Arsenic in the Environment: History, Sources and Perspectives

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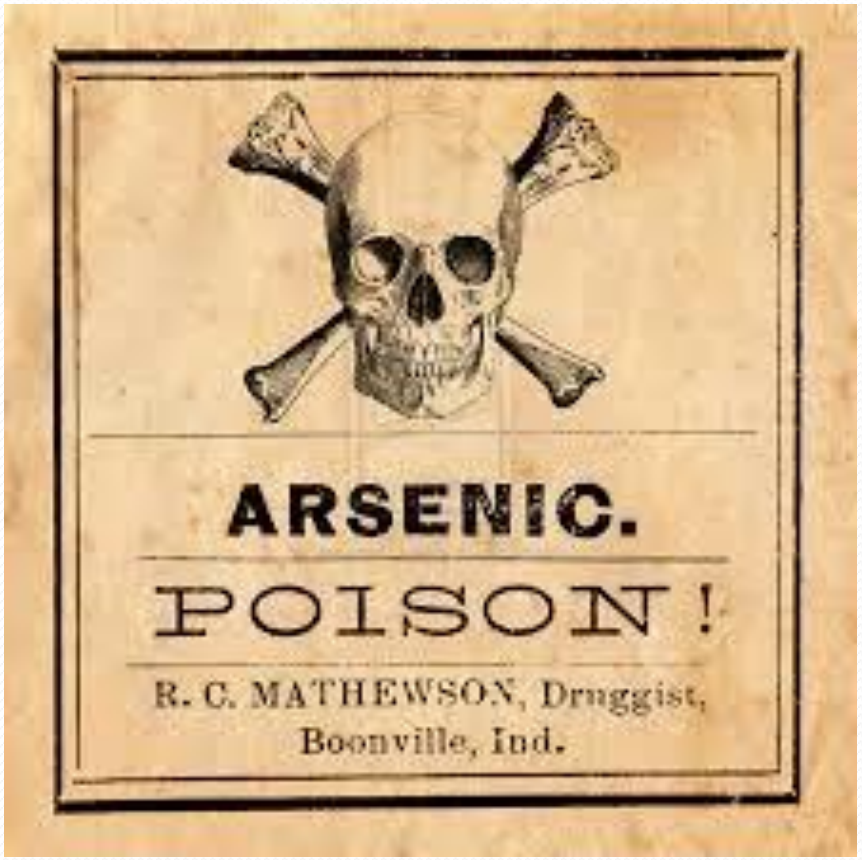
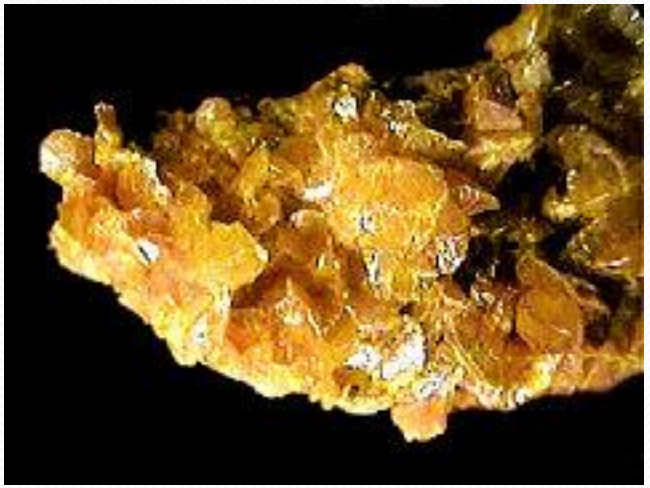
The classic poison……





A bit of History……

- Assassinations - White Arsenic (As_2O_3)
- Greeks and Romans
  - Lucius Corinilius Sulla (82 BC) – *Lex Cornelia*
- Renaissance and Middle Ages
  - Borgias and de Medici' families (14^{th} 15^{th} centuries)
    - Inheritance powder
  - Giulia Toffana/Hieronyma Spara (La Spara) (1600s) - Italy
  - Catherine Deshayes (La Voisin) –France
- Claire Booth Luce(U.S.) Ambassador to Italy (1950s)

So where is it ….?

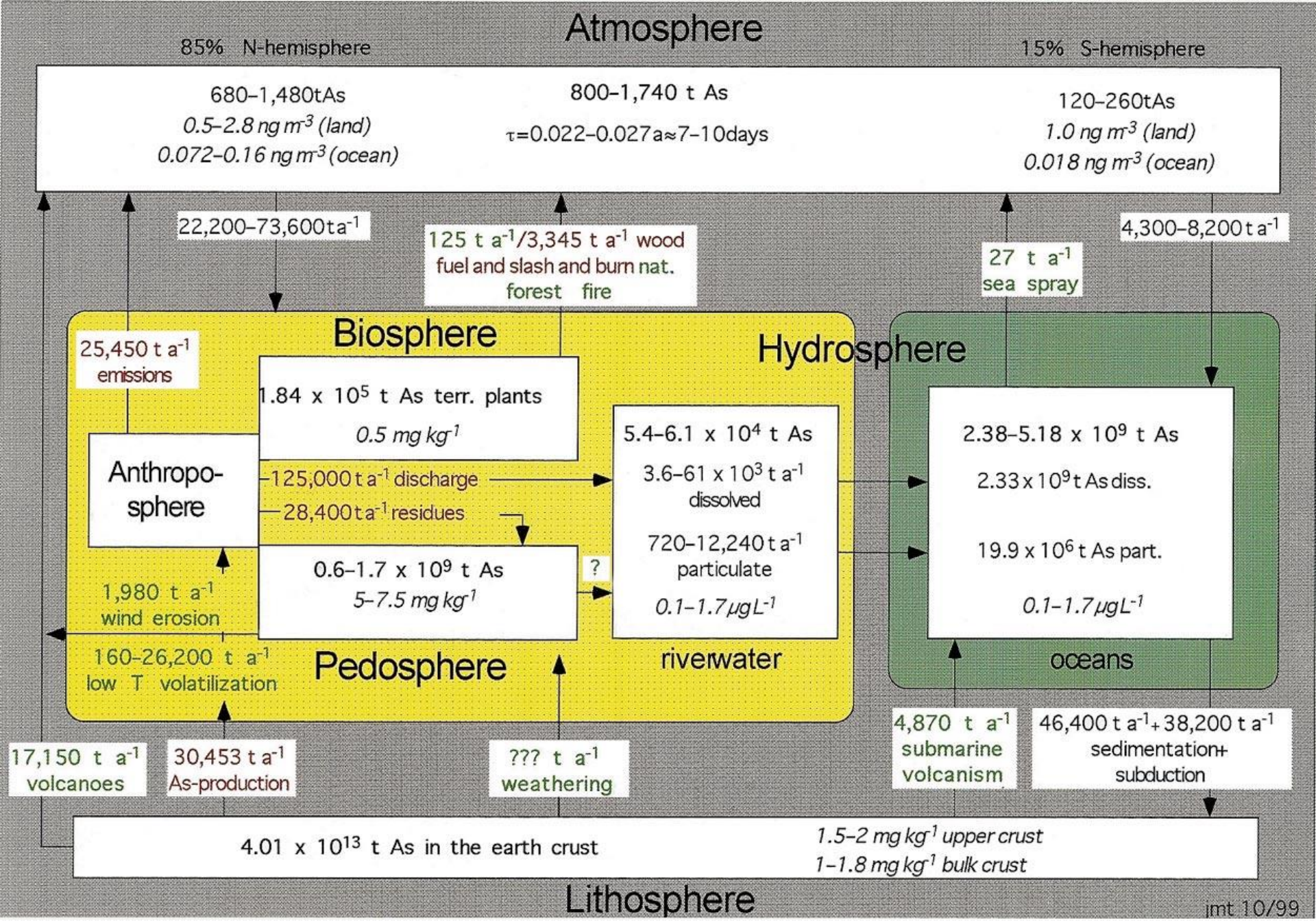
- Lithosphere – 4×10^{13} tons
- Pedosphere – 2×10^{9} tons
- Biosphere – 20,000 tons (mostly plants)
- Atmosphere – 800 – 1700 tons
- Hydrosphere
  - Rivers – 60,000 tons
  - Oceans – $2.4\text{-}5.2 \times 10^{9}$ tons

J. Matschullat, *Sci. Total Env.* (2000)249

Approximate Fluxes

Input to Atmosphere	Input To Hydrosphere	Input to Pedosphere
Soil Bioproductivity – 26,000 t/a	Rivers to sea 54,000 – 90,000 t/a	Natural – 122,000 t/a
Volcanism – 17,000 t/a	Volcanism - 5000 t/a	Natural Weathering - ???
Seaspray – 27 t/a	Atmospheric Deposition – 5-8 t/a	Anthropogenic – 81,000 t/a
Forest fires – 3000 t/a	Soil weathering - ????	
Anthropogenic 25,000 t/a	Anthropogenic 125,000 t/a	

Duce, et al. 1991
Matschullat, 2000
Donet and Bruland, 1995



J. Matschullat, *Sci. Total Env.* (2000)249

How are we exposed?

- **Air**
  - Rural areas (0.02-.2 ug/day)
  - Cities (0.4-0.6/day)
  - Cigarette smoke (0.8-2.4 ug/day)
- **Soil/Dirt** (0.14-0.28 ug/day)
- **Water** (1-5 ug/day)
- **Food**
  - Japan (126-273 ug/day)
  - US (60 ug/day)
  - Belgium (45 ug/day)
  - Canada (7 ug/day)*

WHO, 2000

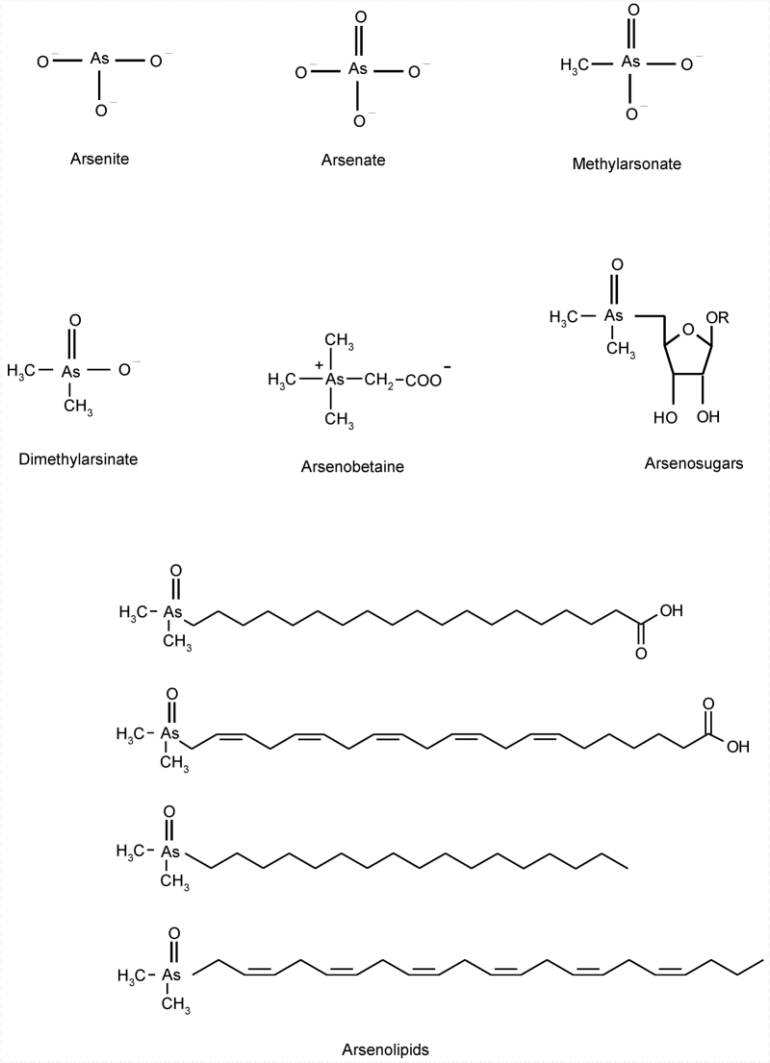
How are we exposed?

Food – (Most less then 0.25 mg/kg)

- **Seafood is highest**
  - Crustaceans (shrimp, crabs) – 30-100 mg/kg
  - Seaweed – 18-124 mg/kg
  - Fish – 2.4 – 17 mg/kg
  - Mollusks – 3- 20 mg/kg
- Mushrooms – 2.5 mg/kg
- Vegetables (misc) – 1.5 mg/kg
- Rice (various) – 0.2-0.9 mg/kg

Rose, et al. *Food Chem Tox*. 2007
J. Matschullat, *Sci. Total Env.* 2000

What happens to it in seafood?



pathway

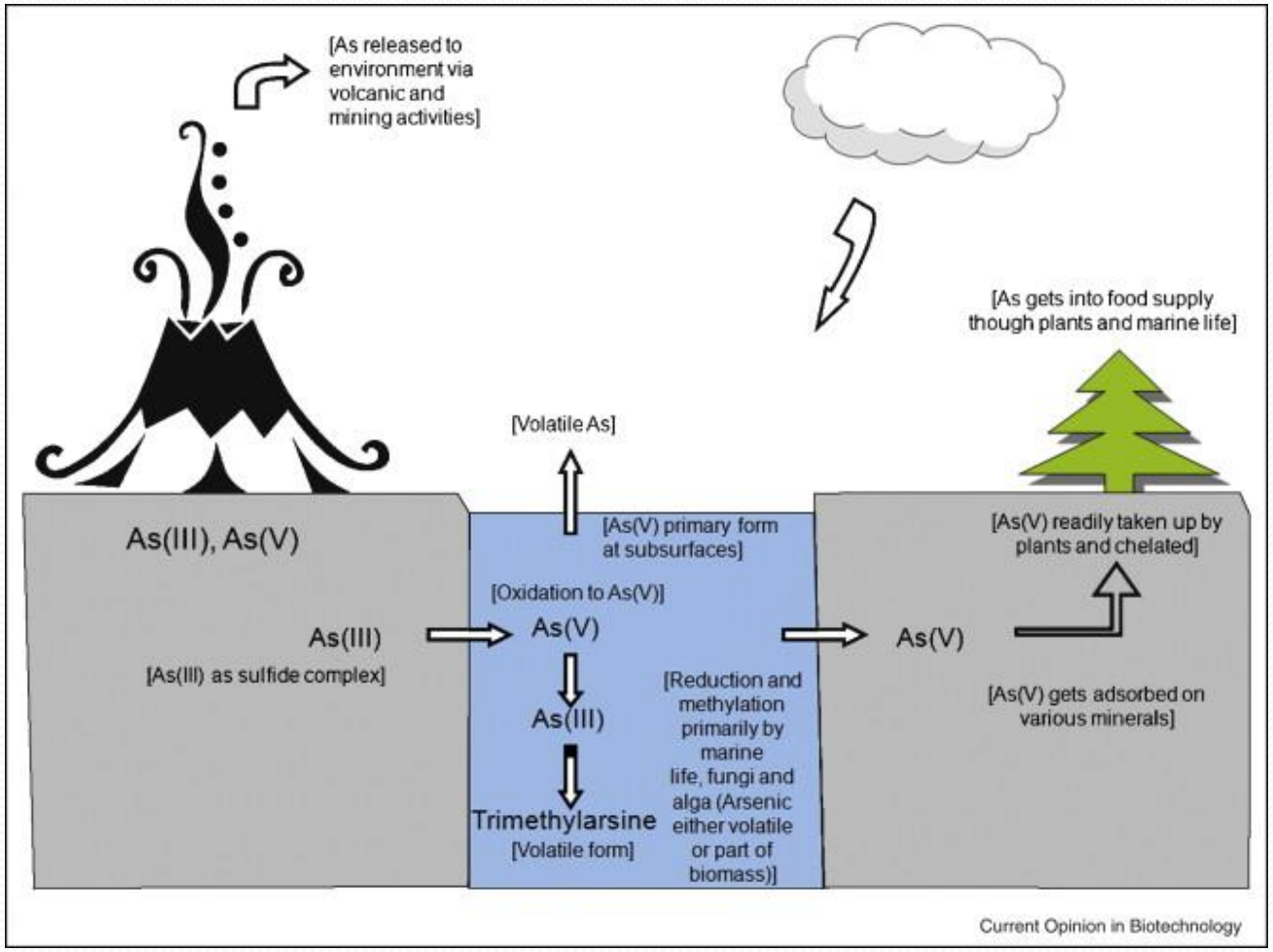
Seawater
Arsenate
1-2 ug/L

Algae
Arsenosugars and
arsenobetaine
And arsenolipids

Fish, mollusks, crustaceans, etc

Francesconi, *Pure Appl. Chem.* 2010

Sources in Soil



Transformations in Soil and Sediment

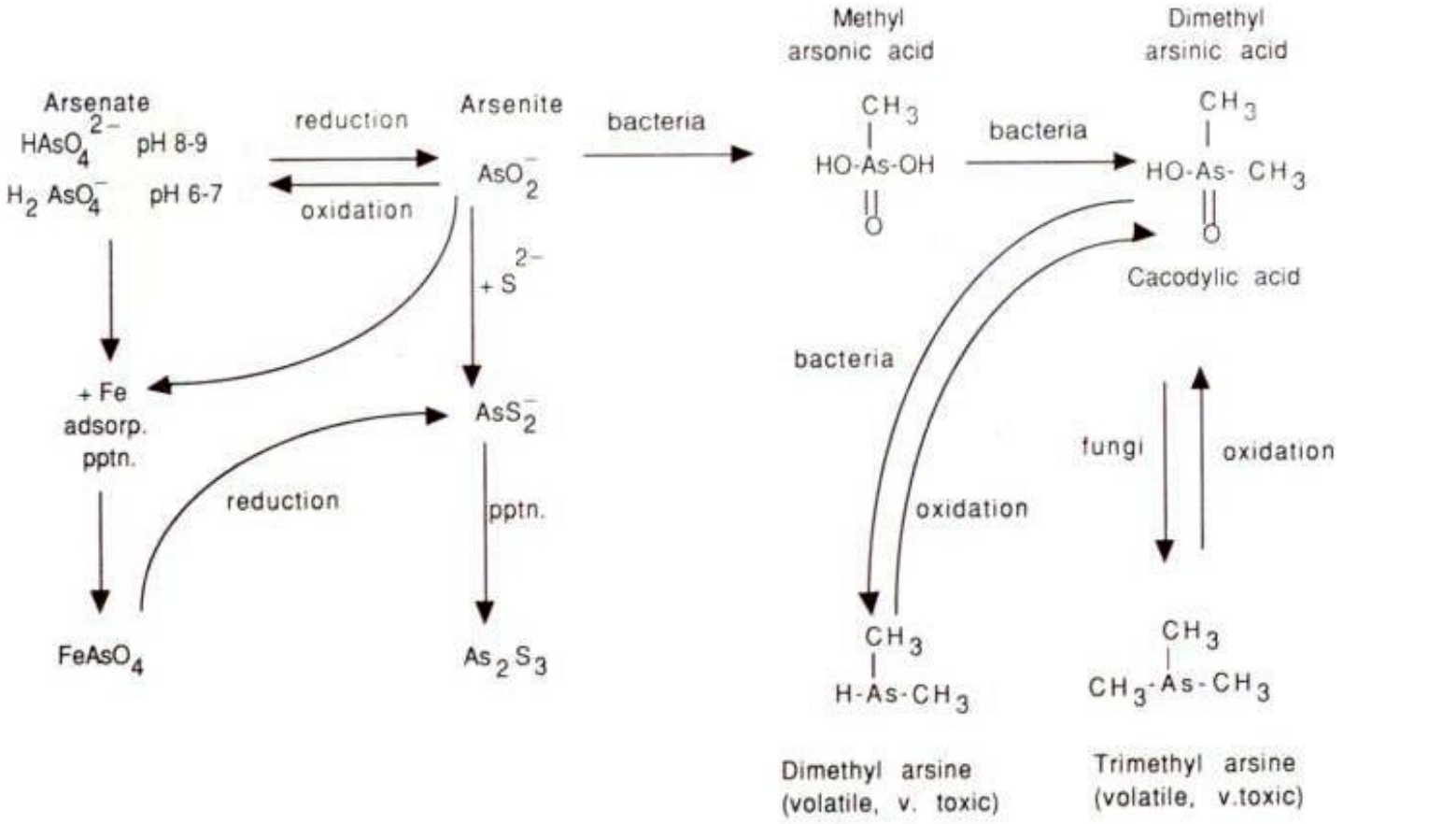


Figure 2. Chemical forms of arsenic and their transformations in soils.

Nriagu, 1990

Amounts in various plant species

- Radish – 30 mg/kg
- Spruce Bark – 10 mg/kg
- Mushrooms – 2.5 mg/kg
- Ferns – 1.3 mg/kg
- Clover – 0.330 mg/kg
- Lettuce – 0.25 mg/kg
- Rice and potatoes – 0.08 – 0.9 mg/kg
- Kale – 0.12 mg/kg
- Carrots – 0.08 mg/kg

Bergqvist, 2011 and Matschullat, 2000

As inputs to Soil (Anthropogenic)

- Mining and smelting waste – 38,000 t/a
  - Water and sludge
- Coal ash – 22,000 t/a
- Atmospheric Deposition – 13,000 t/a
- Animal and Agricultural Waste – 5,800 t/a
  - Pesticides and fertilizers
- Logging and wood waste – 1,700 t/a

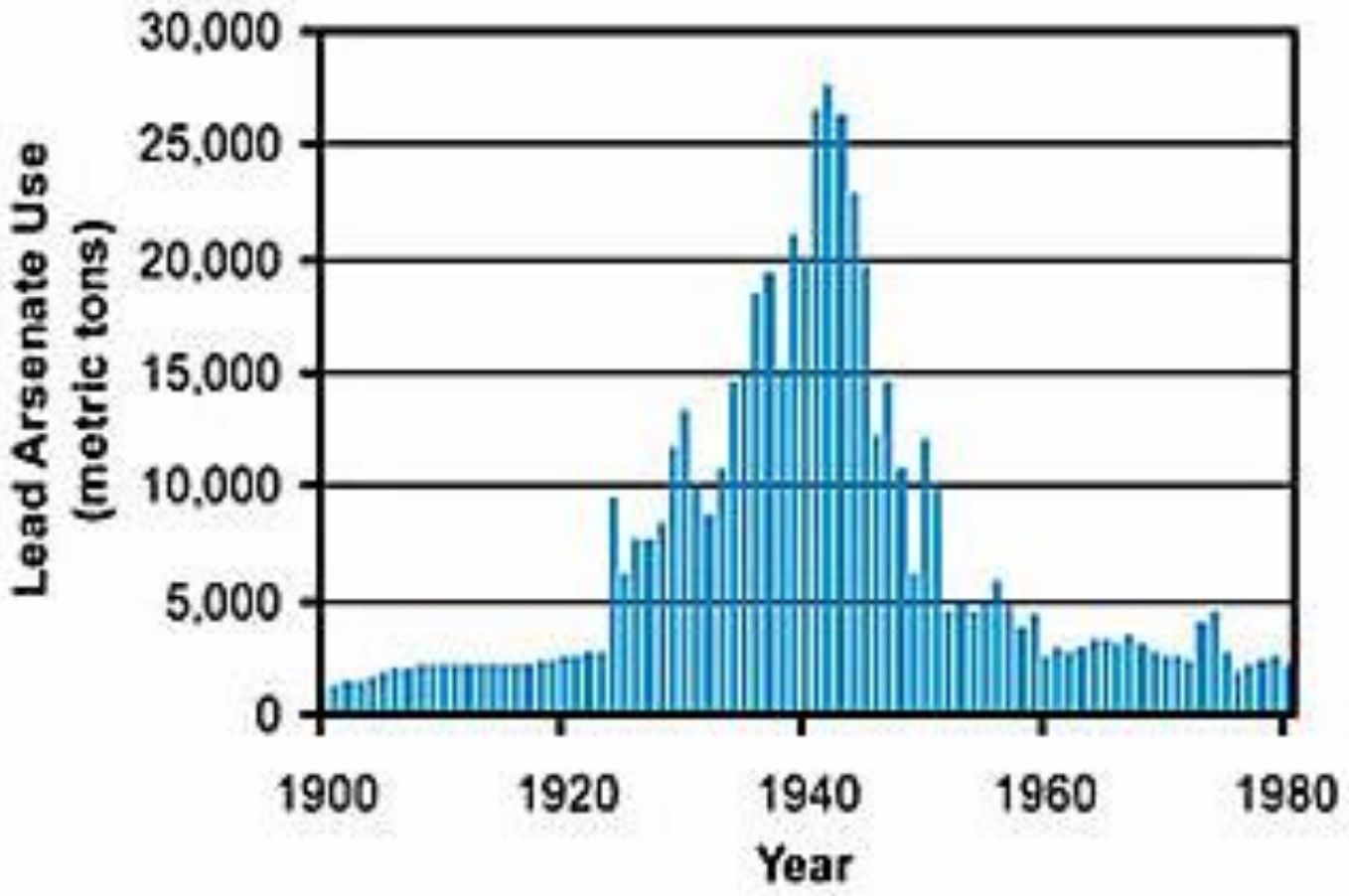
J. Matschullat, *Sci. Total Env.* (2000)249

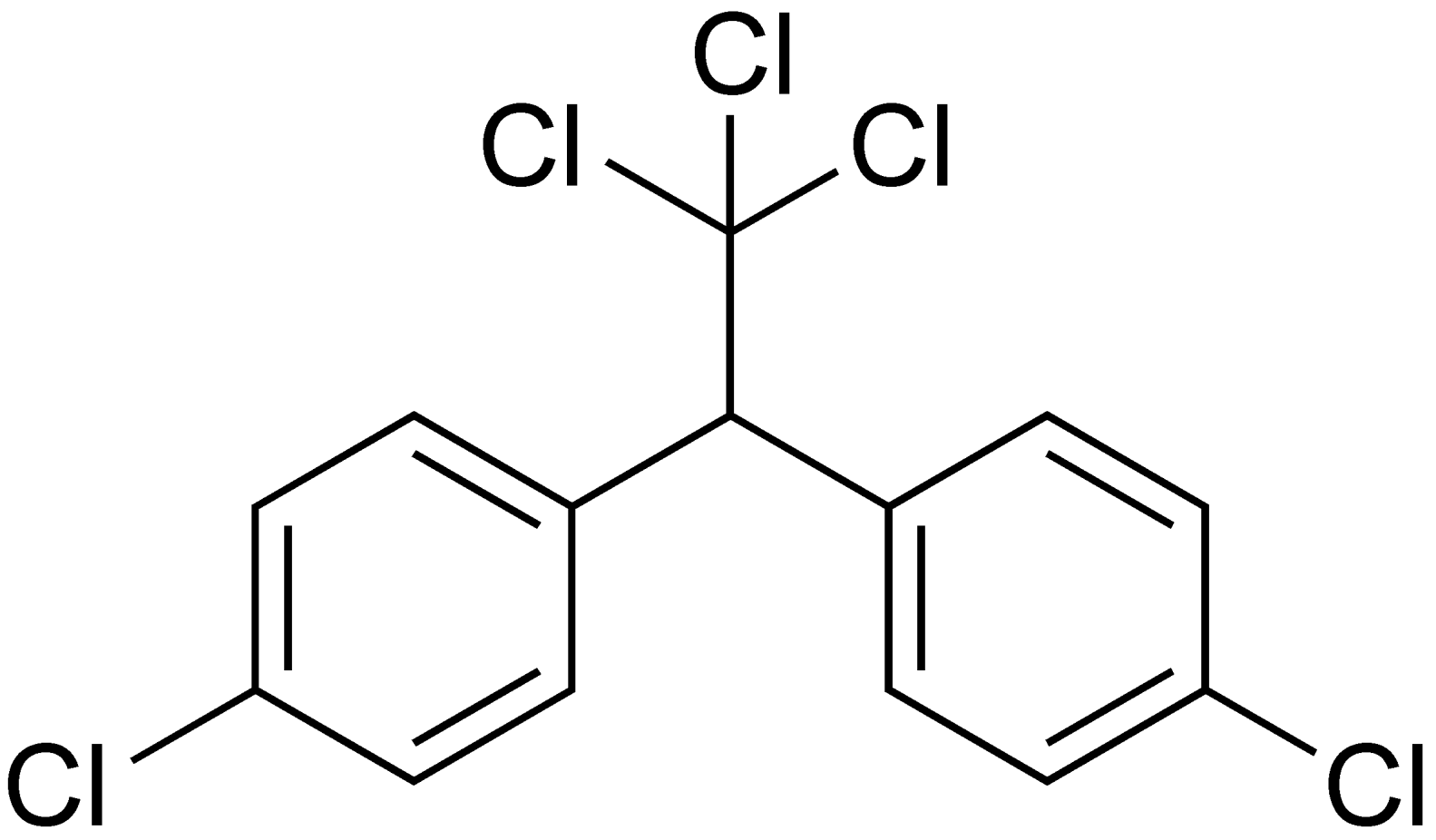
Arsenical pesticides

- Earliest Uses in 1800's (Paris Green)
  - Copper acetate triarsenite - Rodenticide

Cox, 2013

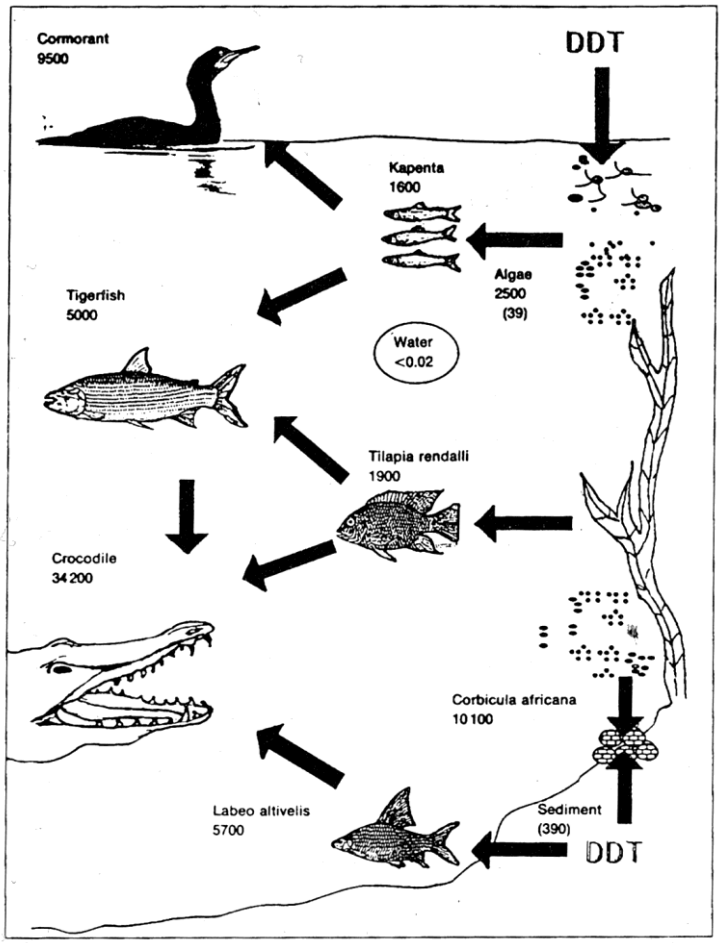

ACME
ARSENATE
OF
LEAD
ONE POUND
NET WEIGHT
POISON

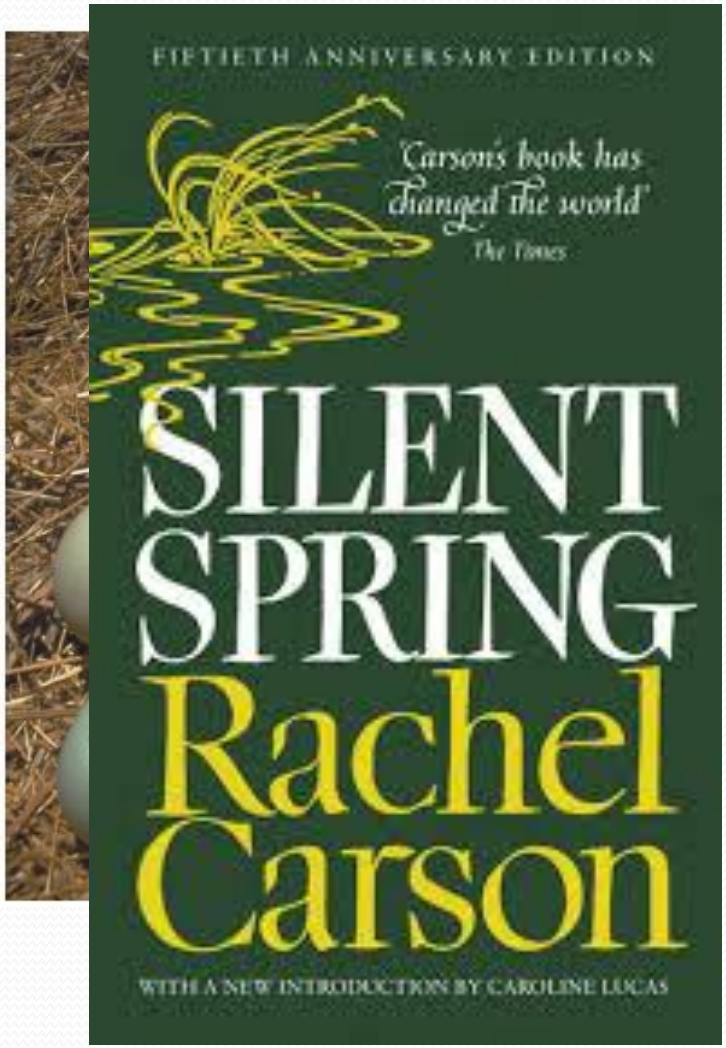

Lead Arsenate Use
(metric tons)
30,000
25,000
20,000
15,000
10,000
5,000
0
1900
1920
1940
1960
1980
Year


Cl
Cl
Cl
Cl
Cl


LIFE


SERVICE


Cormorant
9500
DDT
Kapenta
1600
Algae
2500
(39)
Tigerfish
5000
Water
<0.02
Tilapia rendalli
1900
Crocodile
34 200
Corbicula africana
10 100
Labeo altivelis
5700
Sediment
(390)
DDT


FIFTIETH ANNIVERSARY EDITION
'Carson's book has changed the world'
The Times
SILENT SPRING
Rachel Carson
WITH A NEW INTRODUCTION BY CAROLINE LUCAS

Arsenical pesticides

- Lead Arsenate - banned in 1998
- Chromated Copper Arsenate (CCA)
  - Wood preservative Banned in 2004
- MSMA, DSMA, CAMA, Cacodylic acid (DMAA)
  - Herbicides various AG, turf and ornamental and ROW.
- Roxarsone*

Dissipation of MSMA from Peanuts after Simulated Rainfall

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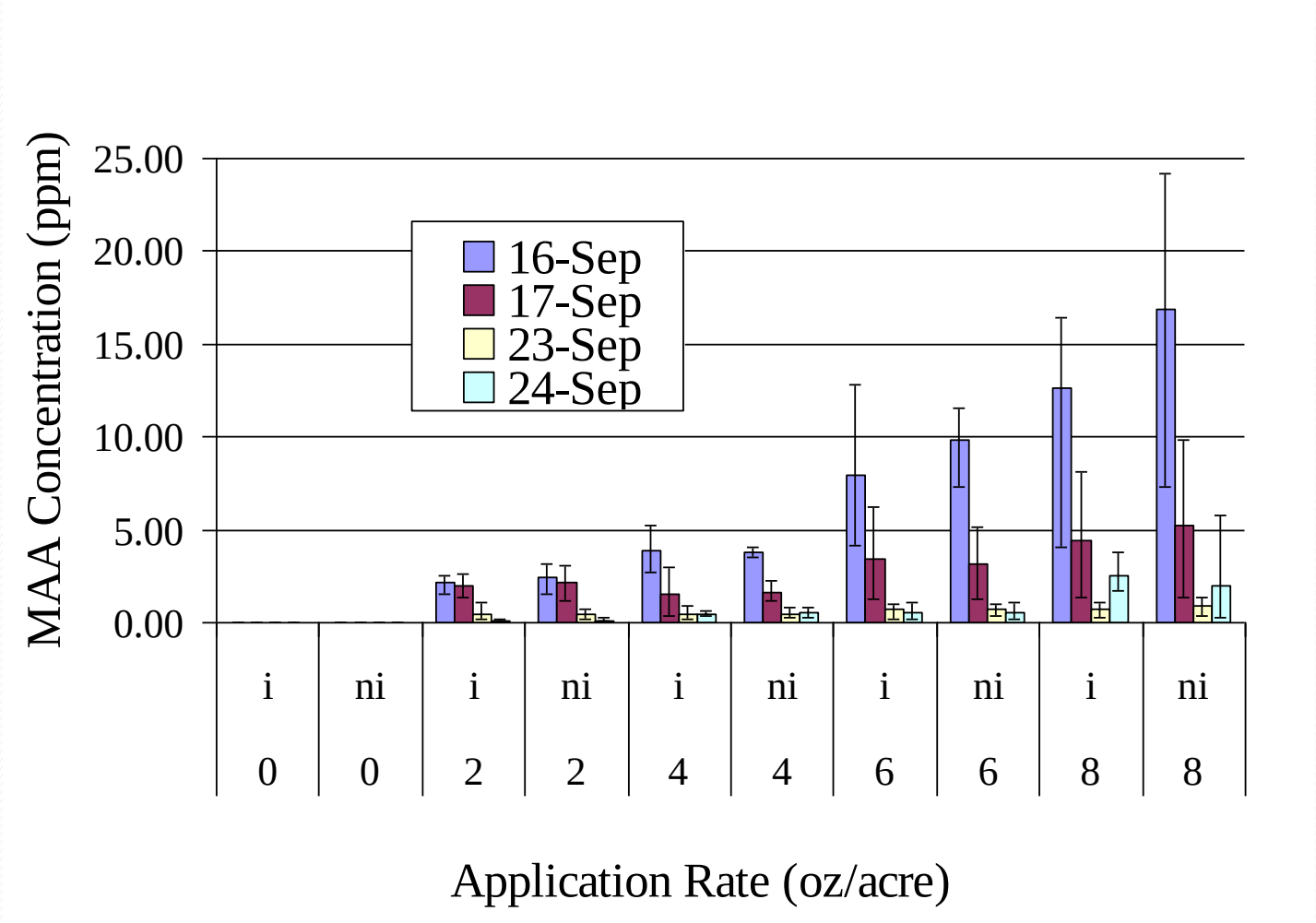
Department of Crop and Soil Sciences
University of Georgia – Griffin Campus
Georgia Department of Agriculture

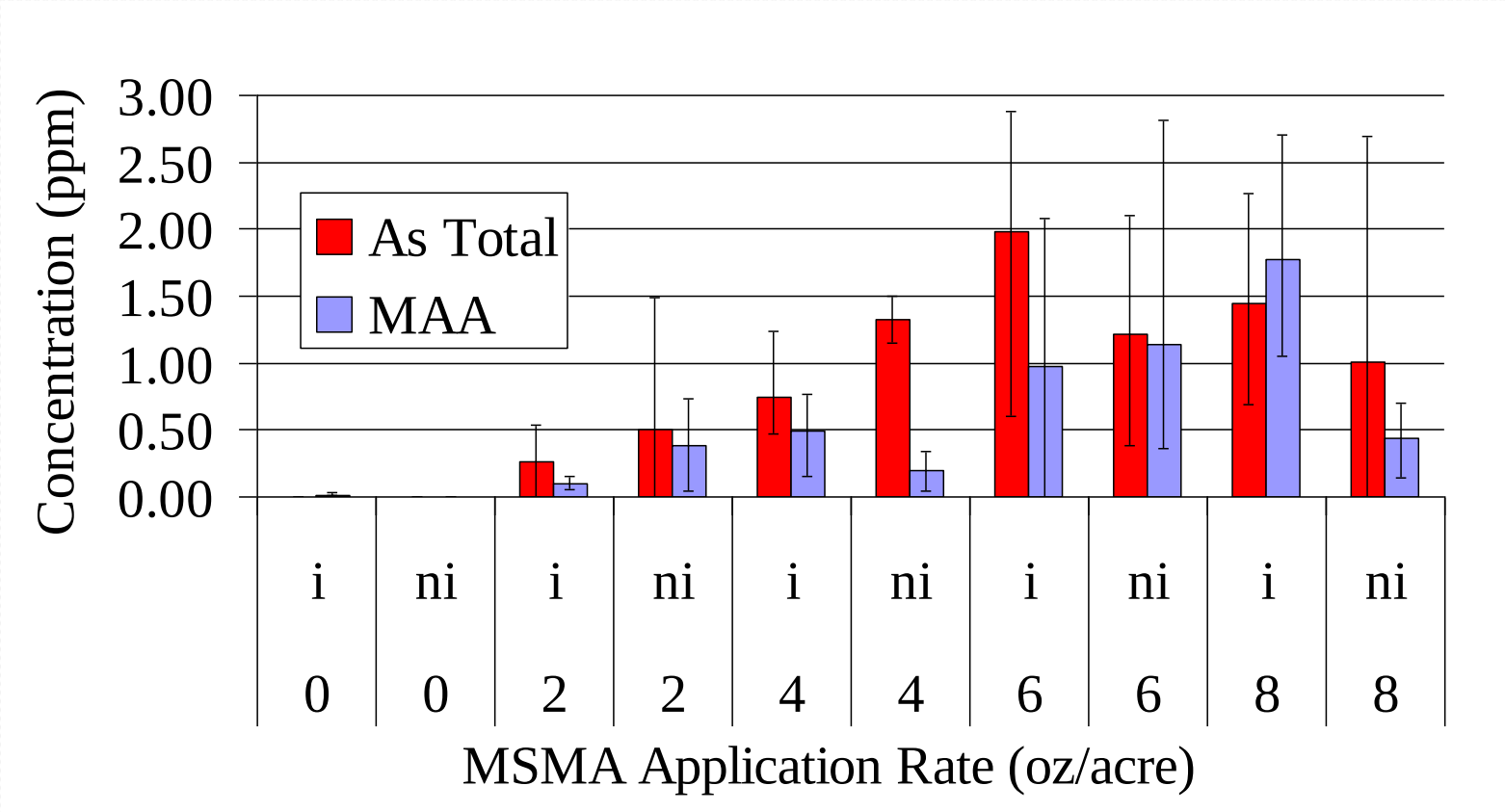
Armbrust and Bridges, *J. Agric Food Chem*. 2002

Decline of Methyl Arsonic Acid (MAA) Residues on Peanut Leaves



Armbrust and Bridges, *J. Agric Food Chem*. 2002

MAA and Total Arsenic in Peanut Meat at Harvest



Armbrust and Bridges, *J. Agric Food Chem*. 2002

So where is arsenic?

Answer: Its everywhere……. Even in you!!!

- Kidneys – 0.005 – 1.5 mg/kg
- Liver – 0.02 – 1.6 mg/kg
- Muscle – 0.009 – 0.65 mg/kg
- Bones – 0.08 – 1.6 mg/kg
- Hair – 0.02 – 3.7 mg/kg
- Finger and toe nails – 0.2 – 3 mg/kg
- Blood and urine – 2 – 10 ug/L
- Overall average person – 0.14 – 0.26 mg/kg
  - Human reservoir on the planet – 108 tons

Summary and take home messages

- Arsenic is natural, exists in many forms in nature, and is mobilized by both man's activities and natural events.
- Greatest sources of inputs today due to mining and smelting activities, however agricultural activities have been historically important.
- Speciation of arsenic is critical. Differing species of As have different toxicities and different bioavailabilities. This will also impact any risk assessment.

Final thoughts…….

- Any risk assessment must include ALL aggregate sources of exposure for it to be of value.
- Route of exposure (air, water, food) and associated bioavailability is important.
- Consideration needs to be given to the analytical method, as certain extraction techniques can alter speciation.