaminated soils, in the low percents in the worst situations, and commonly in the thousands of ppm); average is 5 ppm (ATSDR, http://atsdr1.atsdr.cdc.gov/ToxProfiles/phs8802.html). Soils in mining and smelting sites may have much greater As levels.
- Groundwater: average concentration is 1 ppb, but concentrations in contaminated groundwater and mining areas may exceed 1,000 ppb. Groundwater is more likely to contain high As levels than surface water; As(III) most prevalent; many As compounds dissolve in water
- EPA surface water aquatic discharge standards: chronic = 0.15 mg/L; acute = 0.34 mg/L.
- EPA human heath (carcinogenic) surface water standard: 0.018 mg/L (10<sup>-6</sup> risk factor).

### Fate:

- Persistence: cannot be destroyed; can only change its form
- Solubility: many As compounds dissolve in water; native forms are not very important in natural systems and seldom exist in the environment; they are always associated with metals (Fe) or sulfides (S), etc. As can be dissolved in oxidizing acids.
- Bioaccumulation: by fish and shellfish

**Ecotoxicity**: Terrestrial flora and fauna, birds, and freshwater biota usually contain < 1 mg/As/kg by wet weight (NIWQP); however, much higher concentrations, if contaminated. Freshwater NRWQC – CCC: 150 µg/L; CMC: 340 µg/L. Toxicity in water is determined by water temperature, pH, organic content, phosphate concentration, suspended soils, presence of oxidants, and speciation. As and Se have been found to have an antagonistic interaction in several animal species. Freshwater LOAEL (As-V): 850 µg/L for acute exposure (NIWQP).

**Human Health Effects:** Health organizations advise treating all As compounds as highly toxic. MRLs have been defined as 0.005 mg/kg/day for Provisional Oral Acute (14 days or less), and 0.0003 mg/kg/day for chronic (365 days or less)<sup>1</sup>. **High levels**: Death - as little as 70-200 mg of As(III) ingested by an adult may be lethal; inorganic As can increase risk of cancers (lung, skin, bladder, liver, kidney, prostate); breathing inorganic As causes sore throat, irritated lungs. **Lower levels**: pins and needles in hands/feet; damage to blood vessels, nausea, vomiting; darkening of skin, appearance of 'corns' or 'warts' on palms, soles, torso; skin contact causes redness or swelling As(V) is a carcinogen and skin is a possible absorption route. Inhalation/ingestion causes lung/liver, kidney, bladder cancer.

<sup>&</sup>lt;sup>1</sup> Minimal Risk Levels for Hazardous Substances (MRLs) – Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services, http://www.atsdr.cdc.gov/mrls.html, as accessed 12/21/2003.

# HEALTH & ENVIRONMENTAL EFFECTS OF TRACE ELEMENTS IN METAL-MINING WASTES

# ARSENIC

# Terms<sup>†</sup>:

*CCC*: Criterion Continuous Concentration – an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

*CMC*: Criterion Maximum Concentration – an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.

Persistence: The length of time a compound stays in the environment.

*Solubility*: The amount of mass of a compound that will dissolve in a unit volume of solution.

*Bioaccumulation*: The extent to which substances increase in concentration in contaminated air, water or food because the substances are very slowly metabolized or excreted.

*LD*: Lethal Dose; LD50/Lethal Dose is the dose of a toxicant or microbe that will kill 50% of the test organisms within a designated period. The lower the LD50, the more toxic the compound.

LOAEL: Lowest-observed-adverse effect level.

*MCL*: Maximum contaminant level – an enforceable EPA standard for drinking water contamination.

*MRL*: Minimal Risk Level - an estimate of the daily human exposure to a hazardous substance that is likely to be without an appreciable risk of adverse (noncarcinogenic) health effects over a specified duration of exposure.

**NIWOP:** National Irrigation Water Quality Program Information Report No. 3 (U.S. Department of the Interior)

NRWQC: National Recommended Water Quality Criteria

*SMCL*: Secondary maximum contaminant level – non enforced EPA guidelines to manage water for aesthetic considerations (taste, color, odor).

## FOR FURTHER INFORMATION:

- 1. Arsenic Acid Hazardous Substances Data Bank (http://csi.micromedex.com/DATA/HS/HS431F.htm.
- Arsenic Hazardtext® HazardManagement, http://csi.micromedex.com/DATA/DT/DT1393.htm, TOMES Plus® System, 2003.
- 3. Arsenic in Drinking Water, US EPA, www.epa.gov/safewater/arsenic.html
- 4. Arsenic Treatment Handbook, EPA, www.epa.gov/safewater/ars/asdecisiontree/arsenic\_treatment\_handbook.pdf
- Integrated Risk Information System, US EPA, Arsenic, inorganic, http://cfpub.epa.gov/iris/quickview.cfm?substance\_nmbr=0278
- 6. *Minimal Risk Levels for Hazardous Substances (MRLs)* Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services, http://www.atsdr.cdc.gov/mrls.html, as accessed 12/21/2003.
- 7. *Minor Clarification of National Primary Drinking Water Regulation for Arsenic*, EPA, www.epa/gov/fedregstr/EPA-WATER/2003/March/Day-25/w7048.htm
- 8. National Irrigation Water Quality Program Information Report No. 3, Guidelines for Interpretation of the Biological Effects of Selected Constituents in Biota, Water, and Sediment, Arsenic, www.usbr.gov/niwqp/guidelines/Arsenic.pdf
- 9. National Recommended Water Quality Criteria: 2002, EPA, www.epa.gov/waterscience/pc/revcom.pdf
- 10. Public Health Statement for Arsenic, http://atsdr1.atsdr.cdc.gov/ToxProfiles/phs8802.html
- 11. The Geochemistry of Arsenic and its Use as an Indicator Element in Geochemical Prospecting, R.W. Boyle and I.R. Jonasson, Journal of Geochemical Exploration, 2(1973) 251-296.
- 12. ToxFAQs for Arsenic, Agency for Toxic Substances and Disease Registry (www.atsdr.cdc.gov/tfacts2.html)
- 13. www.arsenic.cr.usgs.gov (Bibliography Search)

<sup>&</sup>lt;sup>v</sup> Source: http://www.epa.gov/OCEPATerms

# HEALTH & ENVIRONMENTAL EFFECTS OF TRACE ELEMENTS IN METAL-MINING WASTES

# CADMIUM

# Quick Facts:

- Description: Cadmium (Cd) is a soft, bluish-white metal easily cut with a knife; also a blue-white solid or grayblack powder
- Usage: Silver solder, metal plating and coating, photography, television phosphors, nickel-cadmium and solar batteries, pigments, stabilizers in plastics, catalysts, dental amalgam, control rods, solar cells
- EPA Drinking Water Standards: 0.005 ppm (mg/L) MCLG; 0.005 ppm (mg/L) MCL
- EPA Classification: Carcinogen and teratogen
- Chemistry Symbol: Cd; CAS Number: 7440439; Class: Metal, Group IIB transition element

**Hardrock Mining Facts**: Most Cd is found in zinc (Zn), copper (Cu) and lead (Pb) ores and is obtained as a by-product in the treatment of these ores. Cd releases are primarily from Zn, Cu and Pb smelting and refining industries. During smelting, Cd volatilizes and condenses into cadmium oxide, a respirable form of Cd. It enters air during mining industry operations and the burning of coal. Best water treatment technologies include coagulation/filtration, ion exchange, lime softening, and reverse osmosis.

**Background**: Cd is found in the earth's crust, usually as a mineral (*e.g.*, greenockite and hawleyite) combined with other elements, *e.g.*, cadmium oxide, cadmium chloride, and cadmium sulfate or sulfide. It is found in coal and other fossil fuels, shales, and is released to the atmosphere during volcanic eruptions. It also enters air during burning of coal and household wastes, and enters water as a byproduct of acid mine drainage.

# **Environmental Availability:**

- Air Cd travels long distances before settling to ground or water.
- Surface Water Cd enters water from waste disposal/spills, leaks at hazardous waste sites. Some Cd dissolves in water. Solutions of Cd and its compounds are toxic.
- Soil Binds strongly to soil particles especially under alkaline conditions. In acidic soils, Cd desorbs and is more mobile in waters with a pH less than 6-7.

### Fate:

- Persistence: Does not break down in the environment, but can change form.
- Solubility: Varies, depending upon form. Cd carbonate is insoluble, whereas Cd nitrate is soluble. Oxides and sulfides are relatively insoluble; chlorides and sulfates salts are soluble.
- Bioaccumulation: Fish, plants, and animals uptake Cd from environment. Bioaccumulation factors vary; rainbow trout BCF=33; mosquito fish BCF = 2213.

**Ecotoxicity** Animals given Cd in food or water develop high blood pressure, iron-poor blood, liver disease, nerve/brain damage. Affects birth weight and skeleton in developing animals. Cadmium is toxic to aquatic organisms at relatively low levels. Freshwater NRWQC – CCC: 0.25 µg/L; CMC: 2.0 µg/L **Toxicity Thresholds** (NIWQP) Cd and its solutions are extremely toxic.

**Human Health Effects**: The Oral Chronic Minimal risk level (MRL) is 0.0002 mg/kg/day.<sup>1</sup> 4 mg of cadmium inhaled can be fatal. Ingestion of more than 100 mg of soluble Cd salt may be lethal. Cd stays in the body a very long time and bioaccumulates from many years of exposure to low levels. The general population can be exposed to Cd in the workplace where Cd products are made, by breathing cigarette smoke, and Cd-contaminated air near the burning of fossil fuels and municipal waste, and also eating Cd-contaminated foods. People who work with lead and lead ores may be exposed to Cd vapors. OSHA PEL is 0.005 mg/m<sup>3</sup> for Cd dust or fume. Lung inflammation results from inhaling air containing 0.5-2.5 mg/m<sup>3</sup> of Cd dust and breathing high levels causes death. Cd is also a severe lung and gastrointestinal irritant. It causes kidney disease, fragile bones, irritates the digestive tract, and causes vomiting, and diarrhea. Long-term exposure to lower levels in air, food, and water leads to buildup of Cd in kidneys, causing kidney and liver damage, anemia and loss of the sense of smell.

<sup>&</sup>lt;sup>1</sup> Minimal Risk Levels for Hazardous Substances (MRLs) – Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services, http://www.atsdr.cdc.gov/mrls.html, as accessed 12/21/2003.

## HEALTH & ENVIRONMENTAL EFFECTS OF TRACE ELEMENTS IN METAL-MINING WASTES

# CADMIUM

### Terms<sup>†</sup>:

*Acid Mine Drainage*: Low pH water drainage from areas that have been mined for coal or other mineral ores. Contact with sulfurbearing material causes the low pH and the water is harmful to aquatic organisms.

Action Level: A contaminant concentration in the environment high enough to warrant action or trigger a response under SARA and the National Oil and Hazardous Substances Contingency Plan.

Antagonism: Two contaminants nullifying each other's toxicity.

*Bioaccumulation*: The extent to which substances increase in concentration in contaminated air, water or food because the substances are very slowly metabolized or excreted.

Biomagnification: The incremental increase in a contaminant's concentration at each level of the food chain.

*CCC*: Criterion Continuous Concentration – an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

*CMC*: Criterion Maximum Concentration – an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.

CDC: Centers for Disease Control

dw: dry weight

Freshwater NRWQC: National Recommended Water Quality Criteria for priority toxic pollutants (EPA)

*LD*: Lethal Dose; LD50/Lethal Dose is the dose of a toxicant or microbe that will kill 50% of the test organisms within a designated period. The lower the LD50, the more toxic the compound.

*MCL*: Maximum contaminant level – an enforceable EPA standard for drinking water contamination.

*MCLG*: Maximum contaminant level goal – a non enforced EPA public health goal; the drinking water contaminant level below which the risk to health is either not known or expected.

*MRL*: Minimal Risk Level – an estimate of the daily human exposure to a substance that is likely to be without an appreciable risk of noncancer adverse health effects over a specified duration of exposure.

NIWOP: National Irrigation Water Quality Program Information Report No. 3 (U.S. Department of the Interior)

NRWQC: National Recommended Water Quality Criteria

*Persistence*: The length of time a compound stays in the environment.

OSHA PEL: Occupational Safety and Health Administration Permissible Exposure Limit

*SMCL*: Secondary maximum contaminant level – non enforced EPA guidelines to manage water for aesthetic considerations (taste, color, odor).

*Solubility*: The amount of mass of a compound that will dissolve in a unit volume of solution.

Teratogen: A substance which causes birth defects by damaging the fetus.

### FOR FURTHER INFORMATION:

- 1. Cadmium Hazardtext® HazardManagement, http://csi.micromedex.com/DATA/DT/DT80, TOMES Plus® System, 2003.
- 2. EPA National Recommended Water Quality Criteria: 2002, www.epa.gov/waterscience/pc/revcom.pdf, p. 12.
- 3. Hazardous wastes from large-scale metal extraction, J.N. Moore and S.N. Luoma, Environ. Sci. Technol., Vol 24, No. 9, 1990.
- 4. List of Drinking Water Contaminants and MCLs, U.S. EPA Groundwater and Drinking Water, www.epa.gov/safewater/mcl.html
- 5. New Jersey Department of Health and Senior Services, Hazardous Substance Factsheet, Cadmium,
- www.state.nj.us/health/eoh/rtkweb/0305.pdf
- 6. Technical Factsheet on Cadmium, US EPA, www.epa.gov/safewater/dwh/t-ioc/cadmium.html
- 7. ToxFAQs for Cadmium, Agency for Toxic Substances and Disease Registry, www.atsdr.cdc.gov/tfacts5.html
- Toxicological Profile for Cadmium, US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, July, 1999. http://www.atsdr.cdc.gov/toxprofiles/tp5.htm and http://www.atsdr.cdc.gov/toxprofiles/tp5.pdf, as accessed 12/21/2003.

<sup>+</sup> See OCEPA (Source: http://www.epa.gov/OCEPATerms/) or listed reports.

### HEALTH & ENVIRONMENTAL EFFECTS OF TRACE ELEMENTS IN METAL-MINING WASTES

# COPPER

# Quick Facts:

- Description: Copper (Cu) is a shiny reddish-brown metal found in various ores, and occurring naturally in its elemental state
- Usage: Heat and electrical conductor; cookware, electrical circuits, household plumbing materials, coins (US penny); compounds to treat plant diseases (mildew); wood, leather, and fabric preservatives
- EPA Drinking Water Standards and Status: 1.3 ppm (mg/L) MCLG; 1.3 ppm (mg/L) MCL; 1.3 ppm (mg/L) Action Level; EPA priority pollutant; carcinogenicity unknown
- Chemistry Symbol: Cu; CAS Number: 7440508; Class: Metallic solid, Group IB transition element

**Hardrock Mining Facts**: Most Cu is mined in open pits of low-grade rock containing chalcopyrite and other Cu sulfides. The ore is concentrated by a flotation process. Acid mine drainage from Cu mine sites have caused massive fish kills and Cu mining and smelting operations are major sources of contamination of source water. Cu is present in acidic waters as  $Cu^{+2}$ . Low pH, soft water, and higher temperature are known to increase Cu toxicity. In MT, contaminated floodplains (slickens) resulting from flood deposition of waste material, extend for over 100 km downstream from its origin in Butte, resulting in a floodplain — largely in Silver Bow Creek, and locally in the Clark Fork River — devoid of biota.

**Background**: Cu is widespread in the environment and has been mined and used by humans for more than 5,000 years in utensils, coins, ornaments, and tools. Common sources of Cu contamination are corrosion of Cu pipes used in home plumbing, as well as mining operations, leachate from municipal landfills, sewage treatment plant sludges, textile mill and cosmetic plant wastes, and burning of coal in power plants. In the environment, it forms cuprous (Cu<sup>+</sup>) or cupric (Cu<sup>+2</sup>) compounds. Cuprous compounds are not common in natural waters. Rhizofiltration may remove Cu from solution and wetland ecosystems (where the pollutants pass through the rooting zone) may remove Cu pollutants.

## **Environmental Availability:**

- Air Cu enters atmosphere from soils, volcanoes, decaying vegetation, forest fires, sea spray and mining/smelting
  operations and is carried over very long distances by particles emitted from smelters and ore processing plants. It
  lands on the ground by snow/rain deposition or gravity.
- Surface Water Tailings ponds and other sources contain Cu. Cu is highly complexed with carbonate and hydroxide ions in natural waters and, as a result, free Cu<sup>+2</sup> ion is usually low in concentration. Complexation of Cu<sup>+2</sup> with inorganic carbon increases with alkalinity and pH; therefore, at high alkalinity and a pH of 8 or more, most Cu<sup>+2</sup> is complexed. Cu affects fish in most life stages, but reproductive adults and embryos are probably most sensitive.
- Soil Strongly attaches to organic materials and minerals; can form both soluble and insoluble complexes with soil
  organic matter.
- Groundwater Significant groundwater contamination can occur but organic complexing agents, if present, can
  reduce Cu<sup>+2</sup> concentrations.

### Fate:

- Persistence:  $Cu^{+2}$  free ion decreases as  $CuCO_3$ ,  $CuOH^+$ , and  $Cu_2(OH)_2^{+2}$  increase.
- Solubility: Solubility depends upon the compound; acidic waters increase solubility.
- Bioaccumulation: Cu does not appear to bioaccumulate except in chicken livers (NIWQP, p. 51).

**Ecotoxicity:** High concentrations of Cu in rivers resulting from metal extraction adversely affect fisheries. Generally more toxic to aquatic organisms than to birds or mammals. Mixtures of Cu and Zinc are known to be additive or synergistic in toxicity to many aquatic organisms (NIWQP, p. 52). High levels of Cu are toxic to soil organisms.

- Freshwater NRWQC CCC: 9.0 μg/L; CMC: 13 μg/L
- The presence of zinc and copper together is known to cause increased toxicity to aquatic organisms
- Toxicity Thresholds (NIWQP)
- Plants (mg/kg dw): >20
- Fish, whole body (mg/kg dw): 13.3
- Birds, liver (mg/kg dw): >540

**Human Health Effects:** Metallic Cu has little toxicity, but Cu's soluble salts are poisonous. Low levels of Cu are essential for maintaining good health (RDA for adults = 900 g/day); high levels can cause harmful effects such as skin allergies and irritation of the nose, mouth, eyes, nausea, diarrhea, vomiting, stomach cramps. The Minimum Risk Level (MRL) of 0.02 mg/kg/day has been derived for acute (duration 1-14 days) oral exposure to Cu.<sup>1</sup> Short periods of exposure can result in gastrointestinal disturbance; long periods can result in kidney/liver damage. It may decrease fertility in adults. Breathing Cu-containing dust or skin contact (in mining Cu or processing ore) can cause death and liver/kidney disease (OSHA exposure limit is 1 mg/m<sup>3</sup> for Cu dust and 0.1 mg.m<sup>3</sup> for Cu fume). Exposure to Cu in tap water (from Cu pipes and brass faucets) can be reduced by running water 15-30 seconds before use.

<sup>&</sup>lt;sup>1</sup> Draft for Public Comment, Toxicological Profile for Copper, Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services, September 2002, http://www.atsdr.cdc.gov/toxprofiles/tp132.html; as accessed 12/21/2003

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# COPPER

### Terms<sup>†</sup>:

*Acid Mine Drainage*: Low pH water drainage from areas that have been mined for coal or other mineral ores. Contact with sulfurbearing material causes the low pH and the water is harmful to aquatic organisms.

Action Level: A contaminant concentration in the environment high enough to warrant action or trigger a response under SARA and the National Oil and Hazardous Substances Contingency Plan.

Antagonism: Two contaminants nullify each other's toxicity.

*Bioaccumulation*: The extent to which substances increase in concentration in contaminated air, water or food because the substances are very slowly metabolized or excreted.

Biomagnification: The incremental increase in a contaminant's concentration at each level of the food chain.

*CCC*: Criterion Continuous Concentration – an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

*CMC*: Criterion Maximum Concentration – an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.

CDC: Centers for Disease Control.

#### dw: dry weight

*Flotation*: A process of agitating a slurry of crusted ore with air; the resulting Cu sulfide is in the form of a froth, which is then treated in several steps resulting in a molten copper sulfide matte. Blister copper (99% pure) is produced when air is blown through the matte.

Freshwater NRWQC: National Recommended Water Quality Criteria for priority toxic pollutants (EPA)

*MCL*: Maximum contaminant level – an enforceable EPA standard for drinking water contamination.

*MCLG*: Maximum contaminant level goal – a non enforced EPA public health goal; the drinking water contaminant level below which the risk to health is either not known or expected.

*MRL*: Minimum Risk Level – An estimate of daily human exposure to a hazardous substance that is likely to be without an appreciable risk of adverse, noncancer health effects over a specified route and duration of exposure.

**NIWOP**: National Irrigation Water Quality Program Information Report No. 3 (U.S. Department of the Interior)

NRWQC: National Recommended Water Quality Criteria

*Persistence*: The length of time a compound stays in the environment.

**OSHA**: Occupational Safety and Health Administration.

**RDA**: Recommended dietary allowances (grams/day).

Rhizofiltration: The use of plant roots to absorb, concentrate, and precipitate heavy metals from polluted effluents.

*SMCL*: Secondary maximum contaminant level – non enforced EPA guidelines to manage water for aesthetic considerations (taste, color, odor).

*Solubility*: The amount of mass of a compound that will dissolve in a unit volume of solution.

Synergism: An interaction of two or more chemicals that results in an effect greater than the sum of their separate effects.

### FOR FURTHER INFORMATION:

- 1. Consumer Factsheet on Copper, US EPA, www.epa.gov/safewater/dwh/t-ioc/copper.html
- Draft for Public Comment, Toxicological Profile for Copper, US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, September 2002, http://www.atsdr.cdc.org/toxprofiles/tp132.html (as accessed 12/21/2003).
- 3. EPA National Recommended Water Quality Criteria: 2002, www.epa.gov/waterscience/pc/revcom.pdf, p. 12.
- 4. Hazardous wastes from large-scale metal extraction, J.N. Moore and S.N. Luoma, Environ. Sci. Technol., Vol 24, No. 9, 1990.
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- 6. ToxFAQs for Copper, Agency for Toxic Substances and Disease Registry, www.atsdr.cdc.gov/tfacts132.html
- 7. New Jersey Department of Health and Senior Services, Hazardous Substance Factsheet, Copper,
- www.state.nj.us/health/eoh/rtkweb/0528.pdf
- 8. United States Department of the Interior, National Irrigation Water Quality Program Information Report No. 3, Guidelines for Interpretation of the Biological Effects of Selected Constituents in Biota, Water, and Sediment, Copper, www.usbr.gov/niwqp/guidelines/copper.pdf, p. 43 and pgs. 41-56.

<sup>+</sup> See OCEPA (Source: http://www.epa.gov/OCEPATerms/ or listed reports.

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# CYANIDE

# Quick Facts:

- Description: Cyanide (CN) is a highly toxic carbon-nitrogen chemical compound; may be combined with various organic and inorganic compounds, such as hydrogen cyanide, a colorless, flammable liquid or gas, or sodium cyanide and potassium cyanide, both solids. Usually stored/transported in dry, solid form.
- Usage: Hydrogen cyanide is used in the manufacture of other cyanides for nylon, fibers, resins; also used in herbicides, as chemical warfare agents, silver plating, dyes, and specialty products. Sodium and potassium cyanide are used in gold/silver ore extraction, and in small amounts to depress pyrite in base metal flotation; hydrogen cyanide is used in fumigation; calcium cyanimide is used in fertilizers.
- EPA Drinking Water Standard: MCLG: 0.2 ppm (mg/L); MCL: 0.2 ppm (mg/L); EPA National Recommended Water Quality Criteria for human health: water + organism, 700 μg/L; Organism only, 220 mg/L.
- Chemistry Symbol: CN<sup>-</sup>; CAS Number: 57125; Class: an inorganic compound although it is composed of nitrogen and carbon.

**Hardrock Mining Facts**: Cyanide has been used since the late 1800s for the recovery of gold, replacing the mercury amalgamation process. Two processes of cyanide leach mining, vat and heap-leaching, now process greater than 90% of US gold ores. CN is also used in small amounts to depress pyrite in the floatation processes of base metal ores (Cu, Ni, Pb, Zn, Mo). For gold, the use of CN allows very low grade deposits to be mined through heap leach techniques. This mining method often produces large amounts of both spent ore and non-ore waste. Gold ore typically runs from ½ oz/ton to as little as 1/20 oz ton. Large open pit mines can produce as much as 20 tons of waste for each ton of ore. These processes often allow unacceptable environmental and health risks, such as spills and widespread contamination, the generation of large amounts of potentially acid-generating waste from huge open pit mines, and water contamination that must be treated in perpetuity. In 1998, and again in 2004, residents of Montana voted to phase out cyanide leach mining, due to rivers, lands and groundwater that became contaminated. Cyanide and other heavy metal pollutants overflowed a dam at Baia Mare, Romania, contaminating 250 miles of rivers, and killing millions of fish.

**Background**: Cyanide is a chemical compound that can be discharged from metal finishing industries, iron and steel mills, and organic chemical industries; in addition, it leaches from landfills and cyanide-containing road salts as well as to the atmosphere from car exhaust (hydrogen cyanide gas). Some foods (almonds and lima beans) contain cyanides naturally and it can be produced by some bacteria, fungi, and algae. It most readily forms compounds with potassium (KCN), hydrogen (HCN), and sodium (NaCN).

# **Environmental Availability:**

- Air CN<sup>-</sup> from natural and human industrial processes usually as hydrogen cyanide gas with small amounts present in dust particles; duration 1-3 years before settling out.
- Surface Water CN<sup>-</sup> oxidizes in the presence of sunlight and oxygen, forming Cyanate (CNO<sup>-</sup>), Thiocyanate (SCN<sup>-</sup>), ammonia (NH<sub>3</sub>), nitrate (NO<sub>3</sub>), and other compounds
- Soil In soils, CN<sup>-</sup> migrates easily to groundwater and at high concentrations is toxic to soil microorganisms
- Groundwater persists in groundwater due to lack of sunlight/oxygen needed to degrade it to benign forms

# Fate:

- Persistence: Most persistent in groundwater, and at higher pH. Cyanate (CNO<sup>-</sup>) and Thiocyanate (SCN<sup>-</sup>) compounds are more persistent than CN<sup>-</sup>, and do have significant toxicity
- Solubility: varies with compound; cyanohydrins and highly soluble; organic cyanides are slightly soluble; hydrogen cyanide is soluble; Ni-, Cu-, Ag-, Zn- and Fe- cyanides are relatively insoluble.
- Bioaccumulation: Does not bioaccumulate in fish

# Ecotoxicity: Freshwater NRWQC - CCC: 5.2 µg/L; CMC: 22 µg/L

**Human Health Effects**: The Minimum Risk Level (MRL) derived for sodium CN is 0.05 mg/kg/day for intermediate duration (15-364 days) for oral exposure.<sup>1</sup> Oral lethal dose of KCN for an adult is 200 mg; airborne concentrations of 270 ppm is immediately fatal and a concentration of 110 ppm for half an hour is life-threatening. In addition, short time high level exposures result in brain and heart damage and can cause coma and death. Long term exposure to lower levels results in heart pains, breathing difficulties, vomiting, blood changes, headaches and thyroid gland enlargement. Salts can be rapidly adsorbed by inhalation; ingestion; through the skin. High blood cyanide levels results in weakness of fingers and toes, difficulty walking, dimness of vision, deafness and decreased thyroid gland function.

<sup>&</sup>lt;sup>1</sup> Minimum Risk Levels for Hazardous Substances (MRLs) – Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services, http://www.atsdr.cdc.gov/mrls.html, as accessed 12/21/2003.

## HEALTH & ENVIRONMENTAL EFFECTS OF TRACE ELEMENTS IN METAL-MINING WASTES

# CYANIDE

### Terms<sup>†</sup>:

*Acid Mine Drainage*: Low pH water drainage from areas that have been mined for coal or other mineral ores. Contact with sulfurbearing material causes the low pH and the water is harmful to aquatic organisms.

*Action Level*: A contaminant concentration in the environment high enough to warrant action or trigger a response under SARA and the National Oil and Hazardous Substances Contingency Plan.

Antagonism: Two contaminants nullify each other's toxicity.

*Bioaccumulation*: The extent to which substances increase in concentration in contaminated air, water or food because the substances are very slowly metabolized or excreted.

Biomagnification: The incremental increase in a contaminant's concentration at each level of the food chain.

*CCC*: Criterion Continuous Concentration – an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

*CMC*: Criterion Maximum Concentration – an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.

*CDC*: Centers for Disease Control.

dw: dry weight

Freshwater NRWQC: National Recommended Water Quality Criteria for priority toxic pollutants (EPA)

*MCL*: Maximum contaminant level – an enforceable EPA standard for drinking water contamination.

*MCLG*: Maximum contaminant level goal – a non enforced EPA public health goal; the drinking water contaminant level below which the risk to health is either not known or expected.

*MRL*: Minimum Risk Level - an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse noncancer health effects over a specified duration of exposure.

NIWOP: National Irrigation Water Quality Program Information Report No. 3 (U.S. Department of the Interior)

NRWQC: National Recommended Water Quality Criteria

Persistence: The length of time a compound stays in the environment.

**OSHA**: Occupational Safety and Health Administration.

**RDA**: Recommended dietary allowances (grams/day).

*SMCL*: Secondary maximum contaminant level – non enforced EPA guidelines to manage water for aesthetic considerations (taste, color, odor).

*Solubility*: The amount of mass of a compound that will dissolve in a unit volume of solution.

*Synergism*: An interaction of two or more chemicals that results in an effect greater than the sum of their separate effects.

#### FOR FURTHER INFORMATION:

- 1. Agency for Toxic Substances and Disease Registry, ToxFAQs for Cyanide, www.atsdr.cdc.gov/tfacts8.html
- 2. Technical Factsheet on Cyanide, US EPA, www.epa.gov/safewater/dwh/t-ioc/cyanide.html
- 3. Cyanide Hazardtext® HazardManagement, http://csi.micromedex.com/DATA/DT/DT12, TOMES Plus® System, 2003.
- 4. EPA National Recommended Water Quality Criteria: 2002, www.epa.gov/waterscience/pc/revcom.pdf, p. 13.
- 5. List of Drinking Water Contaminants and MCLs, U.S. EPA Groundwater and Drinking Water, www.epa.gov/safewater/mcl.html
- 6. New Jersey Department of Health and Senior Services, Cyanide Alert, May 11,2000,
- www.state.nj.us/health/lh/lincs/cyanidealrt.htm
  Toxicological Profile for Cyanide, US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, September 1997, http://www.atsdr.cdc.gov/tp8.html and http://www.atsdr.cdc.gov/tp8.pdf (as accessed 12/21/2003).

<sup>+</sup> See OCEPA (Source: http://www.epa.gov/OCEPATerms/ or listed reports.

HEALTH & ENVIRONMENTAL EFFECTS OF TRACE ELEMENTS IN METAL-MINING WASTES

# LEAD

# Quick Facts:

- Description: Lead (Pb) is a heavy, soft silvery-gray metal; elemental Pb is found in the earth's crust at 15-30 mg/kg, it can be bright silver with a bluish cast; dull gray when exposed to air
- Usage: plumbing/metal products, batteries, ammunition, x-ray shielding devices
- Drinking Water Standards: Current MCLG: zero (EPA) with 15 ppb Action Level
- EPA Classification: Probable human carcinogen; drinking water contaminant regulated by a treatment technique that requires systems to control the corrosiveness of their water. If more than 10% of tap water samples exceed the action level of 0.015 mg/L, water systems must take additional steps to eliminate it. Pb in air may not exceed 1.5  $\mu$ g/m<sup>3</sup>
- Chemistry: Symbol: **Pb**; CAS Number: 7439921; Class: Metal (Group IVA) naturally occurring inorganic element

**Hardrock Mining Facts**: Mined as sulfide ore and often associated with zinc ore deposits. The New Lead Belt in SE Missouri produced 88% of the lead mined in the US. 20<sup>th</sup> century. "Chat" piles (limestone and low-grade ore) in this area were placed in and near streams and are a source of water contamination today. MT, MO, AZ, and UT are among the top twelve states where facilities released greater than 100,000 lbs (1987-1993) of Pb. Lead dust can be a significant hazard at both mines and processing facilities. Total enclosure of ore processing and handling facilities is often required to avoid worker contamination.

**Background**: Pb is produced by smelting galena (PbS), a lead (II) sulfide ore; large quantities are used to make electrodes for storage batteries, in alloys for cable coverings and for solder (with tin). Pb in the environment is due to human activities such as refining and burning fossil fuels, mining, smelting, coal, gasoline, and manufacturing. Grounding of household electrical systems to plumbing may exacerbate corrosion of Pb plumbing, causing tap water contamination. Potential health risks occur from ingestion of Pb-contaminated water (including corrosion of household plumbing systems and erosion of natural deposits), breathing workplace air or dust from mining operations, or eating contaminated foods, soils, or lead-based paint.

### **Environmental Availability:**

- Air may travel thousands of kilometers from the originating source before settling to ground; particles larger than 2 micrometers settle closer to emission source
- Surface Water atmospheric fallout, runoff, and wastewater are major sources in waters; Pb binds to sediments
- Soil sticks to soil particles
- Groundwater movement into groundwater dependent on type of Pb compound and soil characteristics; usually Pb does not migrate to groundwater.

#### Fate:

- Persistence: Does not break down; compounds are changed by sunlight, air, and water
- Solubility: pure Pb has a low solubility in water (least soluble at pH 8-10); compounds vary in solubility; dissolves more easily at low pH
- Bioaccumulation: in plants and animals (does not accumulate in fish, but does in some shellfish, e.g., mussels; and mammal bones)

**Ecotoxicity:** Toxic to all aquatic organisms; as dissolved oxygen levels decrease, Pb increases in toxicity to fish. Toxicity increases if water is acidic or `soft.'

• Freshwater NRWQC - CCC: 2.5 µg/L; CMC: 65 µg/L

**Human Health Effects**: While no acute intermediate or chronic MRLs<sup>1</sup> have been derived for any route of exposure, ATSDR reports a framework to guide public health assessment decisions at lead sites (see Appendix D-1 Toxicological Profile for Lead, www.atsdr.cdc.gov/tp13.pdf) CDC defines elevated level for children as 10  $\mu$ g/dL (ppb) in the blood; greater than 125  $\mu$ g/dL, death results. When blood levels in children is greater than 90  $\mu$ g/dL, acute Pb toxicity occurs with ataxia, coma, and convulsions as symptoms. For adults, it is estimated that death occurs 1-2 days after ingestion of 10-30 g of a lead salt.<sup>2</sup> Pregnant women exposed to Pb can have premature births and smaller babies; infants and children are particularly sensitive to chronic effects of Pb, e.g., decreased mental ability, delays in physical/mental development; attention span deficits, learning disabilities. Chronic effects include stroke, kidney disease, kidney and brain damage, high blood pressure, nervous/reproductive system damage, decreased reaction time, weakness in fingers, wrists, ankles, and probable cancer (if lifetime exposure). Repeated exposure causes Pb to accumulate in human body. OSHA PEL = 0.05 mg/m<sup>3</sup>. EPA lists lead and inorganic compounds of lead as "B2" – a probable human carcinogen. Occupational exposure occurs mainly from breathing dust and fumes, with workers in smelting/refining, battery manufacture/reclamation at higher risk.

<sup>&</sup>lt;sup>1</sup> Toxicological Profile for Lead, US Department of Health and Human Services, ATSDR, www.atsdr.cdc.gov/toxprofiles/tp13.html (and pdf), July 1999.

<sup>&</sup>lt;sup>2</sup> Lead Hazardtext®-Hazard Management – <u>http://csi.micromedex.com/DATA/DT/DT61.htm</u>, p. 12, as accessed November 2003.

# HEALTH & ENVIRONMENTAL EFFECTS OF TRACE ELEMENTS IN METAL-MINING WASTES

# LEAD

Terms<sup>†</sup>:

**Acid Mine Drainage**: Low pH water drainage from areas that have been mined for coal or other mineral ores. Contact with sulfur-bearing material causes the low pH and the water is harmful to aquatic organisms.

*Action Level*: A contaminant concentration in the environment high enough to warrant action or trigger a response under SARA and the National Oil and Hazardous Substances Contingency Plan.

ATSDR: Agency for Toxic Substances and Disease Registry.

*Bioaccumulation*: The extent to which substances increase in concentration in contaminated air, water or food because the substances are very slowly metabolized or excreted.

*CCC*: Criterion Continuous Concentration – an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

CDC: Centers for Disease Control.

*CMC*: Criterion Maximum Concentration - an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.

*MCL*: Maximum contaminant level – an enforceable EPA standard for drinking water contamination.

*MCLG*: Maximum contaminant level goal – a non enforced EPA public health goal; the drinking water contaminant level below which the risk to health is either not known or expected.

*MRL*: Minimal Risk Level - an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse noncancer health effects over a specified duration of exposure.

NRWQC: National Recommended Water Quality Criteria (EPA)

OSHA: Occupational Safety and Health Administration

PEL: airborne permissible exposure limit

*Persistence*: The length of time a compound stays in the environment.

*SMCL*: Secondary maximum contaminant level – non enforced EPA guidelines to manage water for aesthetic considerations (taste, color, odor).

*Solubility*: The amount of mass of a compound that will dissolve in a unit volume of solution.

### FOR FURTHER INFORMATION:

- 1. Consumer Factsheet on Lead, US EPA, www.epa.gov/safewater/dwh/c-ioc/lead.html
- 2. ToxFAQs for Lead, Agency for Toxic Substances and Disease Registry, (www.atsdr.cdc.gov/tfacts13.html)
- 3. Lead and compounds (inorganic) (CASRN 7439-92-1), EPA, http://www.epa.gov/iris/subst/0277.htm
- 4. Lead Compounds, EPA, http://www.epa.gov/ttn/atw/htlthef/lead.htm
- 5. Lead Hazardtext® Hazard Management http://csi.micromedex.com/DATA/DT/DT61.htm, p. 12.
- 6. List of Drinking Water Contaminants and MCLs, U.S. EPA Groundwater and Drinking Water, www.epa.gov/safewater/mcl.html
- 7. National Recommended Water Quality Criteria: 2002 EPA, www.epa.gov/waterscience/pc/revcom.pdf
- 8. New Jersey Department of Health and Senior Services, Hazardous Substance Fact Sheet, Lead, www.state.nj.us/health/eoh/rtkweb/0196.pdf
- 9. Toxicological Profile for Lead, US Department of Health and Human Services, ATSDR, www.atsdr.cdc.gov/toxprofiles/tp13.html (and pdf), July 1999.
- <sup>+</sup> Source: http://www.epa.gov/OCEPATerms

HEALTH & ENVIRONMENTAL EFFECTS OF TRACE ELEMENTS IN METAL-MINING WASTES

# MERCURY

### Quick Facts:

- Description: Mercury (Hg) is a naturally occurring element silvery white liquid; also found as cinnabar (HgS)
- Usage: manufacture of electrical instruments, fungicides, pharmaceuticals, munitions, paper production, extraction
  of gold in mining
- Drinking Water Standards: 0.002 mg/L MCLG; 0.002 mg/L MCL (inorganic)
- EPA Classification: neurotoxin; FDA Classification: 1 ppm seafood; OSHA Classification: 0.1 mg/cm<sup>3</sup> organic Hg;
   0.05 mg/cm<sup>3</sup> metallic Hg vapor
- Chemistry: Symbol: Hg (elemental); CH<sub>3</sub>Hg<sup>+</sup> (methyl-mercury); Hg(II) (ionic); CAS Numbers: (Hg): 7439976; (CH<sub>3</sub>Hg<sup>+</sup>): 22967926; Class: Heavy (transition) metal, Group IIB

**Hardrock Mining Facts:** Hg is no longer mined as a primary mineral, but is produced as a byproduct of processing other minerals, mainly in the processing of gold. Abandoned mercury mines are often explored as potential gold deposits. Historically used in extraction of gold for mining. Placer gold mines can be heavily contaminated with Hg, which was used in processing. Hg is most toxic when converted to methyl-mercury via biotransformation by organic materials. High levels in fish, amphibians, and invertebrates downstream from mines persist, especially where a decrease in pH and/or dissolved oxygen content results in increased mobility of Hg, making it more likely to enter food chain. Treatment technologies, for concentrations less than 10  $\mu$ g/L, include: coagulation/filtration, granular activated carbon, lime softening, and reverse osmosis.

**Background**: Natural sources: volcanoes, volatilization from oceans and erosion of natural deposits and subsequent contamination of waters. Mercury released from human activities has been estimated to be 1/3-2/3 of the total mercury released into the environment. Man-made sources include: stack losses from cinnabar roasting, the working and smelting of metals, and coal fired power plants; discharges from mines, refineries and factories, combustion of coal and municipal wastes, industrial wastes and boilers, medical waste incinerators, pesticides, runoff from landfills/croplands. Sulfate-reducing bacteria uptake inorganic Hg, converting it to  $CH_3Hg^+$  via methylation to eliminate toxic Hg through their cells walls (and into the environment). Species such as  $[Hg(CH_3)_2]$  and  $[HgCH_3]^+$  enter the food chain because they readily penetrate cell walls.

Environmental Availability: Hg undergoes volatilization and biotransformation

- Air: Volatile; widespread (transported hundreds of miles from source) air pollution and rainfall deposits Hg in lakes and other water bodies
- Surface Water: Diffuses throughout water column, particle settling and sinks to sediments, re-volatilize back to atmosphere, rapidly recycles from sediment, to water, to air, and back again; methylation process occurs
- Soil: adsorbs to soil particles; methylation process occurs
- Groundwater: Hg contamination of groundwater is of potential concern because a very low level of Hg contamination can cause human health impacts.

**Fate:** Hg undergoes biogeochemical cycling: it degasses from soils and surface waters, is transported through the atmosphere, deposits on land and surface waters, is sorbed into soil and sediment particulates, and degasses, etc.

- Persistence: can change form, cannot be destroyed
- Solubility: Cinnabar (HgS) is insoluble (and resists weathering); liquid Hg is slightly soluble in water.
- Bioaccumulation: Hg Methylation forms CH<sub>3</sub>Hg<sup>+</sup> which is easily absorbed by organisms and biomagnifies from the bottom to the top of the food chain; concentrates in muscle and tissue of fish and other wildlife, which bioaccumulate it. CH<sub>3</sub>Hg<sup>+</sup> generally increases by a factor of ten or less with each step up the food chain. Bioaccumulation factors of 63,000 for freshwater fish, 10,000 for salt water fish, 100,000 for marine invertebrates, and 1000 for freshwater and marine plants have been found.

**Ecotoxicity**: 0.012 mg/L instream concentration results in chronic effects to aquatic life; concentrations of Hg(0), Hg(II), or  $CH_3Hg^+$  may be low in streams, but due to bioaccumulation and biomagnification,  $CH_3Hg^+$  in fish may be toxic to humans and fish-eating wildlife (such as bald eagles). When Hg and Se interact in various species of wildlife, both antagonistic and synergistic effects have been observed.

- Hg Freshwater NRWQC CCC: 0.77 μg/L; CMC: 1.4 μg/L
- Toxicity Thresholds (NIWQP)
- Fish (cold-water species) (mg/kg ww): 1.0
- Birds, diet (mallards) (mg/kg bw/day: 0.064; loons: 0.3

**Human Health Effects**:  $CH_3Hg^+$  is a neurotoxin and is the most toxic form; consuming Hg contaminated water/wildlife and fish can result in kidney, brain, cardiovascular damage/death. People uptake Hg as  $CH_3Hg^+$  or breathe vapors emitted from metallic Hg, dental amalgams, and ambient air (OSHA PEL=0.1 mg/m<sup>3</sup>). Prenatal effects occur at levels 5-10 times lower than that of adults. The MRL<sup>1</sup> for Hg, for chronic inhalation is 0.0002 mg/m<sup>3</sup> (or 0.2 µg/m<sup>3</sup>). The chronic oral MRL for methyl mercury for a 70 kg adult is 0.0003 mg/kg/day.<sup>2</sup>

<sup>2</sup> Ibid.

<sup>&</sup>lt;sup>1</sup> Minimal Risk Levels for Hazardous Substances (MRL) – http://www.atsdr.cdc.gov/mrls.html.

## HEALTH & ENVIRONMENTAL EFFECTS OF TRACE ELEMENTS IN METAL-MINING WASTES

# MERCURY

### Terms<sup>†</sup>:

*Acid Mine Drainage*: Low pH water drainage from areas that have been mined for coal or other mineral ores. Contact with sulfurbearing material causes the low pH and the water is harmful to aquatic organisms.

Action Level: A contaminant concentration in the environment high enough to warrant action or trigger a response under SARA and the National Oil and Hazardous Substances Contingency Plan.

Antagonism: Two contaminants nullify each other's toxicity.

ATSDR: Agency for Toxic Substances and Disease Registry.

*Bioaccumulation*: The extent to which substances increase in concentration in contaminated air, water or food because the substances are very slowly metabolized or excreted.

Biomagnification: The incremental increase in a contaminant's concentration at each level of the food chain.

*CCC*: Criterion Continuous Concentration – an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

CDC: Centers for Disease Control.

*CMC*: Criterion Maximum Concentration – an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.

*MCL*: Maximum contaminant level – an enforceable EPA standard for drinking water contamination.

*MCLG*: Maximum contaminant level goal – a non enforced EPA public health goal; the drinking water contaminant level below which the risk to health is either not known or expected.

**NIWOP**: National Irrigation Water Quality Program Information Report No. 3 (US Department of the Interior).

OSHA: Occupational Safety and Health Administration

PEL: Airborne permissible exposure limit

Persistence: The length of time a compound stays in the environment.

*SMCL*: Secondary maximum contaminant level – non enforced EPA guidelines to manage water for aesthetic considerations (taste, color, odor).

*Solubility*: The amount of mass of a compound that will dissolve in a unit volume of solution.

*Synergism*: Two contaminants magnify each other's toxicity.

*Toxicity Threshold*: Concentrations exceeding this level seem to cause some adverse effects, including reproductive impairment and sublethal impacts.

#### FOR FURTHER INFORMATION:

- 1. Environmental Geochemistry of Mercury Mines in Alaska, USGS, http://pubs.usgs.gov/fs/fs-0072-94
- 2. EPA Factsheet Update: National Listing of Fish and Wildlife Advisories, EPA, http://www.epa.gov/waterscience/fish/adviseries/factsheet.pdf
- 3. List of Drinking Water Contaminants and MCLs, U.S. EPA Groundwater and Drinking Water, www.epa.gov/safewater/mcl.html
- 4. Mercury, EPA, http://www.epa.gov/mercury/health.htm
- 5. *Mercury and Selenium Poisoning: When 1 + 1 = 2*. USGS, http://www.pwre.usgs.gov/factshts/15mersel.pdf
- 6. Mercury Contamination from Historic Gold Mining in California, USGS, http://ca.water.usgs.gov/mercury/fs06100.html
- 7. Mercury Contamination of Aquatic Ecosystems, USGS, http://wi.water.usgs.gov/pubs/FS-216-95
- 8. Mercury Health Hazards, NIH, http://www.nih.gov/od/ors/ds/nomercury/health.htm
- 9. *Mercury in the Environment*, USGS, http://www.usgs.gov/themes/factsheet/146-00
- 10. New Jersey Department of Health and Senior Services, Hazardous Substance Fact Sheet, Mercury, www.state.nj.us/health/eoh/rtkweb/1183.pdf
- 11. U.S. Department of the Interior, National Irrigation Water Quality Program, Information Report No. 3, Guidelines for Interpretation of the Biological Effects of Selected Constituents in Biota, Water, and Sediment: Mercury, www.usbr.gov/niwqp/guidelines/mercury.pdf, p. 91-113.
- 12. Sources of Mercury, NIH, http://www.nih.gov/od/ors/ds/nomercury/environment.htm
- 13. Technical Factsheet on Mercury, US EPA, www.epa.gov/safewater/dwh/t-ioc/mercury.html
- 14. ToxFAQs for Mercury, Agency for Toxic Substances and Disease Registry (www.atsdr.cdc.gov/tfacts46.html)
- 15. Toxicological Profile for Mercury, US Department of Health and Human Services, ATSDR, www.atsdr.cdc.gov/toxprofiles/tp46.html
- <sup>+</sup> Source: <u>http://www.epa.gov/OCEPATerms</u> and listed references

HEALTH & ENVIRONMENTAL EFFECTS OF TRACE ELEMENTS IN METAL-MINING WASTES

# SELENIUM

### Quick Facts:

- Description: Selenium (Se) is a semi-metallic element with an average crustal abundance of 0.05 mg/kg, and commonly
  occurring mixed with sulfide ores. Most common forms in natural waters are Se<sup>4+</sup> (selenite) and Se<sup>6+</sup> (selenate)
- Usage: Metal alloys, petroleum, rubber, pigments in glass, dye and paint, mineral supplement for humans, livestock and poultry. Gray Se is a photoconductor and is used to make photoelectric cells and rectifiers for electronic equipment. Also used in photography, xerography and telephotography.
- Drinking Water Standards: MCLG: 0.05 ppm (0.05 mg/L); MCL: 0.05 ppm (0.05 mg/L)
- EPA Classification: EPA Priority Pollutant ; NRWQC Freshwater CCC: 5 μg/L
- Chemistry Symbol: Se, CAS Number: 7782492; Class: Semi-metallic trace element; Group VIA element

**Hardrock Mining Facts:** Se typically does not occur in pure elemental form. It is a trace element found in natural deposits such as ores containing other minerals, having no true geologic deposits and occurs in sulfide ores of heavy metals. It is the most strongly enriched trace element in coal. Se is obtained from the flue dusts from the roasting of sulfide ores and from the anode mud formed by the electrolytic refining of Cu. It is a common waste product from uranium, bentonite, and coal mining. Soils, surface waters, and ground waters around mining operations can become contaminated. May also be concentrated in coal deposits and carbonaceous shales. Mining operations increase the element's mobility and solubility. Treatment technologies include: activated alumina, coagulation/filtration (Se[VI] only), lime softening, reverse osmosis, electrodialysis.

**Background**: Traces of Se are naturally found in most waters and soils. In community drinking water, concentrations range from 0-0.01 ppm. Se is released to air when coal and petroleum fuels are combusted and during metal smelting and refining (especially copper). In its oxidized form and in alkaline soils, it is highly mobile and biologically active. Plants uptake it. Widely distributed in rocks, soils, water and living organisms. Irrigation drainage return flow can increase Se concentrations in rivers, wetlands, and lakes. Se is also found in neutral drainage from mining waste rock. Se dioxide is the primary source of health problem from industrial exposures; it forms selenous acid, an irritant, with water/sweat.

## **Environmental Availability:**

- Air Se dust is airborne and settles out on land/water; Se particles may bind to other particles or fly ash; Se dioxide, produced from burning fossil fuels, may form selenous acid in water.
- Surface Water Se in fresh water is usually 0.02 ppm; Se content is greatly influenced by pH; high in acidic (pH <3) and alkaline (pH >7.5).
- Soil Volatilizes from soil upon conversion by microorganisms to volatile Se compounds
- Groundwater can be become contaminated with leached Se

#### Fate:

- Persistence: cannot be destroyed
- Solubility: both insoluble and soluble forms; Selenite and selenate are the predominant aqueous species.
- Bioaccumulation: bioaccumulates up the food chain in living tissues; may biomagnify in aquatic organisms.

**Ecotoxicity**: Se typically occurs as oxidized form in alkaline soils making it biologically active; less toxic to plants and invertebrates than vertebrates. Causes congenital deformation and death in birds and fish (which have similar toxicity thresholds for Se). Overt deformities, reproductive failure, cachexia in wildlife. Se contamination caused by irrigation has been observed in arid/semi arid climates. When Hg and Se interact in various species of wildlife, both antagonistic and synergistic effects are observed. Se more poisonous than As and Hg. The threshold of ecotoxicity for Se is similar for fish and birds (NIWQP). Se is toxic to livestock when they eat locoweed/milkvetch; both concentrate Se

#### Toxicity Threshold (NIWQP)

- Fish (mg/kg dw): > 4 (warm and cold water species); Waterbird eggs (mg/kg dw): > 6
- Freshwater NRWQC CCC: 5.0 µg/L; CMC: none

**Human Health Effects:** Too much or too little Se has adverse effects for most people. While Se is an essential nutrient at low levels (Adult RDA= 400 mg/d), at levels above the MRL, some chronic and short term effects include damage to peripheral nervous system, skin lesions, hair and fingernail loss and changes, fatigue, irritability. Keshan Disease (a form of juvenile cardiomyopathy), and Kashin-Beck Disease (a form of abnormal bone growth) affects people who live in areas with abnormally low levels of Se. In drinking water, the MCLG has been set at 0.05 ppm (US EPA). The MRL is oral chronic 0.005 mg/kg/day.<sup>1</sup> Brief exposures to high levels cause respiratory tract irritation, bronchitis, difficulty breathing, and stomach pains. OSHA exposure limit for Se compounds in air is 0.2 mg/cm<sup>3</sup>.

<sup>&</sup>lt;sup>1</sup> Minimal Risk Level for Hazardous Substances, US Department of Health and Human Services, ATSDR, http://www.atsdr.cdc.gov/mrls.html.

# HEALTH & ENVIRONMENTAL EFFECTS OF TRACE ELEMENTS IN METAL-MINING WASTES

# SELENIUM

## Terms<sup>†</sup>:

Acid Mine Drainage: Low pH water drainage from areas that have been mined for coal or other mineral ores. Contact with sulfurbearing material causes the low pH and the water is harmful to aquatic organisms.

Action Level: A contaminant concentration in the environment high enough to warrant action or trigger a response under SARA and the National Oil and Hazardous Substances Contingency Plan.

Alkaline: Having a pH greater than 7 (basic).

Antagonism: Two contaminants nullify each other's toxicity.

*Bioaccumulation*: The extent to which substances increase in concentration in contaminated air, water or food because the substances are very slowly metabolized or excreted.

Biomagnification: The incremental increase in a contaminant's concentration at each level of the food chain.

Cachexia: A condition of starvation and wasting (even though food may be abundant).

#### CDC: Centers for Disease Control.

**Freshwater CCC** – National Recommended Water Quality Criteria for Priority Toxic Pollutants – CCC is the Criterion Continuous Concentration, an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

*MCL*: Maximum contaminant level – an enforceable EPA standard for drinking water contamination.

*MCLG:* Maximum contaminant level goal – a non enforced EPA public health goal; the drinking water contaminant level below which the risk to health is either not known or expected.

MRL: Minimal Risk Level (US Department of Health and Human Services)

NIWOP: National Irrigation Water Quality Program

**NRWQC**: National Recommended Water Quality Criteria for Priority Toxic Pollutants (EPA)

*Persistence*: The length of time a compound stays in the environment.

Photoconductor: A material that is a good conductor of electricity when light falls upon it.

**RDA**: Recommended Dietary Allowance

*SMCL*: Secondary maximum contaminant level – non enforced EPA guidelines to manage water for aesthetic considerations (taste, color, odor).

*Solubility*: The amount of mass of a compound that will dissolve in a unit volume of solution.

*Synergism*: Process wherein two contaminants magnify each other's toxicity.

### FOR FURTHER INFORMATION:

- 1. Consumer Fact Sheet on Selenium, EPA, www.epa.gov/OGWDW/dwh/c-ioc/selenium.html
- 2. EPA Factsheet Update: National Listing of Fish and Wildlife Advisories, EPA, http://www.epa.gov/waterscience/fish/adviseries/factsheet.pdf
- 3. Food and Nutrition Information Center, Dietary Reference Intakes and Recommended Dietary Allowances, NIH Clinical Center, <u>www.cc.nih.gov/ccc/supplements/selen.html/#rda</u> and <u>www.nal.usda.gov/fnic/etext/000105.html</u>
- 4. Hazardous Trace Elements in Petroleum Source Rock, <u>http://wrgis.wr.usgs.gov/wreg/env/faq.html</u>
- 5. List of Drinking Water Contaminants and MCLs, U.S. EPA Groundwater and Drinking Water, www.epa.gov/safewater/mcl.html
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+ Source: http://www.epa.gov/OCEPATerms

### HEALTH & ENVIRONMENTAL EFFECTS OF TRACE ELEMENTS IN METAL-MINING WASTES

# ZINC

# Quick Facts:

- Description: Zinc (Zn) is a bluish-white shiny metal; pure Zn is rarely seen in nature, because Zn is highly reactive. Most common zinc ore is sphalerite (or zinc blende), ZnS
- Usage: protective coatings of iron and steel with zinc and cadmium for rust prevention; in dry cells, as metal alloys (US penny, with Cu); compounds are used to make paint, rubber, dye, wood preservatives, and ointments; Zn oxide is used for photoconductive surfaces in photocopiers
- EPA Drinking Water Standards and Status: Secondary standard: 5 ppm (mg/L) drinking water contaminant
- Chemistry Symbol: **Zn**; CAS Number: 7440666; Class: metal, Group IIB element

**Hardrock Mining Facts**: Most common ore is sphalerite which is roasted to form zinc oxide, then heated with coke to produce a vapor that is condensed to form the solid metal upon freezing. Residuals from smelting produce waste rock, mill tailings, furnace slag, and flue dust. High concentrations of Zn (Cd, Cu, Pb and As) in rivers resulting from metal extraction have adversely affected fisheries in more than 21,0000 km of rivers. Zinc from mines/mineral deposits is easily dissolved into surface and ground waters. For example, acid mine drainage from Iron Mountain Mine and Penn Mine, both in CA, have resulted in numerous fish kills; during a fish kill in the Mokelumne River in 1958, zinc concentrations of 1.4 mg/L were measured 6.4 km downstream from the mine.

**Background**: Zn is widespread in the environment (mean surface soil concentrations = 64 mg/kg; background concentrations in soils/sediments = 200 mg/kg; in fresh water, < 40-60  $\mu$ g/L). Some Zn is released by natural processes; artificial sources include mining and smelting operations, steel production, electroplaters, smelting and ore processes, acid mine drainage, domestic and industrial sewage, road surface runoff, corrosion of zinc alloys and galvanized surfaces, erosion of agricultural soils, and coal and waste burning.

## **Environmental Availability:**

- Air Attaches to dust particles in air; can be removed by rain/snow and falls to earth
- Surface Water Compounds can move into lakes, streams, rivers; most Zn is eventually deposited in sediments; In acidic waters, Zn is present is Zn<sup>2+</sup>; in soft waters, as ZnOH<sup>+</sup>.
- Soil Most Zn stays bound to soil particles; sulfides immobilize Zn
- Groundwater Compounds can move into groundwater

### Fate:

- Persistence: Cannot be broken down
- Solubility: Zn metal is not soluble; some compounds of Zn are water soluble
- Bioaccumulation: varies greatly; BCF for insects ~ 107-1,130; BCF fish ~51-432

**Ecotoxicity** Mixtures of Cu and Zinc are known to be additive or synergistic in toxicity to many aquatic organisms (NIWQP, p. 52, 190). Other metals that are additive to zinc in toxicity are lead and nickel; cadmium is known to be antagonistic to zinc (NIWQP, p. 190). Zn toxicity in water is affected by hardness, pH, temperature, dissolved oxygen, and alkalinity. Dissolved Zn is toxic to fish.

• Freshwater NRWQC - CCC: 120 μg/L; CMC: 120 μg/L

### Toxicity Thresholds (NIWQP - mg/kg dw)

- Plants: > 300; oak/maple seedlings died when Zn soil levels were > 100 mg/kg dw
- Fish, white sucker muscle tissue: 20
- Birds, liver/kidney: > 2,100
- Mammals, Kidney: >274; Liver: >465

**Human Health Effects**: Low levels of Zn are essential for maintaining good health: RDA for adults = 8 mg/day (females); 11 mg/day (males); too little and too much Zn are harmful to health. Inhalation or contact with decomposition products, vapors, or substance may cause death or severe injury. Signs of deficiency include growth retardation, hair loss, diarrhea, delayed sexual maturation, eye and skin lesions (slow wound healing), damaged immune system, and loss of appetite. Zn toxicity has acute and chronic forms: 150-450 mg have been associated with low copper status, altered iron function, reduced immune function. Eating large amounts, even for a short time, causes stomach cramps, nausea, and vomiting; chronic use can cause anemia, pancreas damage, and lower levels of high density lipoprotein cholesterol (the good form of cholesterol). Breathing zinc dust or fumes causes `metal fume fever'; OSHA PEL for Zinc chloride fumes = 1 mg/m<sup>3</sup>; PEL for Zinc oxide fumes=5 mg/m<sup>3</sup>. An MRL of 0.3 mg/kg/day (Oral, Intermediate duration (15-364 days) and 0.3 mg/kg/day, chronic (365 days or more) has been derived.<sup>1</sup>

<sup>&</sup>lt;sup>1</sup> Minimal Risk Levels for Hazardous Substances (MRLs) – Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services, http://www.atsdr.cdc.gov/mrls.html, as accessed 12/21/2003.

# HEALTH & ENVIRONMENTAL EFFECTS OF TRACE ELEMENTS IN METAL-MINING WASTES

# ZINC

### Terms<sup>†</sup>:

Acid Mine Drainage: Low pH water drainage from areas that have been mined for coal or other mineral ores. Contact with sulfurbearing material causes the low pH and the water is harmful to aquatic organisms.

Action Level: A contaminant concentration in the environment high enough to warrant action or trigger a response under SARA and the National Oil and Hazardous Substances Contingency Plan.

Antagonism: Two contaminants nullify each other's toxicity.

**BCF**: Bioconcentration factors (NIWQP)

*Bioaccumulation*: The extent to which substances increase in concentration in contaminated air, water or food because the substances are very slowly metabolized or excreted.

Biomagnification: The incremental increase in a contaminant's concentration at each level of the food chain.

*CCC*: Criterion Continuous Concentration – an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

*CMC*: Criterion Maximum Concentration – an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.

**CDC**: Centers for Disease Control.

dw: dry weight

Freshwater NRWQC: National Recommended Water Quality Criteria for priority toxic pollutants (EPA)

*MCL*: Maximum contaminant level – an enforceable EPA standard for drinking water contamination.

*MCLG*: Maximum contaminant level goal – a non enforced EPA public health goal; the drinking water contaminant level below which the risk to health is either not known or expected.

*MRL*: Minimal Risk Level – an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse noncancer health effects over a specified duration of exposure.

**NIWOP**: National Irrigation Water Quality Program Information Report No. 3 (U.S. Department of the Interior)

*Persistence*: The length of time a compound stays in the environment.

OSHA: Occupational Safety and Health Administration.

RDA: Recommended dietary allowances (grams/day).

**Secondary Standard**: An EPA classification (also known as the National Secondary Drinking Water Regulations [NSDWRs] that is a non-enforceable guideline regulating contaminants that may cause cosmetic effects (skin or tooth discoloration) or aesthetic effects (taste, color, odor) in drinking water

*SMCL*: Secondary maximum contaminant level – non enforced EPA guidelines to manage water for aesthetic considerations (taste, color, odor).

*Solubility*: The amount of mass of a compound that will dissolve in a unit volume of solution.

Synergism: An interaction of two or more chemicals that results in an effect greater than the sum of their separate effects.

#### FOR FURTHER INFORMATION:

- 1. EPA National Recommended Water Quality Criteria: 2002, www.epa.gov/waterscience/pc/revcom.pdf, p. 13.
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- 9. Zinc Hazardtext® HazardManagement, http://csi.micromedex.com/DATA/DT/DT892, TOMES Plus® System, 2003.

<sup>+</sup> See OCEPA (Source: http://www.epa.gov/OCEPATerms/ or listed reports.