Challenges of the Global Water Shortage: Contamination of Water Resources by Inorganic Pollution

Janet G. Hering, Ph.D.

- Sources of inorganic contaminants
- Types of inorganic contaminants: speciation and health hazards
- Mobility and fate
- Occurrence and remedial options
- Concluding comments

Eawag: Swiss Federal Institute of Aquatic Science and Technology
Sources of inorganic contaminants

USE OF FERTILIZER AND BIOCIDES

MINING AND SMELTING

EFFLUENT DISCHARGE AND WASTE DISPOSAL

INDUSTRIAL PROCESSING AND MANUFACTURE

GEOGENIC CONTAMINANTS
Sources: Mining and smelting

Anaconda smelter

Clark Fork Superfund Site (Montana)

BP-ARCO repository
Sources: Industrial discharges
Sources: Legacy of nuclear weapons production

Hanford Nuclear Reservation (Washington)
Sources: Agriculture

Historical use of arsenic- and lead-containing biocides in orchards and vineyards.

Current-day use of organic arsenicals in animal feed as growth promoter.
Pre-1970: surface water used for drinking water
1970-1990: installation of ca. 3 million shallow tubewells
Since 1997: recognition of hazard associated with geogenic arsenic
Types of inorganic contaminants

Hazard limited to particular molecular species
  • nitrate, nitrite, perchlorate

Hazard associated with radioactivity

Particular hazard associated with organic forms
  • tetraethyl lead, dimethyl mercury, tributyl tin
  • Note: for some elements (e.g., arsenic), organic forms are less hazardous

Hazard associated (primarily) with element
  • Note: mobility often varies with oxidation state
United Nations Environment Programme Global Mercury Assessment, 2002, using J. Pacyna 1995 data, as presented by the Arctic Monitoring and Assessment Programme

Source: http://www.epa.gov/mercury/control_emissions/global.htm
Hg in the environment

Major exposure route

Source: http://www.mercuryinschools.uwex.edu/curriculum/national-curriculum.htm
Fish Consumption Advisories for Mercury

NOTE: This map depicts the presence and type of fish advisories issued by the states for mercury as of December 2002. Because only selected waterbodies are monitored, this map does not reflect the full extent of chemical contamination of fish tissues in each state or province.

Source: http://epag.gov/waterscience/fish/map.htm
Health hazards

Mercury
Minamata disease
(Japan)

Fluoride
dental fluorosis
(Ethiopia)

Arsenic
blackfoot disease
(Bangladesh)
Transmutation: Not a reliable strategy
Protein of receptors by sequestration

arsenic partitioning between mobile and immobile phases

Mobility of constituent X (in dissolved or colloidal form) depends on its partitioning between mobile and immobile phases.
Factors affecting mobilization and sequestration

Environmental conditions (e.g., pe, pH, OC, microbial community)
  
  - stability of carrier phases
  - microbial activity
  - arsenic oxidation state

*Shift from mobilization to sequestration requires a gradient in environmental conditions.*
Greater effect of Fe(III) solid on abiotic vs. microbial reduction

Fig. 1. Initial (2–3-day incubation) surface area-specific rates of bacterial (A) and abiotic (B) reduction of synthetic Fe(III) oxides

Microbial As(V) and Fe(III) reduction

As Respiration

As Detoxification

Fe Reduction

ArrA  MtrB  OmcB
ArsB
ArsC
ArrA gene detected in isolate from field (sediment)

Expression of ArrA genes during As(V) reduction by *Shewanella* sp. strain ANA-3

Peak in ArrA expression corresponds to maximal As(V) reduction

Preferential microbial reduction: As(V) vs. Fe(III)

**Haiwee sediment**

HFO = 2 g/L, 0.002 mol As(V):mol Fe, pH = 7.2, 19 mM lactate

With Haiwee sediment inoculum, As(V) reduction precedes Fe(III) reduction. With ANA-3, both proceed simultaneously.

**ANA-3**

HFO = 2.8 g/L, 0.001 mol As(V):mol Fe, pH = 8.0, 14 mM lactate

Note: NO measurable dissolved As or Fe in these experiments.

In situ reductive dissolution examined using gel probes doped with hydrous manganese oxide (HMO)
Comparison of porewater composition and HMO reduction

Correspondence between depth of maximum Fe concentration and HMO loss.

Comparison with solid phase Fe and Mn and speciation determined by sequential extraction

As(V) reduction in sediments precedes mobilization

XANES signature of As in sediments

Porewater profile

In situ sampling of porewater composition and sorption behavior

- Clear gels
- HFO-doped gels
Comparison of porewater and *in situ* sorption profiles

Calibration of As XANES signal using HFO-doped gels equilibrated with As(III) and As(V)

Calibration used to quantify the ratio of As(III)-to-As(V) on HFO-doped gels deployed in the field

Correlation of Fe and As release

Note: observed at Haiwee reservoir but not in all sediments

Despite mobilization >97% of Fe and As remains in the solid phase in (these) sediments

Mobilization of naturally-occurring As due to molasses injections at Ft. Devens (Massachusetts)

Objective: stimulation of biodegradation of chlorinated solvents

Unintended consequence: mobilization of As, Fe, and Mn

Observation: plume attenuation
Footprints of arsenic, organic carbon, and iron

Migration of As and Fe lag OC (which lags groundwater)
Observations of groundwater and sediments

**Elevated Mn concentrations downgradient of apparent sequestration of Fe and As**

No signature of sequestration in solid phase except (possibly) in extractable Fe(II).

(XANES shows only As(V) signal in sediments)

Column experiments with sediments


- Column 1: As(III) only ($C_0 = 0.1$ mM)
- Column 2: As(III) + Fe(II) ($C_0 = 1$ mM)
- Column 3: As(III) + Fe (buffered)

As(III) transport retarded in presence of Fe(II) but sorption is reversible.

Mn release observed in presence of Fe(II).

Ratio of signals at ~6557 and ~6553 eV shift when sediment (SMW-3) is exposed to As(III) particularly in the batch experiments.

As XANES indicates accumulation of "excess" As(V) (i.e., above As(V) signature of native sediments).

No observable changes in Fe XANES.

arsenic at background levels

manganese still elevated relative to background levels

Reliability of arsenic attenuation will depend on the amount and duration of organic carbon loading.
Augmentation of attenuation

Birnessite amendment to sediment suspensions containing dissolved As(III) and Fe(II) results in oxidative sequestration of Fe and As.

Geogenic contaminants in groundwater in South and Southeast Asia

http://www.bdix.net/sdnbd_org/world_env_day/2002/current_issues/arsenic/maps/arsenic.gif
Geologic information used to predict arsenic occurrence in groundwater.

New risk areas can be identified.

But does not account for local heterogeneity.

L. Winkel
Heterogeneity of As occurrence

A. Van Geen

C. Harvey
Possible options: deep tubewells, treatment

S. Hug, M. Berg, M. Ahmed
Behavior

Personal Factors
• Vulnerability
• Fear
• ...

Social Factors
• Norms
• Values
• ...

Structural Factors
• Distance
• Cost
• ...

Social science aspects

Disadvantages of deep tube wells

<table>
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<th>Disadvantage</th>
<th>N</th>
<th>% yes of N=222</th>
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<tbody>
<tr>
<td>needs much time</td>
<td>74</td>
<td>33.3</td>
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<tr>
<td>rainy season</td>
<td>61</td>
<td>27.5</td>
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<tr>
<td>social barriers for women</td>
<td>35</td>
<td>15.8</td>
</tr>
<tr>
<td>laborious</td>
<td>25</td>
<td>11.3</td>
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<tr>
<td>is near a mosque</td>
<td>23</td>
<td>10.4</td>
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<tr>
<td>owner gets angry</td>
<td>18</td>
<td>8.1</td>
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<tr>
<td>is frequently out of order</td>
<td>14</td>
<td>6.3</td>
</tr>
<tr>
<td>rush area</td>
<td>12</td>
<td>5.4</td>
</tr>
<tr>
<td>gives less water than shallow</td>
<td>9</td>
<td>4.1</td>
</tr>
<tr>
<td>water is salty</td>
<td>5</td>
<td>2.3</td>
</tr>
</tbody>
</table>

H. Mosler
WRQ

Current use of groundwater for drinking water supply without sufficient assurance of quality.

Mapping can draw attention to potential risks.

Risks can be managed by substitution or treatment of source water.
Concluding comments

There are multiple sources of inorganic contaminants to the environment.

The mobility of inorganic contaminants can be strongly influenced by redox conditions because of the dependence of solubility on oxidation state.

Microbes play a key role in redox cycling in environmental systems. Many factors influence the rate of microbial redox reactions; a key factor is the availability of organic carbon.

Since the hazards of inorganic contaminants are often associated with toxic elements, risk reduction depends on decreasing exposure (e.g., through sequestration, elimination of use, water treatment, etc.).

Problems of inorganic contaminants are old but not yet solved and new aspects arise (e.g., metal-containing nanoparticles).
Statistics (2008)

Personnel
- 6 Full Professors (5 at ETHZ)
- 1 Assistant Professor at EPFL
- 13 Adjunct Professors
- 146 Research Staff

Student supervision
- 119 PhD students
- 97 MS students

Publications, Spin-offs, External Funding
- publications: 253 ISI, 75 non-ISI
- 1 spin-off
- 13.6 Mio. CHF third-party funding
Visitors welcome!

http://www.eawag.ch/index_EN

Dübendorf

http://www.eawag.ch/services/publikationen/jahresbericht/eawag-jb_08d.pdf

Kastanienbaum