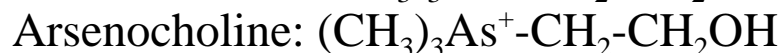


## Issue #3: Arsenic

- 20th most abundant element in Earth's crust, but few uses
- toxic: essentially no known role as micronutrient
- unlike Hg and Pb, organoarsenicals are less toxic than inorganic arsenic
- seaweeds contain various arseno-sugars (little known about their toxicity)
- Shellfish contain arsenobetaine and the related arsenocholine; these are non-bioavailable, water-soluble, and hence readily excreted.

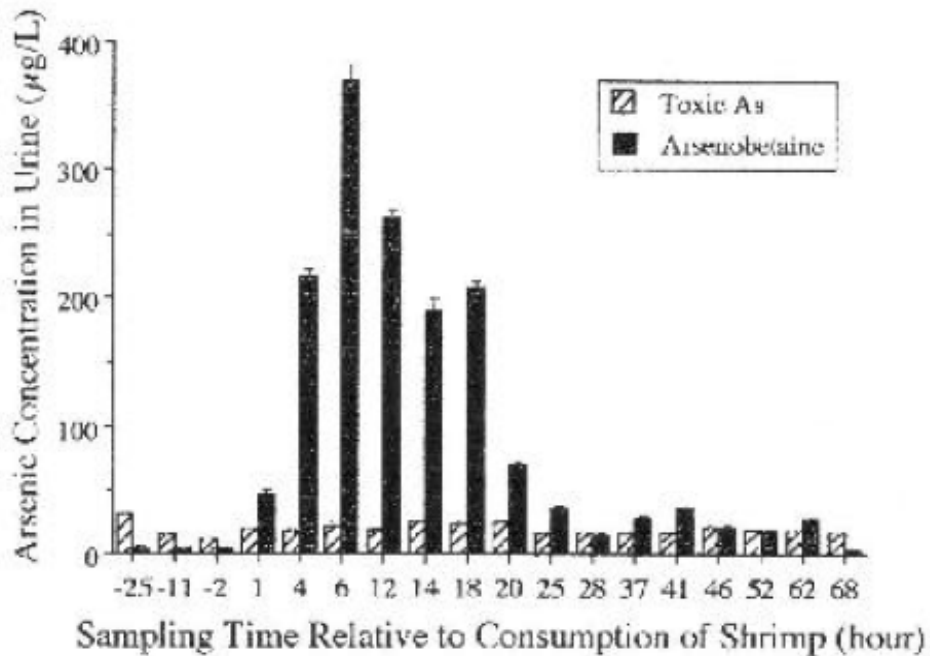


## Canadian exposure to arsenic

(Canadian Chemical News, September 1999, p. 18)

- Food, usually < 0.04 mg/day in North America
- With high seafood, up to 0.2 mg/day (mostly “non-toxic” forms).
- **Food:**
  - fish 1700 ng/g
  - meat, poultry, cereals, fats 20 ng/g
  - shellfish ~20 :g/g
  - e.g., 1 lobster meal could give ingestion of 5 mg of As, but principal form is the relatively non-toxic arsenobetaine

Arsenic is excreted rapidly:



- **Water:** Maximum Canadian contaminant level 25 µg/L suggests < 50 µg/day
  - “old” WHO guideline = North American standard/guideline = 50 µg/L
  - “new” WHO guideline = 10 µg/L
  - controversy in US over implementation of new standard because many DW sources (and many mine effluents) have  $10 < [As] < 50$  ppb. Removal of As to 10 ppb would be very expensive: what technology??

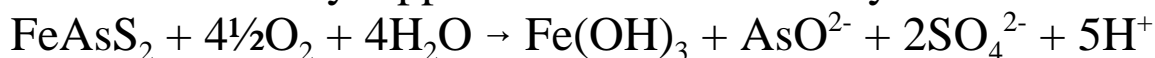
**Issues in many parts of Asia** (West Bengal, Bangladesh, Taiwan, Vietnam: Chem. Eng. News, December 6, 1999, pp.128-131)

- 1970s: UNICEF program to provide new wells; success in reducing water-borne disease
- 1990s: thousands of cases of skin disorders (clinical sign of arsenicosis), fatigue/lethargy; cancers
- levels up to 1-5 mg/L; no good (cheap) methods for arsenic removal
- difficulty of analysis for As (no simple test)
  - occurs in water as arsenite (As(III) =  $\text{AsO}_2^-$ ) and arsenate (As(V) =  $\text{AsO}_4^{3-}$  and protonated species, like  $\text{PO}_4^{3-}$ )

### **Origin of arsenic in water**

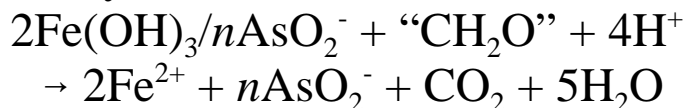
- naturally occurring arsenopyrite ( $\text{FeAsS}_2$ ) is the usual source
- details of the solubilization chemistry are unclear and controversial

Oxidation chemistry: approximate stoichiometry



However,  $\text{Fe}(\text{OH})_3$  adsorbs inorganic arsenic quite strongly

Reduction chemistry, anaerobic conditions in sediments



Significance of this controversy (New Scientist, February 12,

2000, pp. 16-17):

- If oxidation chemistry predominates, dig the wells deeper
- If reduction chemistry predominates, deeper wells mean more anaerobic conditions

### Metabolites

- Major metabolites from inorganic As in human urine:
  - unchanged inorganic forms, 20-25%
  - monomethylated As,  $\text{CH}_3\text{AsO}(\text{OH})_2$ , MMA, 20%
  - dimethylarsinic acid  $(\text{CH}_3)_2\text{As}(\text{O})\text{OH}$ , DMA, 40-60%, also called cacodylic acid
- For As compounds, methylation is a detoxification mechanism
- Rat LD50's (Canadian Chemical News, Sept. 1999, p.18)

$\text{AsO}_2^-$ (arsenite, As(III))	14 mg/kg
$\text{AsO}_4^{3-}$ (arsenate, As(V))	20
$\text{CH}_3\text{AsO}(\text{OH})_2$ (methylarsonic acid)	700-1800
$(\text{CH}_3)_2\text{AsO}(\text{OH})$ (dimethylarsinic acid)	700-2600
arsenocholine	6500
arsenobetaine	>10,000

## **Uptake**

- Efficient (95%) oral uptake of soluble inorganic As
- Low availability from insoluble salts (lead arsenate, arsenic sulfide), and from As in soil.
- Inorganic As: colourless, tasteless; a favourite potion for poisoners until the development of the “Marsh test” (1836) in which As compounds reduced to arsine ( $\text{AsH}_3$ ) which was decomposed in a capillary to (black) As metal. Length of black deposit " As concentration.

## **Inhalation toxicology**

- Dusts of  $\text{As}_2\text{O}_3$  are the commonest form in air
- Emphasis is on  $\text{As}_2\text{O}_3$  (metal smelters, since As minerals occur along with many metal ores, e.g.,  $\text{FeAsS}_2$ )
- Chronic animal studies and human epidemiological studies (workers at Chilean copper smelters, 1995) → clear evidence of increased risk of lung cancer
- Uptake: Although exposure estimates have uncertainty, workers exposed to  $\text{As}_2\text{O}_3$  in smelters absorb 40-60% of the amount inhaled. Most (80%) of the  $\text{As}_2\text{O}_3$  deposited in the lung is then absorbed.
- Time weighted TLV =  $0.5 \text{ mg/m}^3$  “Canadian content”
- Bankrupt Royal Oak Giant gold mine (Yellowknife): As sulfides →  $\text{As}_2\text{O}_3$ . ~ 200,000 tonnes  $\text{As}_2\text{O}_3$  presently buried in the mine + ~ 40,000 tonnes As in tailings ponds  
<http://www.carc.org/whatsnew/cleanup.htm>

## **Effects**

- Doses of 0.05-0.5 mg/kg/day for weeks or months → GI upset. Symptoms disappear after exposure ceases
- Acute high doses 6 neurotoxin: encephalopathy; clinical signs confusion, impaired memory, emotional upset. Peripheral neuropathy from lower doses, numbness, pins and needles at first; later, loss of reflexes and weakness
- Dermal effects: hyperkeratosis, hyperpigmentation, warts and corns on the soles and palms which may lead to squamous cell carcinoma
- Long term oral exposure ~0.02 mg/kg/day in drinking water also → skin cancer, also lung, bladder, liver. Not understood why pulmonary and oral cause cancer at different sites.

## **Metabolism and mechanism of action**

- Problem of finding suitable animal model for human toxicity
- Humans more susceptible to As intoxication than lab animals

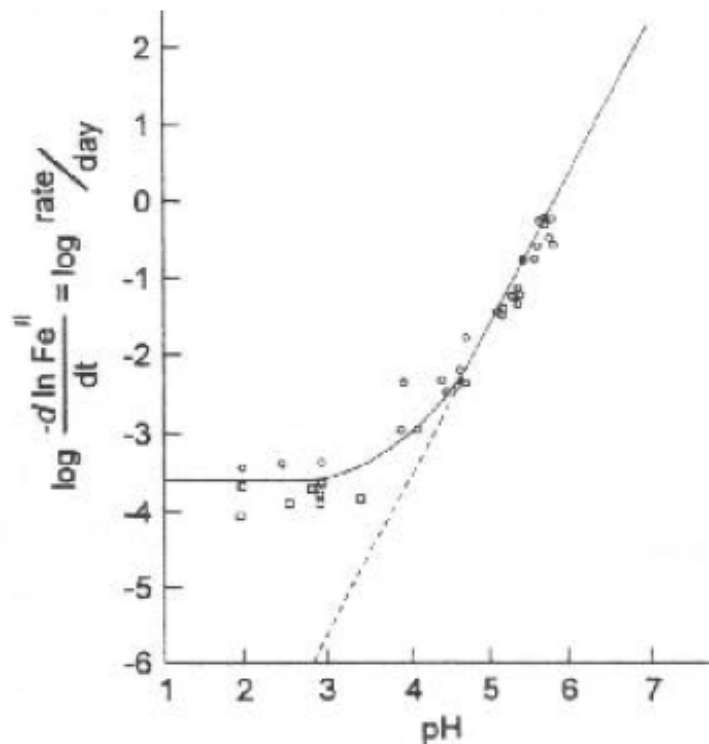
## **Biomarkers for exposure**

- Analysis of hair and fingernails (Mee's lines = transverse white lines) allows estimation of past exposure, since fingernails grow ~0.3 cm/month. Important to avoid surface contamination
- Analysis of blood does not give useful data.
- No preferential accumulation in specific organs. Some deposition of As(V) in bone (analog of phosphate)

CHEM/TOX 336 - W05  
Week12-7

## Issue #4: Acid Mine Drainage (AMD)

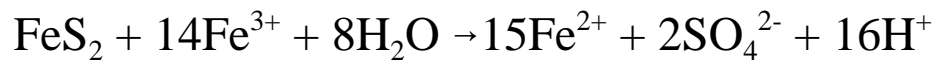
- Major problem, Canada and elsewhere, (abandoned) mine sites – both metal ore mines and coal mines
- Biological origin of AMD – microbial oxidation of sulfides  
 $\text{FeS}_2(\text{s}) + 3\frac{1}{2}\text{O}_2(\text{g}) + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$
- AMD problems are:
  - toxicity due to low pH
  - toxicity due to solubilization of metals Cu, Pb, Zn, Cd, Ni etc
  - deposition of  $\text{Fe}(\text{OH})_3$  downstream



Oxidation of Fe(II) as a function of pH

## Dimensions of the AMD problem

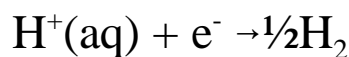
- The Clark-Fork site, Montana (see text) 50,000 acres, contaminated with As, Cu, Cd, Pb, Zn from 100 years of mining
- Richmond Mine, Iron Mountain, California: in the subsurface, extreme acidity pH to  $-3.6!!!$  and metal concentrations to 200g/L,  $\text{SO}_4^{2-}$  to 760 g/L (Environ. Sci. Technol., 2000, 34, 254) — the most acidic environmental water known
- Proposed sequence of events:
  - $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  by conventional AMD formation and oxidation
  - further reaction by exothermic process below



- heat released evaporates water and increases concentrations of all solutes

## AMD remediation

- Exclude air through:
  - submersion of tailings
  - cover the tailings with soil and grow grass
- Cathodic protection of the ore body using sacrificial Fe or Zn anode
- Remediate seepage via:
  - neutralization, usually with limestone: sludge handling problems, repeated treatment required
  - Neutralization: anoxic limestone drains (ALDs): how long will they last?
  - wetlands as filters: remove metals by precipitation and/or biomass incorporation; how long before they become choked?
  - phytoremediation using engineered wetlands: use of “hyperaccumulators”; what to do with the contaminated plants?
  - electrochemical technologies: finding suitable electrodes, current efficiencies; anode reaction?



Read remaining text material pp. 356-360