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"water for life…"

Assoc.Prof. TorOve Leiknes

The Removal of Arsenic from Drinking Water

presented by

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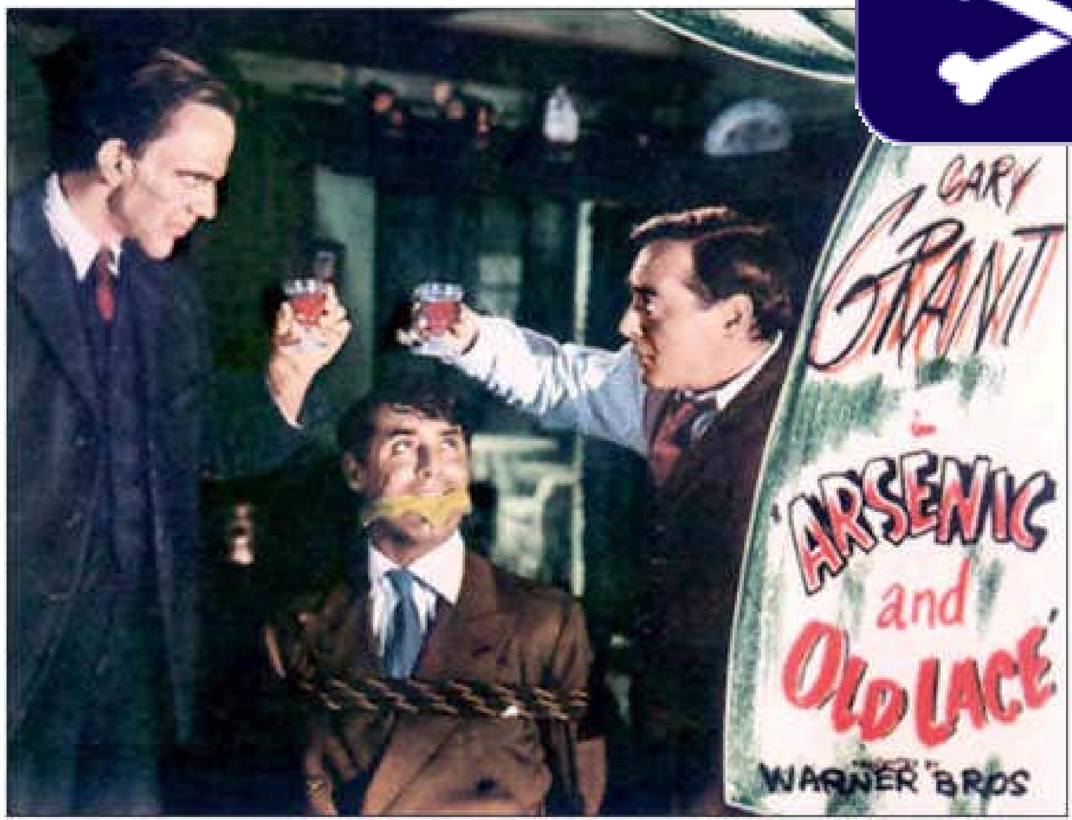
Arsenic associations?



By Joseph Kesselring

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Arsenic (As) – Fact Sheet:

- Common metal in earths crust – avg.concentration 2 mg/kg
- > 200 mineral species, most common arsenopyrite (FeAsS)
- Found as inorganic As and in organic compounds. Some species have an affinity for clay mineral surfaces and organic mater
- As in drinking water first found in 1938 (Argentina)

Essentials:

- Arsenic (As)
- Atomic nr: 33
- Atomic weight 74.9
- Std state: solid at 298 K
- metalloid – brittle, crystalline

Toxicity

$$As(III) \xrightarrow{60\times} As(V)$$

$$\text{inorganic As} \xrightarrow{100\times} \text{organic compounds}$$

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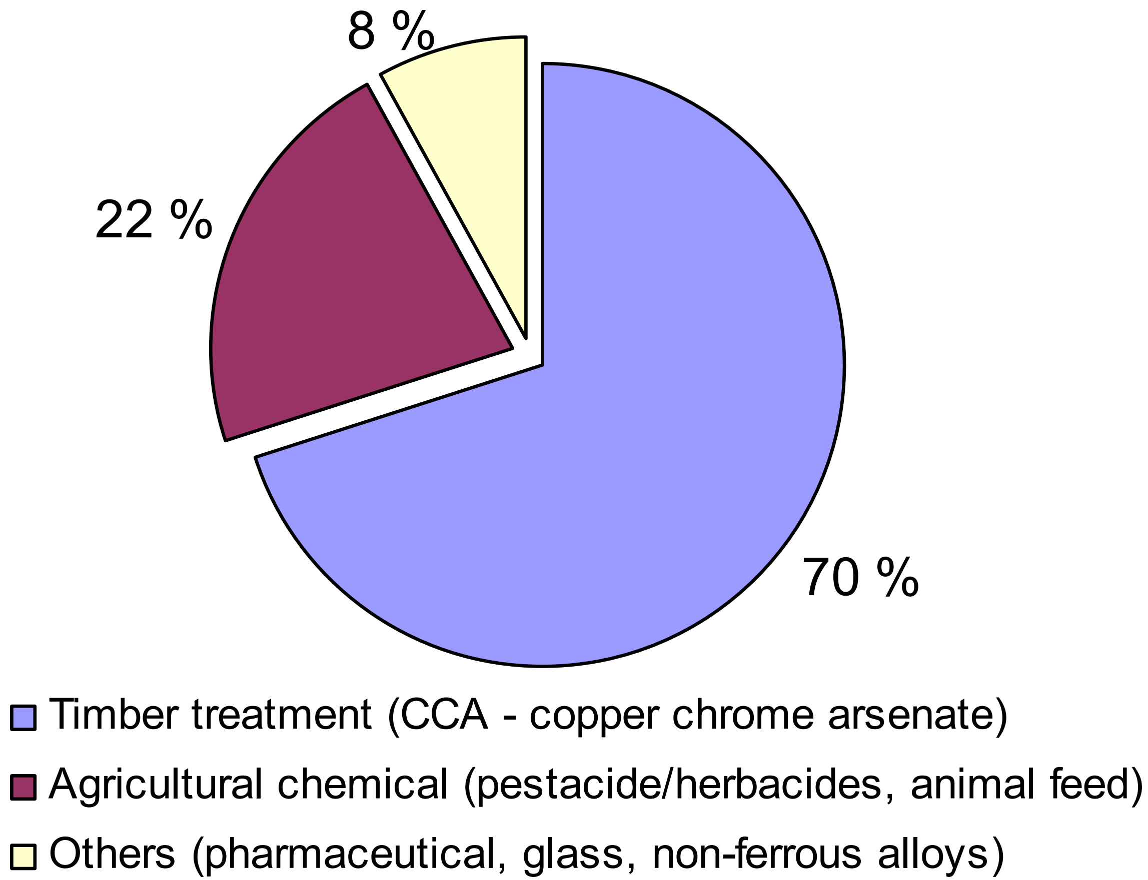
Arsenic (As) – production and use

Sector	*Use examples*
Lumber	Wood and timber preservatives (copper chrome arsenate - CCA)
Agriculture	Pesticides, insecticides, herbicides, defoliants, debarking agents, soil sterilant
Livestock	Feed additives (weight gain, feed efficiency – swine/poultry), disease preventives, dips, algaecides
Medicine	Antisyphilitic drugs, treatment of trypanosomiasis, amebiasis, sleeping sickness
Industry	Glassware, electrophotography, catalysts, pyrotechnics, antifouling paints, dye and soaps, ceramics, pharmaceutical substances, alloys, battery plates, solar cells, optoelectronic devices, semiconductor application, light emitting diodes in digital watches, mining and smelting, fossil fuels

Arsenic (As) – production and use



Arsenic (As) – Environmental levels:

Air:

- rural areas – 0.02 – 4 ng/m^3
- urban areas – 3 – 200 ng/m^3
- industrial areas > 1000 ng/m^3

Open sea water:

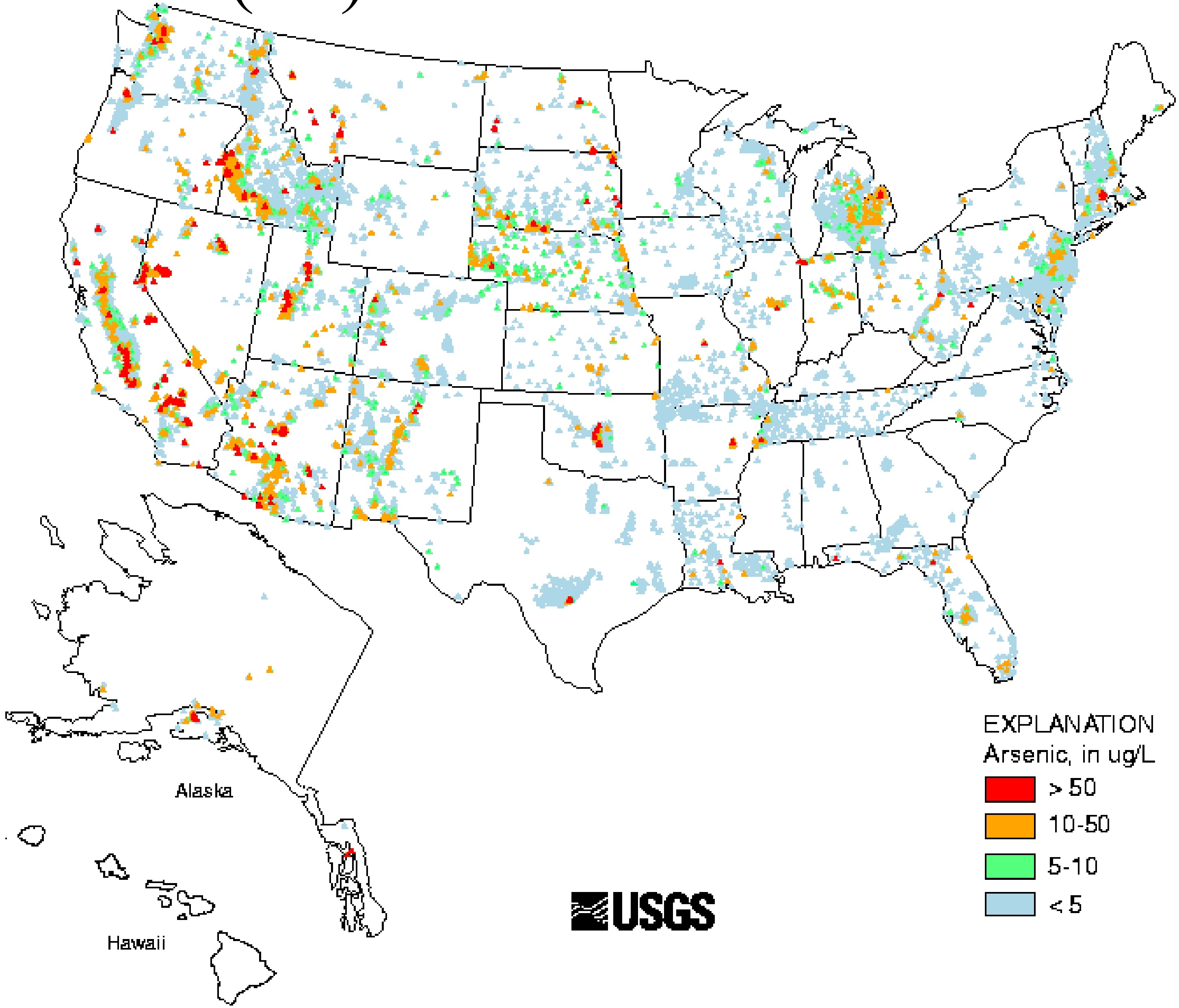
- average concentration – 1 – 2 μg/liter

Arsenic (As) – Environmental levels:

Fresh water:

- generally below 10 µg/liter
- near anthropogenic sources – 5 mg/liter
- ground water average – 1-2 µg/liter
- geology dependent – up to 3 mg/liter

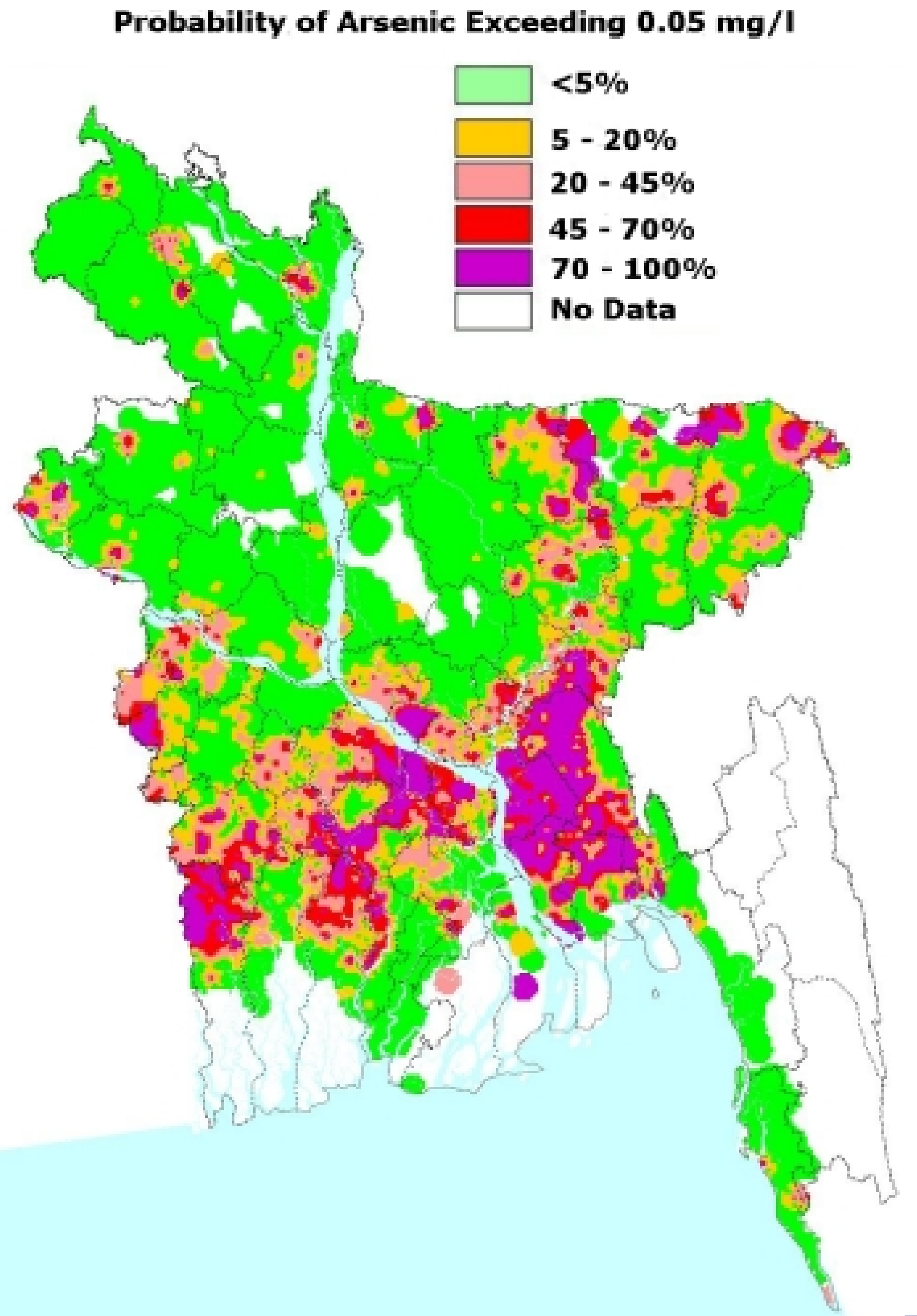
Arsenic (As) – in USA:



Arsenic (As) – Bangladesh:

Geochemical map of Bangladesh:

As first measured in groundwater in 1993



Arsenic (As) – Environmental levels:

Sediments:

- site specific 5 – 3000 mg/kg

Soil:

- background concentrations 1 – 40 mg/kg
- mean values 5 mg/kg

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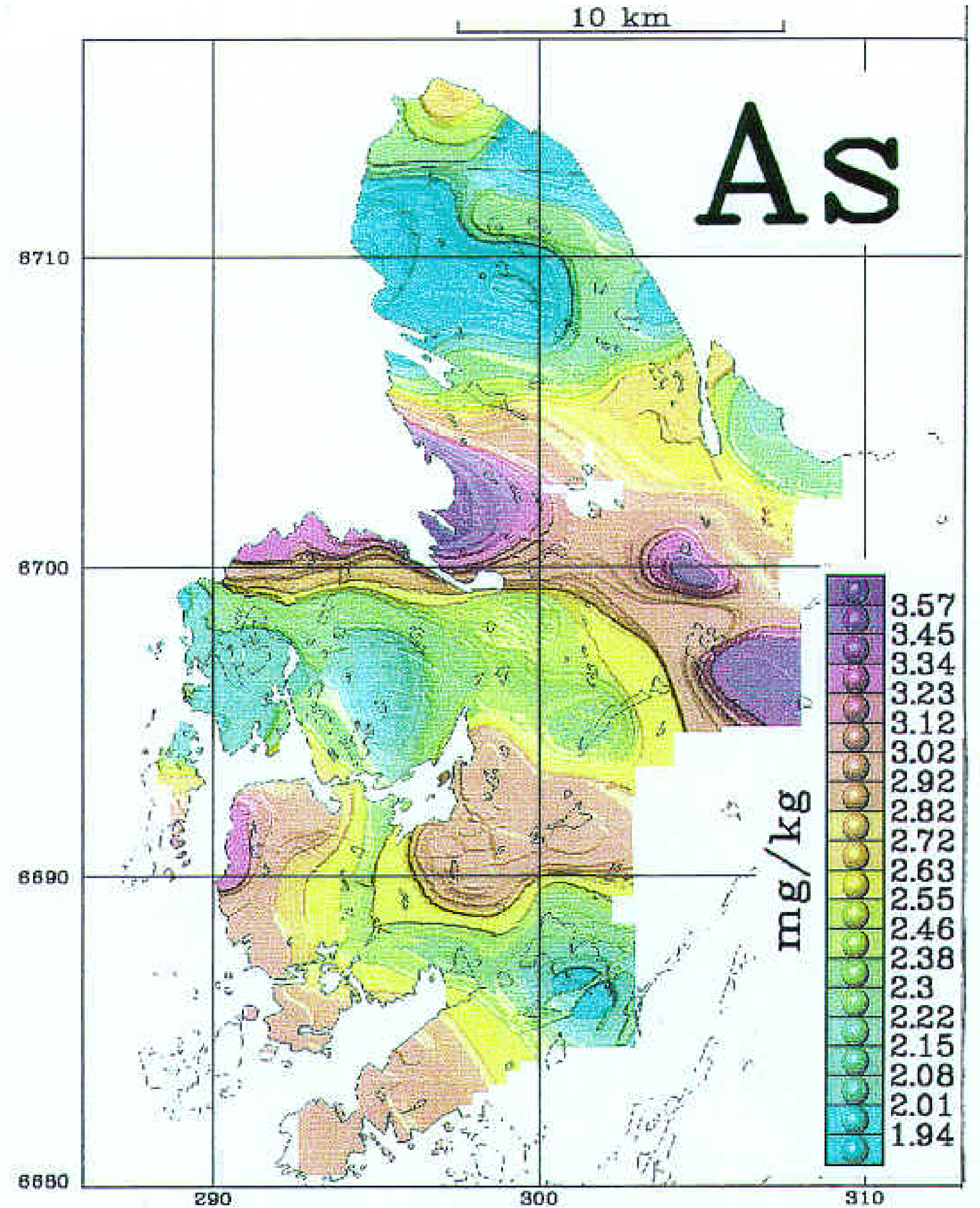
Arsenic (As) – case study:

<u>Bergen, Norway</u>

Survey of arsenic levels in the soil.
(1998)



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Arsenic (As) – Exposure:

- Primarily food and water – non-occupational exposure
- Apart from obvious point sources of As contamination, high concentration is mainly found in groundwater
- Daily intake – 20-300 µg/day (~25% inorganic As)
  (meat, poultry, dairy products, cereals)
- Pulmonary exposure – burning of fossil fuels, tobacco smoke
  (smoker 10 µg/day vs. 1 µg/day for non-smokers)
- Average daily intake: *water = food*

⇨ *Drinking water probably poses the greatest threat to human health*

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Arsenic (As) – drinking water

Drinking water standards:

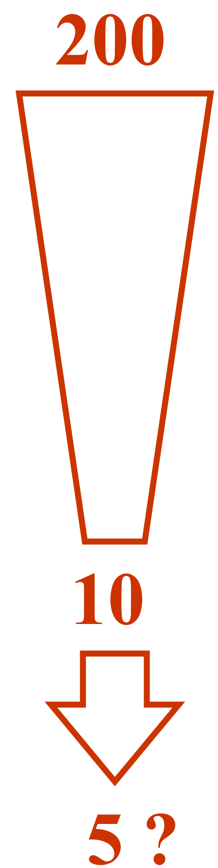
WHO

”International Standards for Drinking Water”

- 1958 – published As 200 µg/l
- 1963 – revised As 50 µg/l, (toxic substance)
- 1971 – revised, status as toxic substance reaffirmed

”WHO Guidelines for Drinking Water Quality (GDW)”

- 1984 – guidelines ”*significance to health*” - 50 µg/l
- 1993, 1996, 1997 – 2nd edition, As 10 µg/l
- 1998 – updated As 10 µg/l, (1.7 µg/l)



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Arsenic (As) – drinking water

National drinking water standards:

Standard variations – 50 µg/l → 10 µg/l or stricter

Standard	*Countries*
< 10 µg/l	Australia (1996) – 7 µg/l
10 µg/l	USA (2001), European Union (1998), Japan (1993), Jordan (1991), Laos (1990), Mongolia (1998), Namibia, Syria (1994)
50 > std > 10	Canada (1999) – 25 µg/l
50 µg/l	Mexico (1994), Bahrain, Bangladesh, Bolivia (1997), China, Egypt (1995), India, Indonesia(1990), Oman, Philippines (1978), Saudi Arabia, Sri Lanka (1983), Viet Nam (1989), Zimbabwe

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Arsenic (AS) – Health risks

Arsenicosis – chronic poisoning over 5-20 years

Long-term exposure: skin diseases → cancer (liver, bladder, kidney)

Development of arsenicosis:
Stage 1:
Dermatitis, keratitis, conjunctivitis, bronchitis and gastroenteritis
Stage 2:
Peripheral neuropathy, hepatopathy, melanosis, depigmentation and hyperkeratosis
Stage 3:
Gangrene in the limbs, malignant neoplasm, and cancer

1:100 persons drinking > 50 µg/l will die from arsenic related cancers

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Water quality issues: (global perspective)

(WHO – assessment report 2000)

1. Diarrhea – 4 billion cases/year, 2.2 million deaths
2. Intestinal worms – effects ~ 10% of population in the developing world
3. Trachoma – 6 million blind, 500 million at risk
4. Schistosomiasis – 200 million affected, 20 million severely
5. Arsenicosis – complete extent unknown, well documented in certain areas

Press Release WHO/55
8 September 2000

RESEARCHERS WARN OF IMPENDING DISASTER FROM MASS ARSENIC POISONING

Example surveys:

1. USA – 13 million > 10 µg/l
2. Bangladesh – 28-35 million > 50 µg/l
   46-57 million > 10 µg/l
3. Inner Mongolia - ~35% of pop. (96% of water undrinkable)
4. South Japan (Fukuoka Prefecture) ~43% well water > 10 µg/l

Arsenic (AS) – Treatment:

Fundamental aspects of treating inorganic arsenic :

Arsenite	Arsenate
Oxidation state: +III	Oxidation state: +V
As(III) species: – $H_4AsO_3^+$ – H_3AsO_3 – $H_2AsO_3^-$ [pH > 9.2] – $HAsO_3^{2-}$ – AsO_3^{3-}	As(V) species: – H_3AsO_4 – $H_2AsO_4^-$ [pH 6-9] – $HAsO_4^{2-}$ [pH 6-9] – AsO_4^{3-}
Primarily soluble, no charge	Primarily soluble, negative charge
Anaerobic conditions	Aerobic conditions

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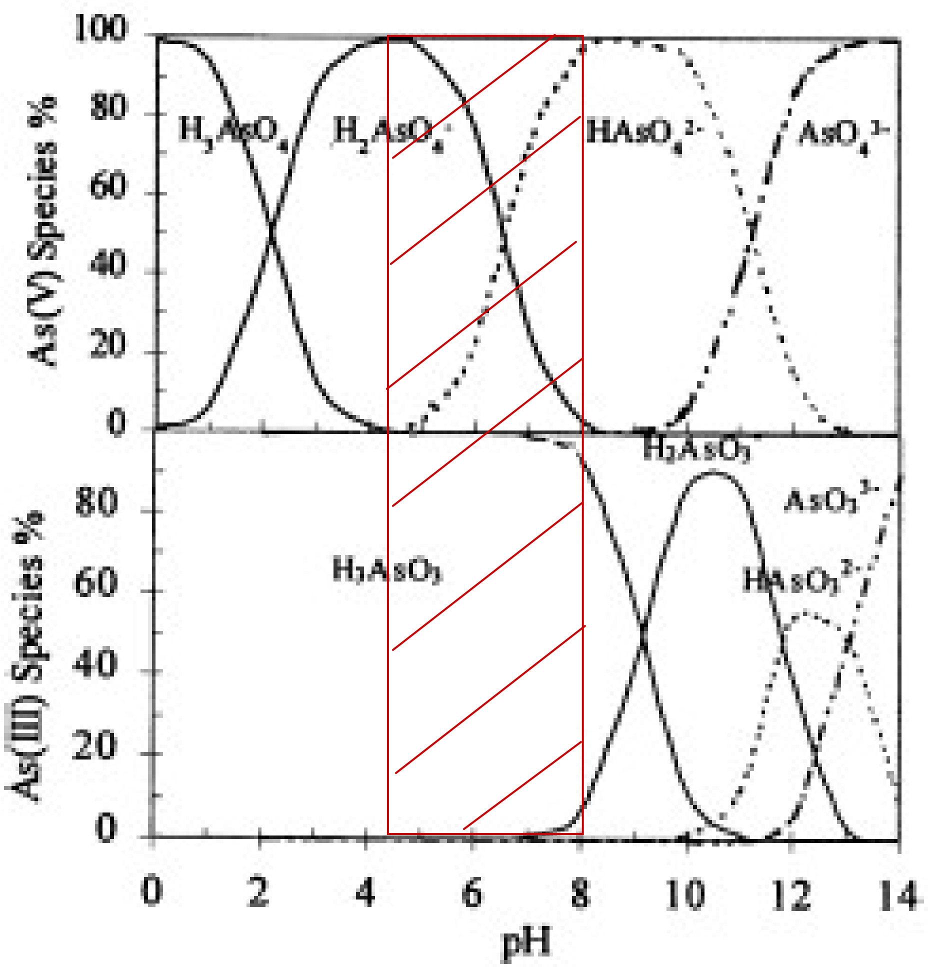
Arsenic (As) – inorg. As species in water



$[As] = [As(III)] + [As(V)]$

Dominant species in water

$[As(III)] \rightarrow [H_3AsO_3]$

$[As(V)] \rightarrow [H_2AsO_4^-]$

$\rightarrow [HAsO_4^{2-}]$

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Arsenic (AS) – Treatment options:

Treatment technology for arsenic removal:

- precipitative processes:
  - coagulation/filtration
  - direct filtration
  - lime softening
- adsorption processes:
  - metal oxides / hydroxides
  - activated alumina
- ion exchange processes:
  - specifically anion exchange
- membrane processes:
  - MF, UF, NF, RO, EDR
- biological processes:

Arsenic (AS) – treatment studies:

Case New Zealand, Waikato River:
ALUM based coagulation

- Geo-chemical source
- Thermal active area
- Surface water

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Arsenic (AS) – Coagulation:

ALUM-based – case New Zealand, Waikato River:

Initial concentration ~ 30 µg/l (90% as As(V))

→ Coagulation/flocculation – Clarification – Filtration – Disinfection →

$As(III)_{sol}$ ⟶ $As(V)_{sol}$

$As(V)_{sol}$ ⟶ $As(V)_{part}$ ↓ **> 90% removed**

Removal mechanisms

1. *Precipitation* – formation of insoluble compounds ($Al(AsO_4)$, $Fe(AsO_4)$)
2. ✔ *Coprecipitation* – incorporation into the MeOH phase
3. ✔ *Adsorption* – binding of soluble As(V) onto MeOH

Arsenic (As) – Coagulation

<u>Alternative coagulants;</u>

Ferric chloride – $FeCl_3$ → *Mechanisms*;
- coprecipitation
- adsorption

Process issues:
- coprecipitation through formation of inner sphere complexes
- adsorption onto metal oxides and hydroxides
- affected by other anions – silicate, sulfate, carbonate, NOM

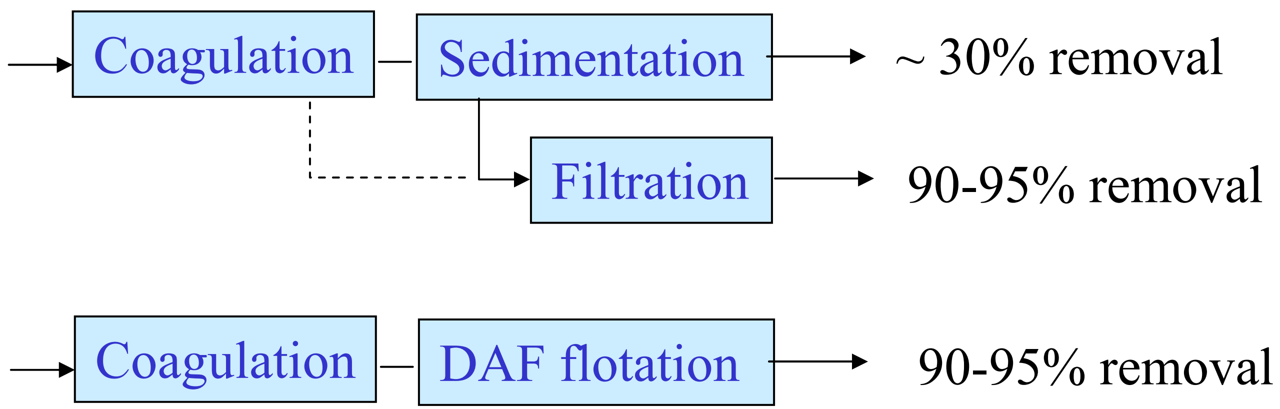
Ferric sulfate – $Fe_2(SO_4)_3$ → Found to be less effective

Polymers and clays → Used to improve As removal

Arsenic (As) – Coagulation

Removal of particulates an important process step;

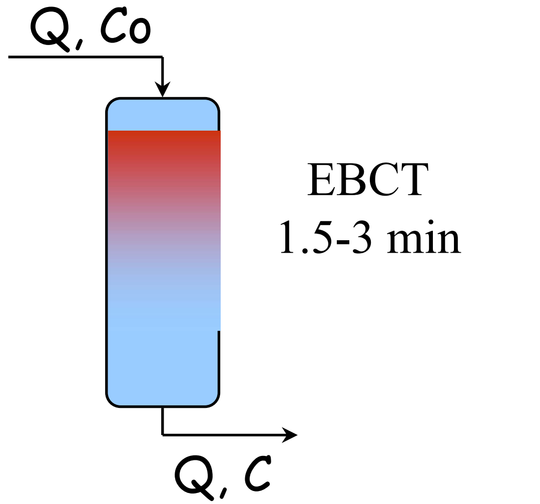
Conventional treatment processes

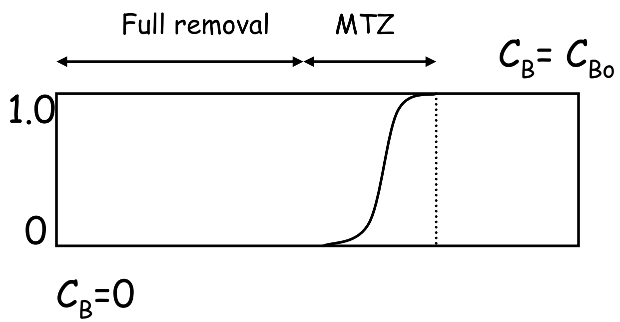


Laboratory / pilot studies:
- 99% removal under optimal conditions

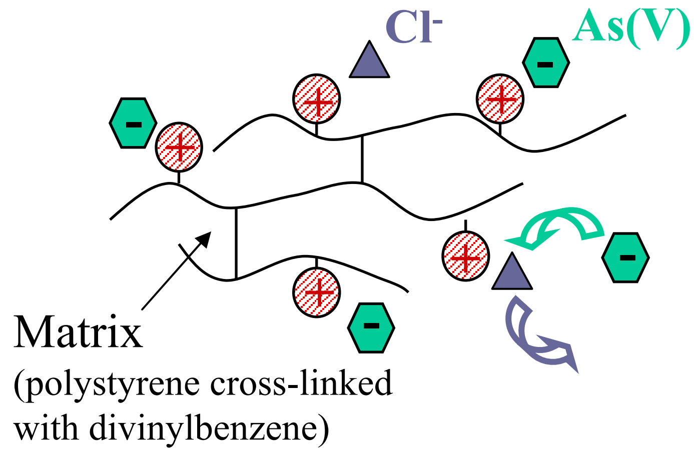
Full-scale plants:
- report 50-90% removal

Arsenic (AS) – Ion exchange:





Principle mechanism



$$R \cdot Cl^- + As(V)^- \rightleftarrows R \cdot As(V)^- + Cl^-$$

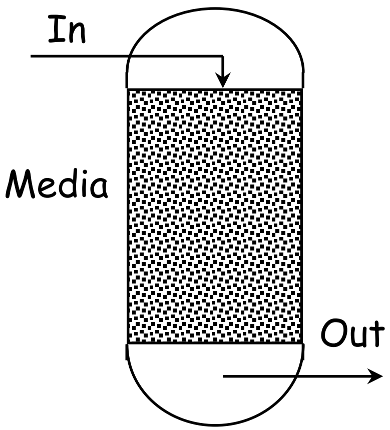
$C_{effluent} < 1\ \mu g/l$

Process issues:

- Strong-base anion exchanger
- independent of pH and initial concentration
- easily regenerated (1.0 M NaCl)
- MeOH – fouling/short circuiting
- competing ions have a strong effect

$$SO_4^{2-} \gg NO_3^- > Br^- > HAsO_4^{2-} > NO_2^- > Cl^- > H_2AsO_4^-$$

Arsenic (As) –Adsorption processes:



Activated Alumina (AA) – Al_2O_3:

- dehydration of $Al(OH)_3$ at high temperature
- granulated form – high surface area (200-300 m^2/g)
- exhibits ion exchange properties
- efficiency typically > 95% removal
- narrow optimum pH range (5.5 – 6)
- controlled by pH, initial concentration and speciation

Operational considerations:

- acidic conditions preferable
- EBCT varying between 3-8 minutes
- regeneration with NaOH (not always effective, *i.e.* 50-70%)
- AA dissolves during regeneration, cementing tendencies
- residual metal, formation of colloids, resin fouling (iron precipitation)
- selectivity and competing ions

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Arsenic (As) –Adsorption alternatives:

Granular Ferric Hydroxide (GFH) – $Fe(OH)_3$ and α-FeOOH:

- poorly crystallized α-FeOOH with water-filled pores
- granulated form (0.2-2.0 mm) – high surface area (250-300 m^2/dm^3)
- 40000-60000 bed volumes, adsorption capacity 5-10 > AA
- efficiency typically > 95% removal
- operated like a conventional filter, disposed of when spent
- raw water quality and phosphates affect performance

Conventional Fe/Mn removal:

- most methods for Fe/Mn removal should work for As as well
- Green sand (mineral coated with MnO_2) – strong oxidizing agent
- without Fe: ~ 40% removal, with Fe; ~ 80%

⇒ Ferric hydroxides appear to be most applicable

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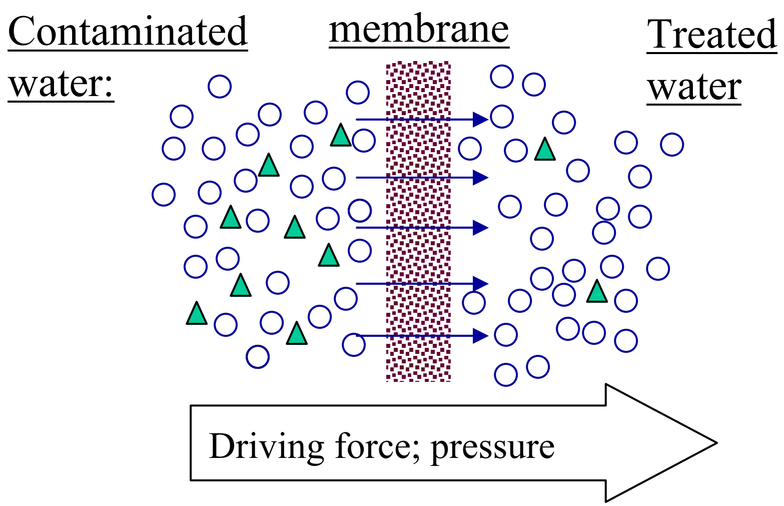
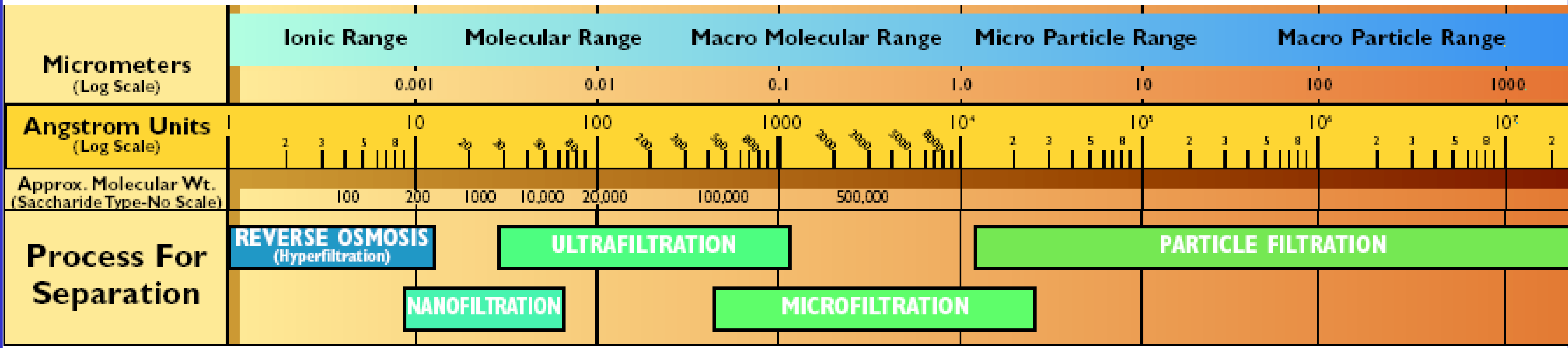
Arsenic (AS) – membrane methods:

Principle:



Defined by 4 categories:

1. RO – reverse osmosis
2. NF – nanofiltration
3. UF – ultrafiltration
4. MF – microfiltration



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Arsenic (As) – membrane methods:

Process performance:

matching membrane properties to source water characteristics

[As] → dissolved → colloidal → particulate

- dissolved → RO/NF
- colloidal → NF/UF
- particulate → MF (C-MF)

General observations:

- As(III) – 9% (UF) to >90% (RO) rejection
- As(V) – >98% (RO/NF) rejection
- negatively charged membranes enhance As(V) rejection
- oxidation/coagulation necessary for efficient removal with UF/MF
- DOC and more complex forms of arsenic relevant

Arsenic (As) – Oxidation:

As(V) → readily removed
As(III) → difficult

→ As(III) —oxidation→ As(V)

Autoxidation (O_2):

- kinetics slow (weeks) – species relatively unchanged for days
- can be catalyzed by bacteria, strong acids/alkali solutions, copper

Chemical oxidation:

- chlorine, hypochlorite, ozone, permanganate, hydrogen peroxide, Fenton's reagent (H_2O_2/Fe^{2+}), UV-radiation
- Oxidation by products, undesired residuals

NB! Oxidation does not remove [As]

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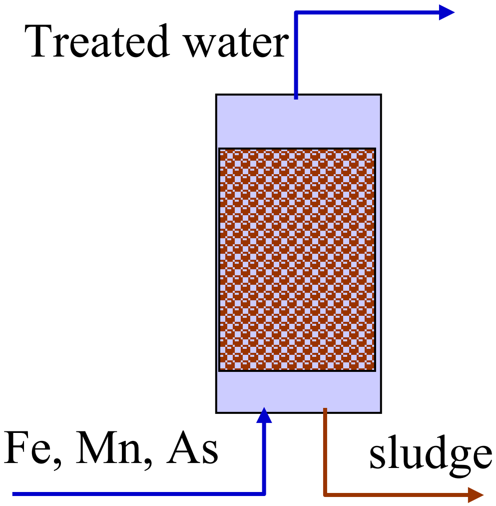
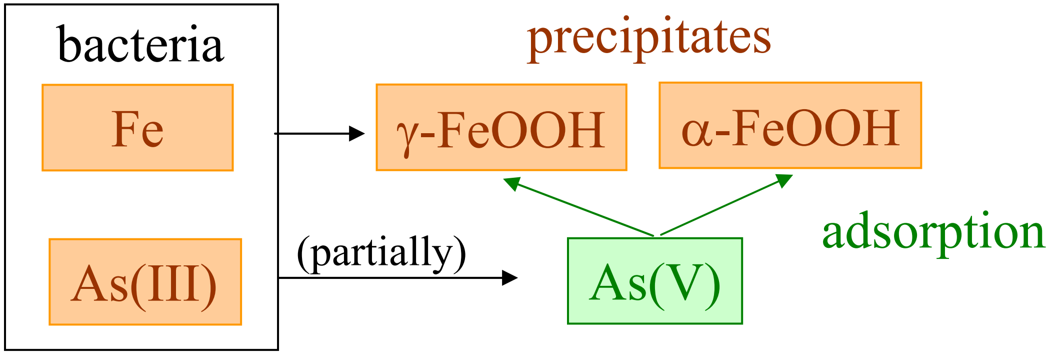
Arsenic (As) – biological processes:

Biological oxidation of Fe and Mn - an alternative for As(III) removal?

Process description:



Fixed-bed upflow bioreactor



Process issues:

- [As] removal ~ 80%
- biological oxidation → adsorption on MeOH
- no addition of chemicals necessary
- MeOH continuously produced during the process
- potential for simultaneous removal of Fe, Mn, As

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Arsenic (As) – treatment summary:

Technology	*Removal efficiency*		*Comments*
	As(III)	As(V)	
Coagulation 1. ALUM 2. Iron salts 3. Lime softening	 - ++ +	 +++ +++ +++	pH dependent, water quality effects (phosphates/silicates), generates As-rich sludge, centralized systems
Ion exchange	-	+++	Choice of resin, competing ions, regeneration, waste disposal, cost
Adsorption 1. AA 2. GFH 3. Combined Fe/Mn	 +/++ ++ -/+	 +++ +++ +++	pH dependent, media life-time, residuals, fouling, process optimization
Membranes	-/+++	+++	Match membrane/water, costs, dissolved/particulate, operation
Biological processes	++/+++	+++	Biological oxidation of As(III), methods still under development

+++ - > 90% removal, ++ - 60-90% removal
+ - 30-60% removal, - - < 30% removal

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We have the technology, so what's the problem?

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Arsenic (As) – solutions?

BAT - implement / optimize processes!

- better understanding of As removal processes
- improving known technology, finding novel approaches
- centralized / decentralized strategies
- new, simpler measuring techniques

Find another source!

Rain water? → • site dependent
• safe storage and treatment facilities

Drink bottled water! → ~ 47.8 ±11.2 µg/l (April – August 2000)

Water policies and public awareness

- centralized treatment strategies
- Point-of-use (POU) and point-of-entry (POE)

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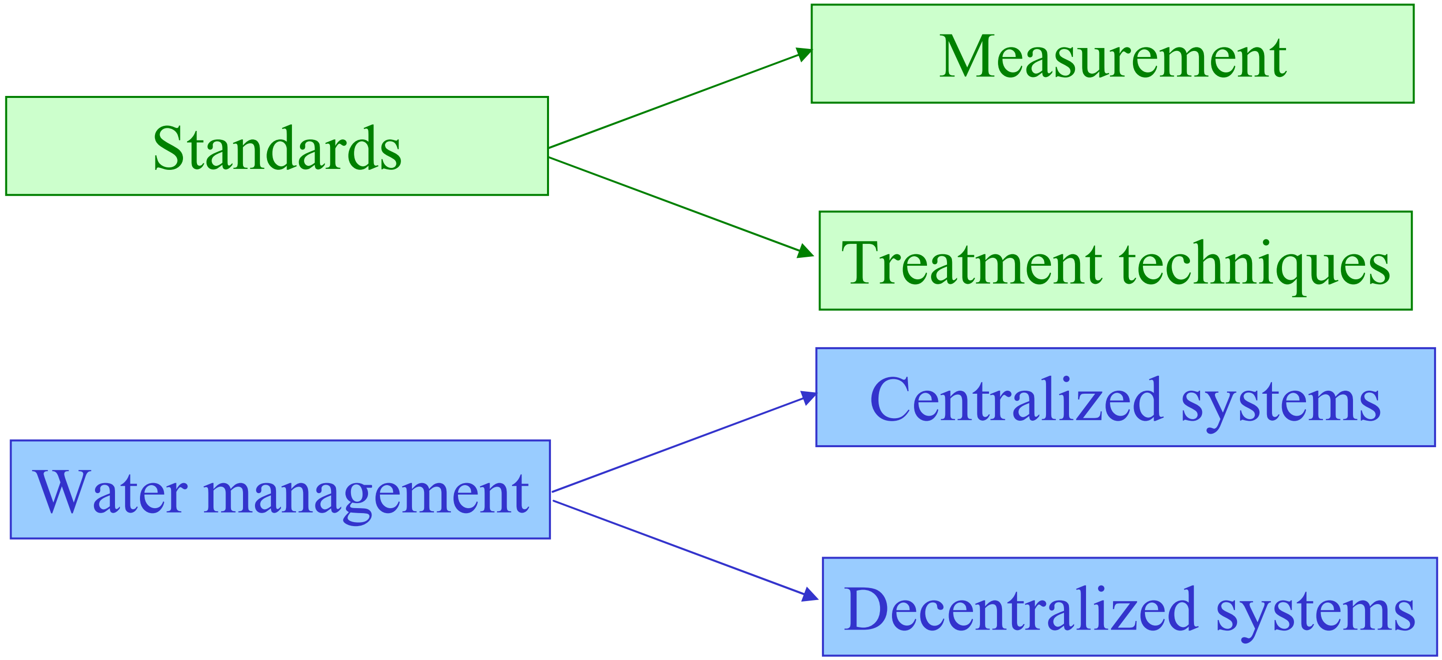
The Removal of Arsenic from Drinking Water



Challenges:

- research to identify and improve technologies that effectively remove As
- implementation of stricter drinking water standards
- find sustainable solutions for decentralized systems
- public awareness and education on arsenic health impacts

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