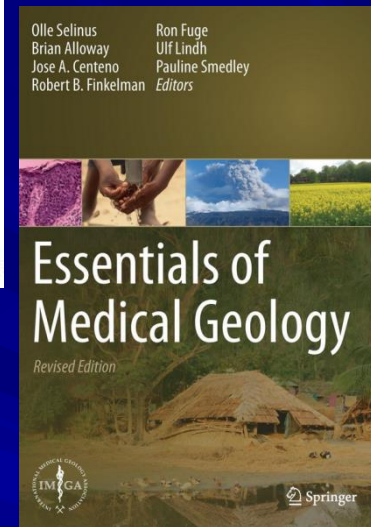
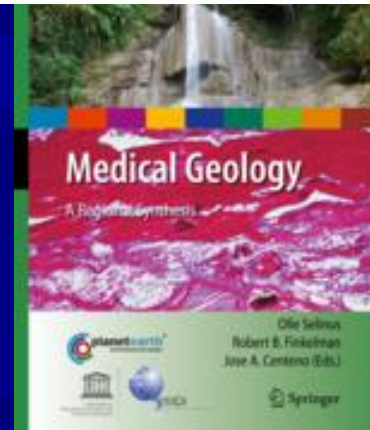
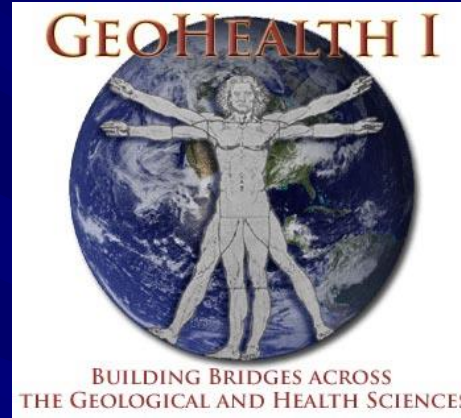
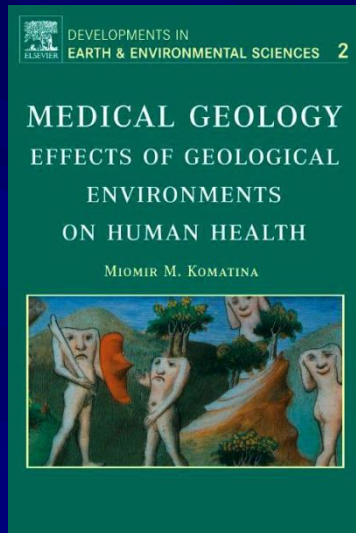


# Geologia e Salute: quando la natura ci minaccia



# What is Medical Geology ?

“The science that deals with the relationships between natural geological factors and human and animal health” (*Selinus, 2005*)



[www.medicalgeology.org](http://www.medicalgeology.org)

It is a dynamic re-emerging discipline bringing together geoscientists and biomedical/public health researchers to solve a wide range of environmental health problems.

# **Environmental health problems**

- **Exposure to natural dust and to radioactivity**
- **Identification and effects of volcanic emissions**
- **Exposure to toxic levels of trace essential and non-essential elements**
- **Nutrient trace element deficiencies**
- **Naturally occurring toxic organic and inorganic compounds in drinking water**

# NATURALLY OCCURRING DUSTS

Exposure to mineral dust can cause a wide range of respiratory problems. The dust can be generated by mining rocks or coal, sandstorms, and smoke plumes from fires (both natural and man-made) or simply from the wind dispersing fine-grained minerals from the earth's surface.

Some aspects have been well known for decades:

- General effects of industrial / commercial asbestos
- Silicosis (hard rock mining)
- Black lung (coal mining)

New issues and problems are arising:

- Effects of trace asbestos in other rocks, industrial products
- Valley fever
- Trans-oceanic dust transport



Diameters of airborne particles: solids, liquids, gases, inorganic, and biologic Earth materials and the techniques usually employed in detection and analysis.

Particle diameter →										
Meters	10 <sup>-10</sup> (1Å)	10 <sup>-9</sup>	10 <sup>-8</sup>	10 <sup>-7</sup>	10 <sup>-6</sup>	10 <sup>-5</sup>	10 <sup>-4</sup>	10 <sup>-3</sup>	10 <sup>-2</sup>	
Microns (μ, 10 <sup>-6</sup> meter)	0.0001	1 μm, 1 nm 0.001	0.01	0.1	1	10	100	1 mm 1,000	1 cm 10,000	
Solids			Clay		Silt	Fine sand	Coarse sand		Gravel	
				Volcanic and industrial ash						
				Lung-damaging dusts Combustion nuclei, fly ash, colloidal silica, coal dust						
Water-related	H <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub> O	Smog		Clouds and fog		Mist	Drizzle	Rain
Biological		CO <sub>2</sub>		Proteins	Viruses	Bacteria, spores, and pollen		Cells	Hair	
Sampling and analysis methods							Visible to the eye			
					Impinger		Sieving			
				Electron microscope · · · light microscope						
	Spectroscopy			X-ray diffraction						

Of greatest concern for its effects on human health are the finer particles of respirable (inhalable) dusts. In this regard, considerable work is being conducted to identify dust particles derived from soils, sediment, and weathered rocks

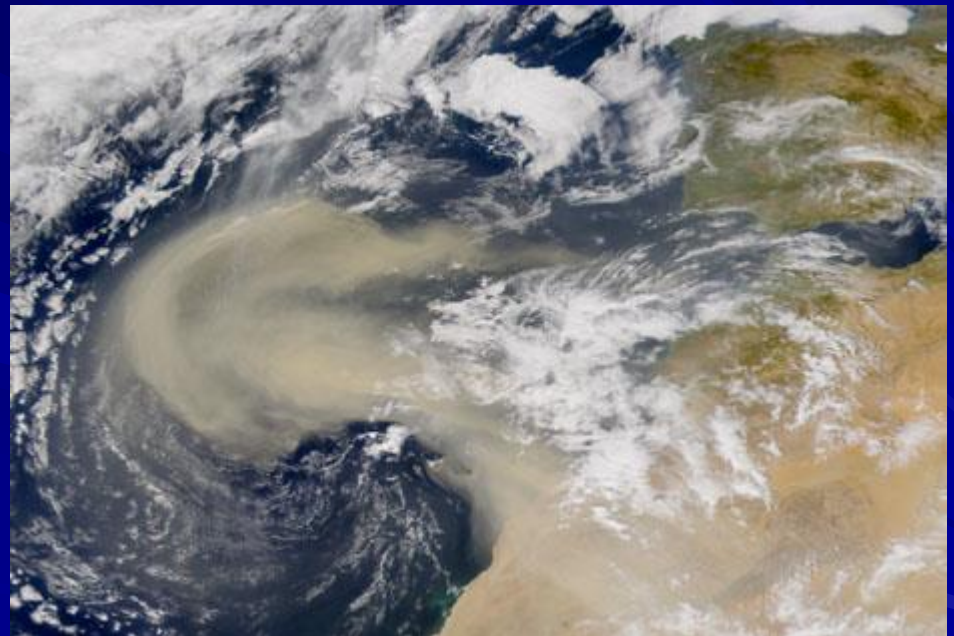
# NATURALLY OCCURRING DUSTS

Dust exposure can even take on global dimensions.

Ash ejected from volcanic eruptions can travel many times around the world, and recent satellite images have shown wind-borne dust from the Sahara and Gobi deserts blown halfway around the world.



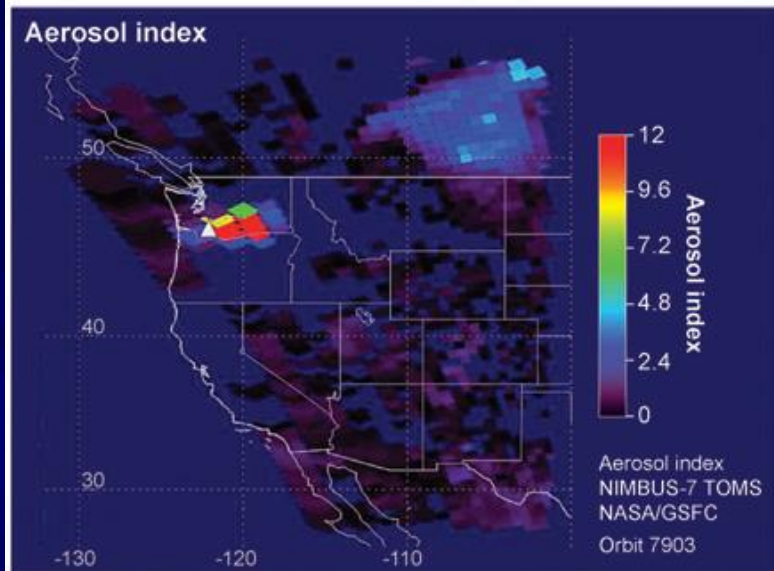
Eruption in Kamchatka peninsula (Russia). Dust column 20 km high is a dense cloud extending for 800 km and covering a 150,000 km<sup>2</sup> area (from *Space Shuttle Endeavour*, October 1994)



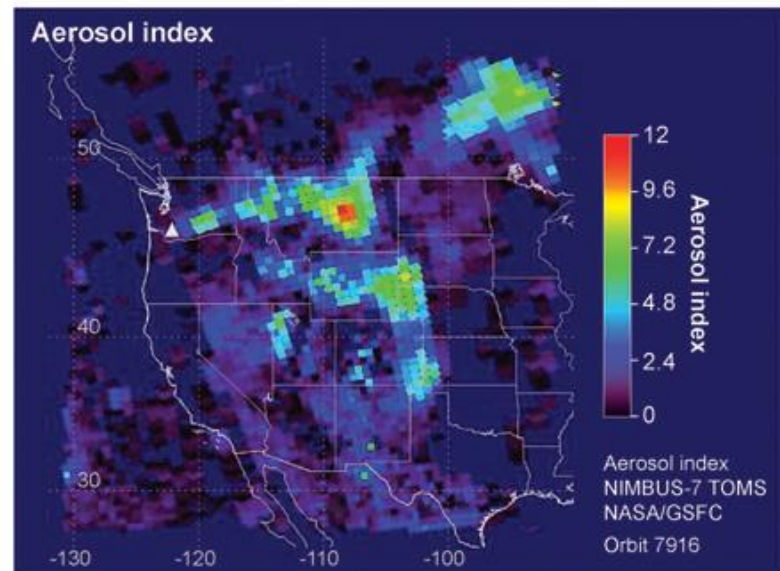
A large dust cloud heads east over the Atlantic Ocean from the West Coast of Africa on February 26, 2000. (SeaWiFS satellite image courtesy of NASA).

Satellite images of the Mt. St. Helens eruption May 18 and 19, 1980, showing eastward trend of aerosols and SO<sub>2</sub> over the two days.

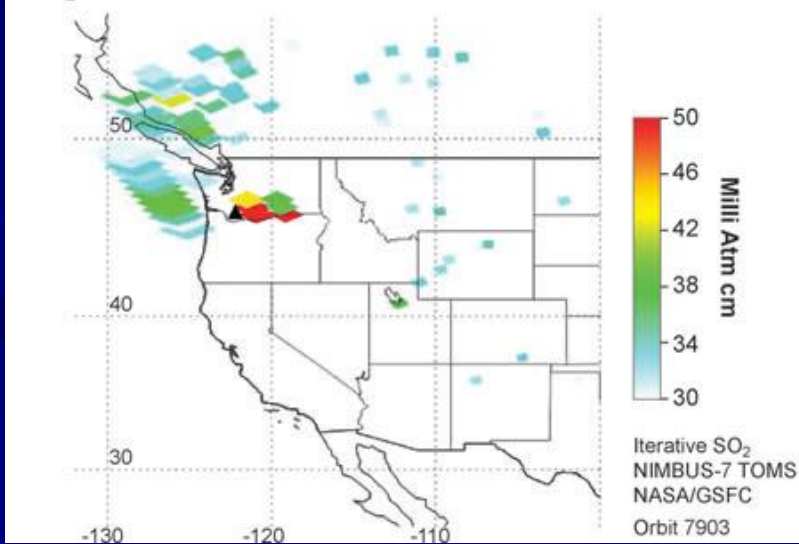
May 18, 1980



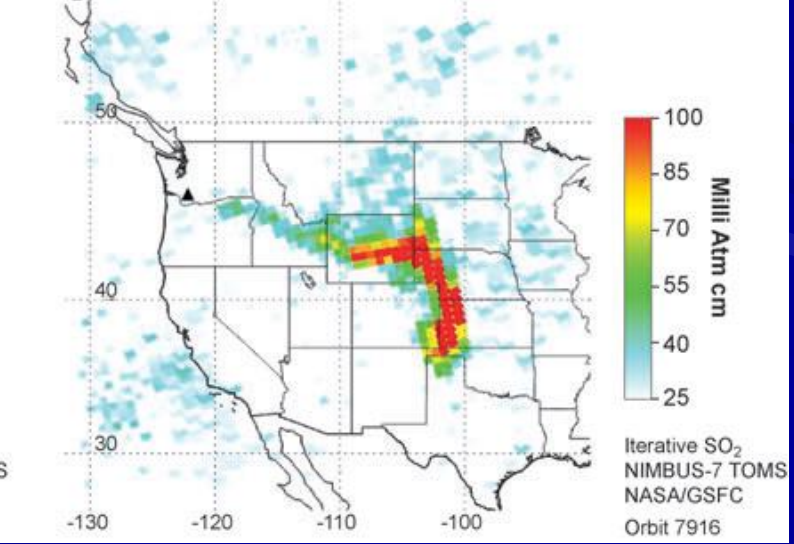
May 19, 1980



SO<sub>2</sub> concentrations



SO<sub>2</sub> concentrations



# Volcanic gas

Water, CO, CO<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>, SO<sub>3</sub>, HCl, HF, CH<sub>4</sub>

One of the most dramatic demonstrations of the suffocating effect of CO<sub>2</sub> was the explosion of *Lake Nyos* in *Cameroon* on August 12, 1986.

More than 1700 people and 3500 livestock were killed by the flow of CO<sub>2</sub> gas cloud emitted as a result of convective turnover of a stratified lake in a crater of a defunct volcano.



**How to avoid future disaster?**

**To know past events and to set up a monitoring system**



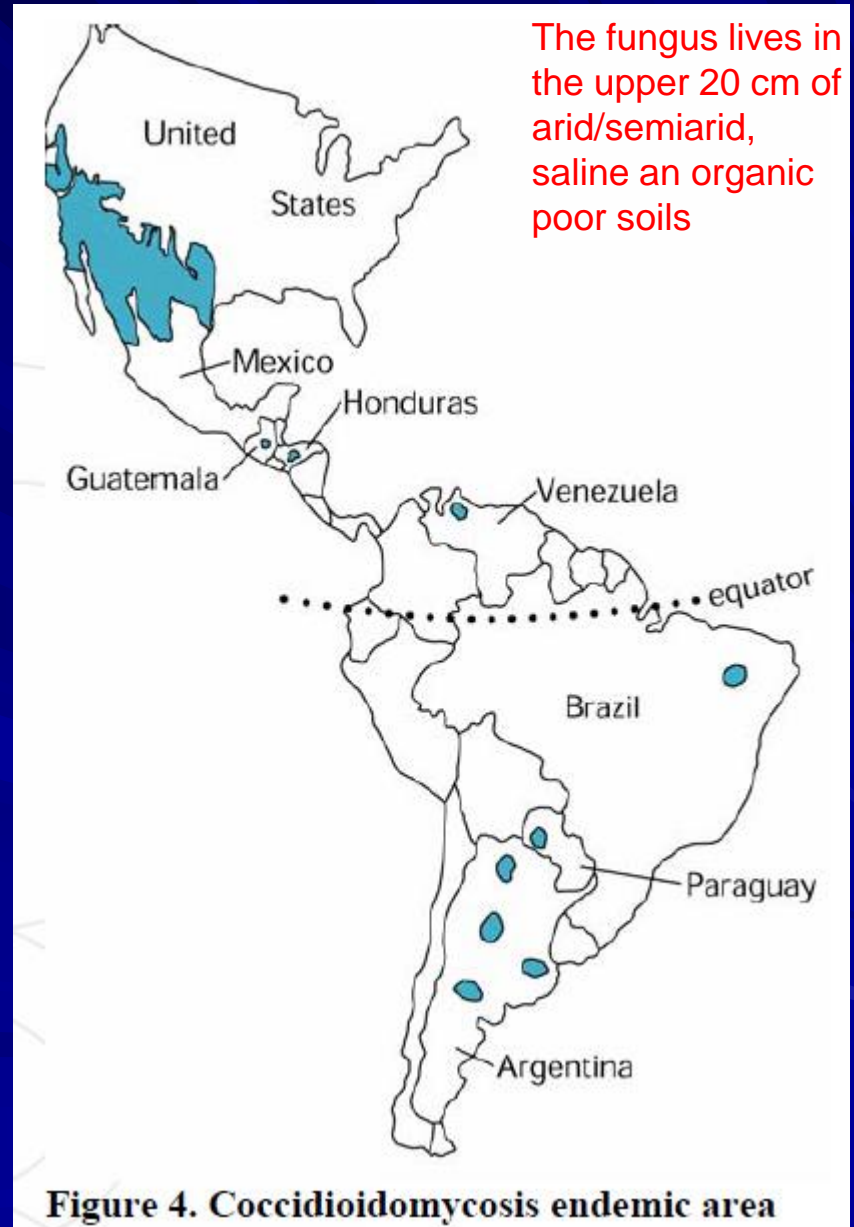
# Valley Fever (*Coccidioidomycosis*)

7,500 new cases of Valley Fever occur annually in the U.S.A, with a hospitalization cost in excess of \$60 million a year



Figure 1. *Coccidioides* sp. hyphae showing initial formation of arthroconidia

VF results from an infection caused by inhaling specific airborne pathogenic fungi (*Coccidioides immitis*) spores which can be transported by wind as far as 700 km, causing outbreaks



# Valley Fever (Coccidioidomycosis)

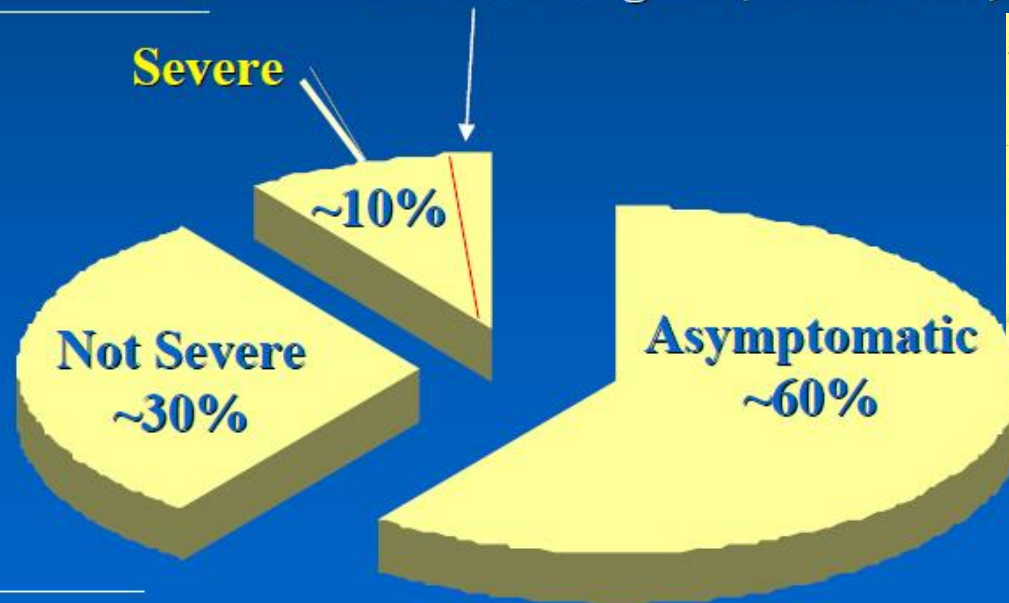
Clinical manifestations occur in ~40% of infected persons



self-limited  
influenza-like  
illness to  
pneumonia

fatigue  
cough  
chest pain  
fever  
rash  
headache  
joint ache

In ~1% to 2% of cases the disease becomes disseminated, and affects skin, bones, or joints, or develops into meningitis (<1 % fatal)



Fungus > maturation (spores) > soil disturbance > transport > inhalation > infection

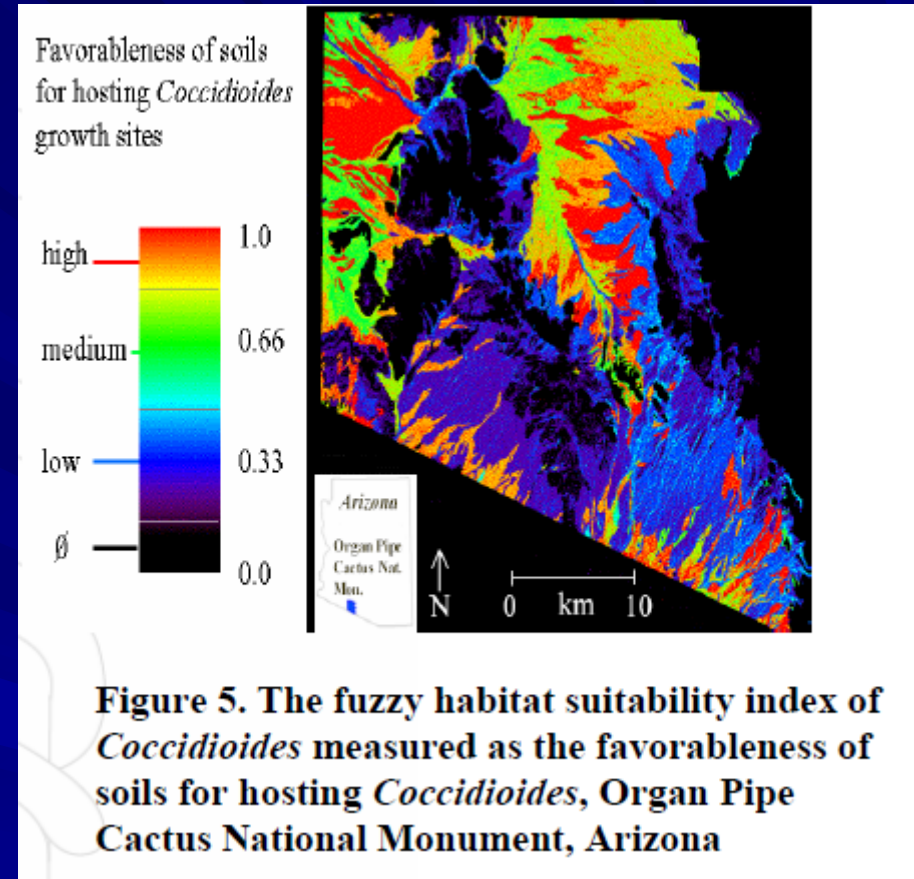
# Valley Fever (*Coccidioidomycosis*)

How to mitigate the risk ?

- 1) Defining the geological/ecological habitat for the fungi (**the key !**)
- 2) Spatial and temporal models of the habitat to delineate favorable conditions in soils
- 3) To monitor and to model dust emissions

The goal

- To predict possible epidemics
- Allowing the use of biological and chemical control methods
- To allow dust abatement methods



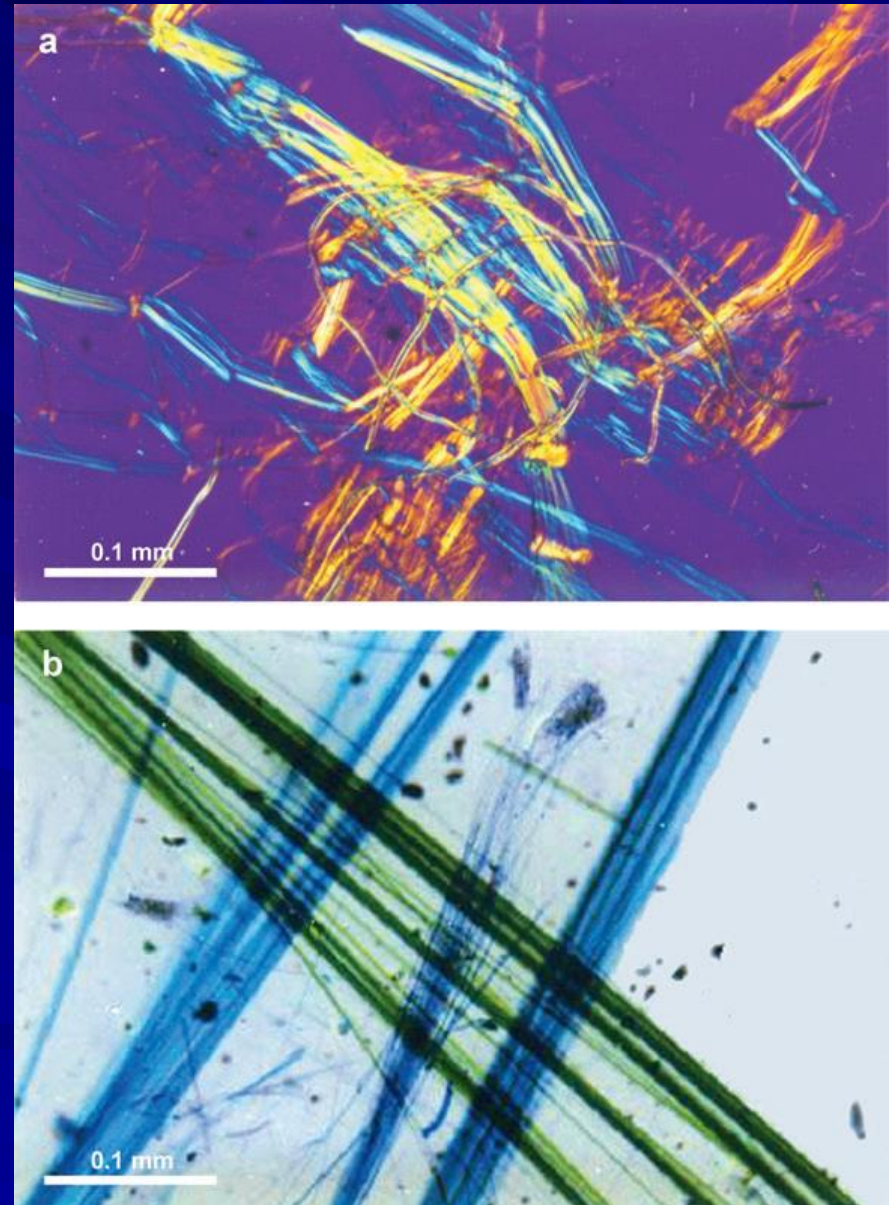
# ASBESTOS

Asbestos is a diverse group of minerals with several common properties; separation into long thin fibers, heat resistance, and chemically inertness.

In the 1980s the U.S. medical community recognized that exposure to respirable asbestos fibers can cause severe health problems including *mesothelioma*, *lung cancer*, and *asbestosis*.

(a) Bundles of flexible fibers of chrysotile or "white asbestos." Optical photomicrograph under crossed polarization. The different colors are related to the thickness of the fiber bundles.

(b) Fibrous crocidolite, the asbestos form of the mineral riebeckite also known as "blue asbestos." Optical photomicrograph under crossed polarization. Straight parallel fiber bundles are typical of the amphibole mineral group. Courtesy of Malcolm Ross, USGS.



# ASBESTOS

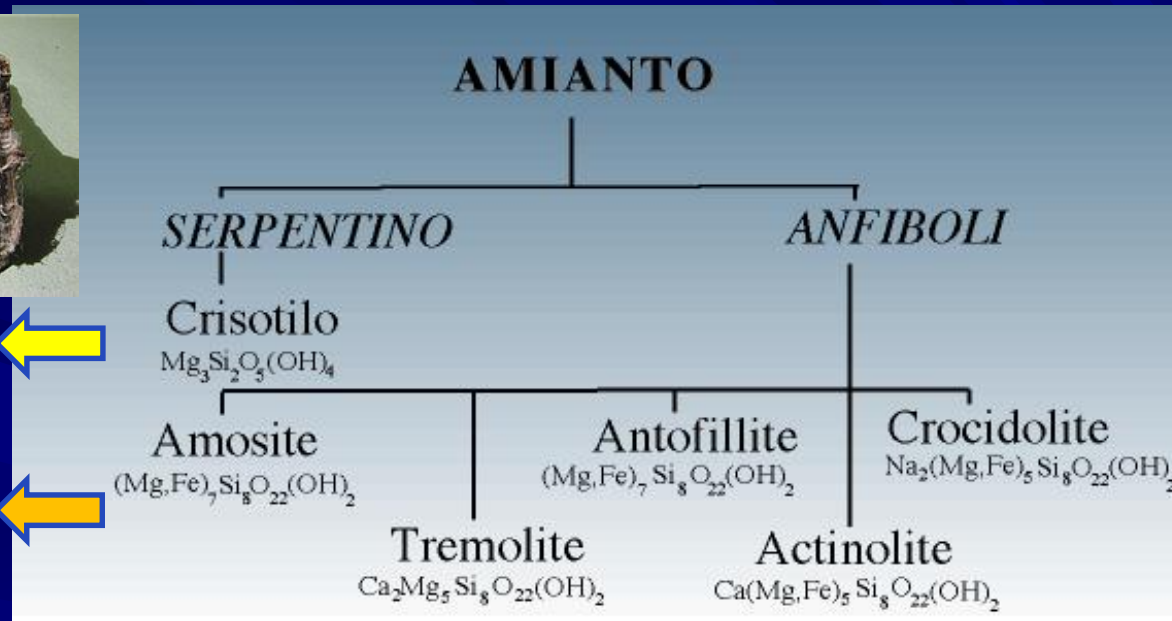
Not all forms of asbestos are equally carcinogenic and deleterious to health



Less toxic



More toxic







Chrysotile can break more easily into shorter fibers, and therefore can be cleared more easily by the lungs.

The asbestos amphiboles are less soluble than chrysotile in the bodily fluids, and therefore cannot be cleared as easily by the body.

# ENVIRONMENTAL ASPECTS OF CHEMICAL ELEMENTS

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu									

-  Elementi con valenza tossicologica non ben definita
-  Elementi tossici
-  Elementi potenzialmente tossici
-  Elementi tossici e radioattivi

# TRACE ELEMENT EXPOSURE: DEFICIENCY AND TOXICITY

Trace elements play an essential role in the normal metabolism and physiological functions of animals and humans.

## **Macronutrients (C H N O P S)** and **micronutrients**

16 elements are established as being essential for good health!

**Ca, P, Mg** and **F** are required for structural functions in bone and membranes.

**Na, K** and **Cl** are required for the maintenance of water and electrolyte balance in cells.

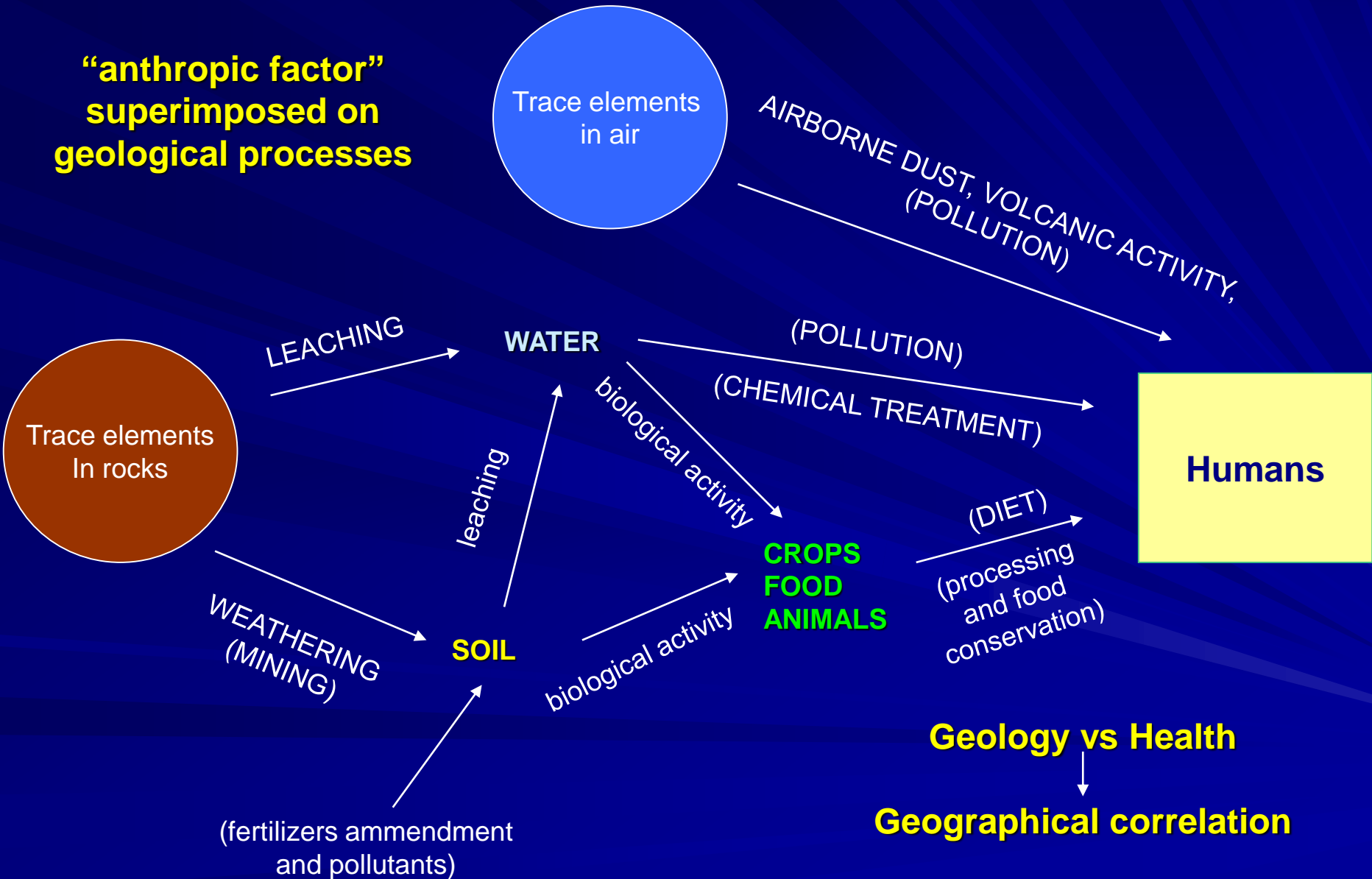
**Zn, Cu, Se, Mn** and **Mo** are essential constituents of enzymes or serve as carriers (iron) for ligands essential in metabolism.

**I** is an essential component of the thyroid hormone thyroxine.

**Cr** is the central atom of the hormone-like glucose tolerance factor.

# Pathways through which trace elements enter the body

**“anthropic factor”  
superimposed on  
geological processes**





# Diseases Due to Trace Elements

## Endemic diseases due to trace element deficiency

- Iodine
- Selenium

## Cronical exposure to essential and non-essential elements

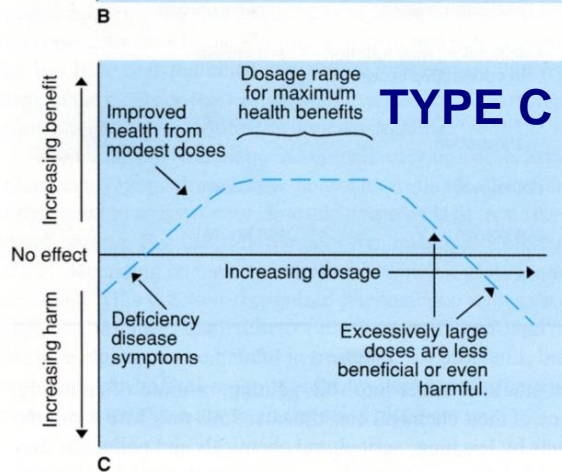
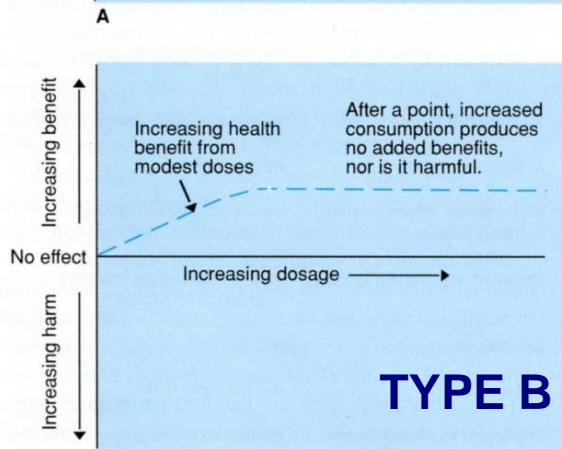
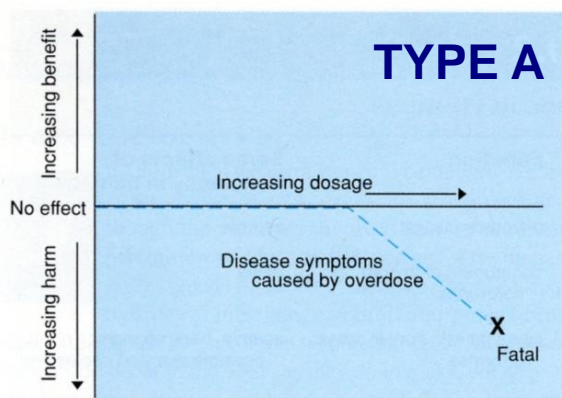
- Fluorine
- Cadmium
- Arsenic

# The effects of short-term dietary deficiencies or excess of trace elements

← **No essential elements:** no effects at low concentrations, lethal at high levels (ex. Cd, Pb, Hg, As)

← Beneficial effects at the beginning and lower than a limit concentration; no effects at high level (ex. Ca)

← Diseases due to trace element deficiencies as well as excesses (ex. Cu, Mo, Mn)



## Iodine (curve type C)

Necessary for thyroid gland → Iodine Deficiency Disorders (IDD) → goiter, cretinism, reduced IQ, miscarriages and birth defects

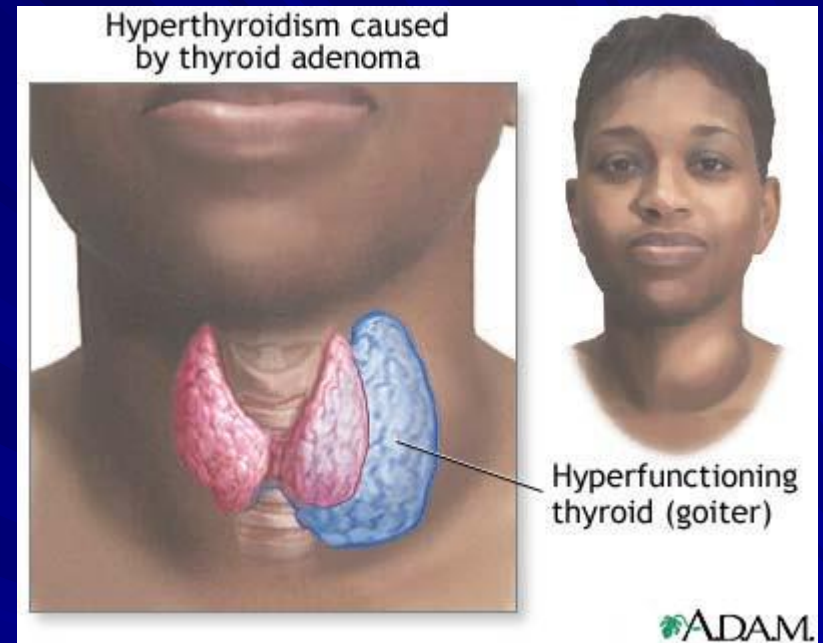
effect: lack of iodine in soil → crop and animals → diet

causes: geology ?

Leaching due to melting waters from the ice cap after the last glaciation era (USA);

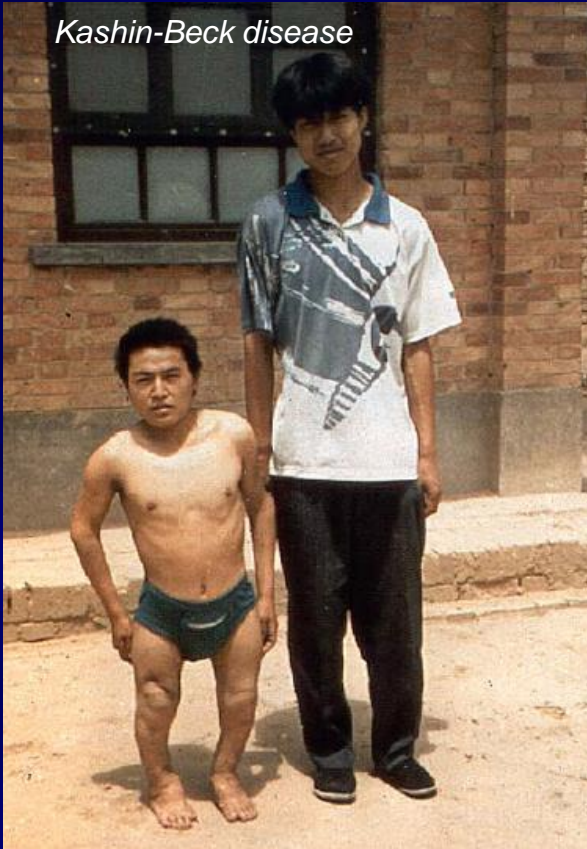
70 % of Iodine in sedimentary rocks (marine);  
seawater reach in Iodine (58 ppb)

remediation: salt amended with iodide of Na and K



At risk: populations from developing countries and tropical areas (weathering)

Kashin-Beck disease



## Selenium (curve type C)

- terrestrial crust  $< 0.1$  ppm (basalts, schists)
- essential at low concentrations: antioxidant protective functions
- $0.006-0.2$  mg/day = daily intake variable on the diet basis  $\rightarrow$  soil
- vegetables (ex. cauliflower, onion, cereals) are Se bioaccumulator
- deficiency: muscular abnormalities (*Kashin-Beck disease*), liver necrosis, juvenile cardiomyopathy (*Keshan disease*)
- overexposure ( $>5$  mg/day): gastrointestinal disorders, liver and spleen damage, carcinogenic.



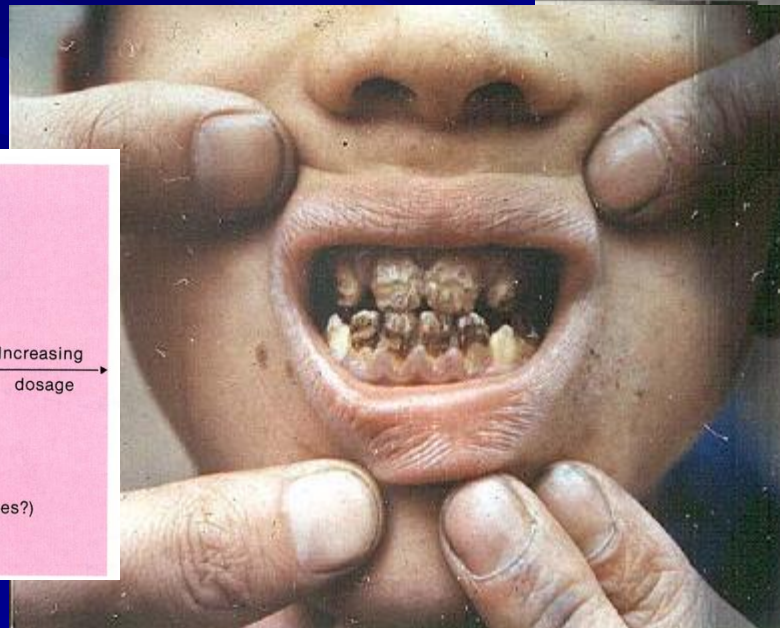
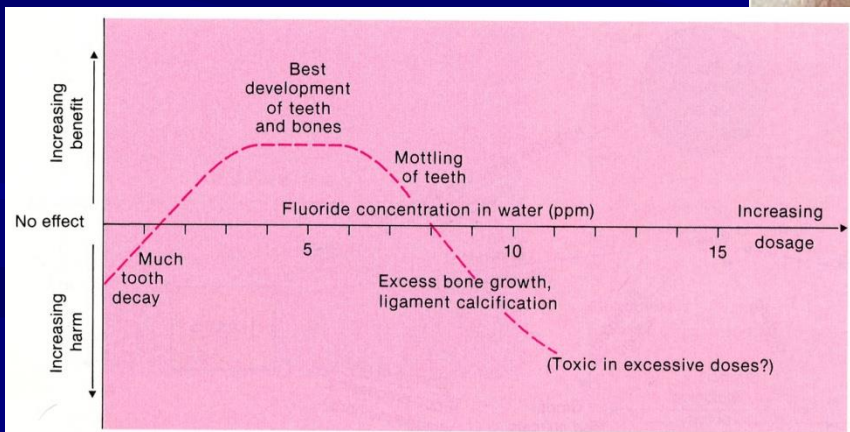
# Fluorine (curve type C)

- about hundreds of ppm in the continental crust, a few ppm in natural waters
- necessary to reduce dental caries (ideal concentration in drinking waters 1 ppm → 1 mg/l)
- 0.3-5 mg/day = intake on dietary basis → soils
- important in osteosclerosis reduction

**Anomalous dosis:** 2-8 x normal contents

**cause:** fluoride ions rich water (in igneus rocks)

**effects:** mottling of teeth dental (20-40 x) and skeletal fluorosis



(from J.A. Centeno, Armed Forces Institute of Pathology)

# Cadmium (curve type A)

- Incorporated in trace amounts in Zn minerals (ZnS) and separated as by product of mining operations.
- Uses: to prevent corrosion, Ni-Cd batteries.
- The expense of mining and refining Cd has encouraged recycling.
- It is promptly taken up by plants (ex. lettuce, spinach, tobacco leave).
- Cd can accumulate in the body tissue since it easily associates to sulfur-containing amminoacids (cysteine)

**Itai-itai disease was caused by Cd poisoning due to mining in Japan (1968)**



**The affected population consumed rice containing elevated contents of Cd grown in paddies irrigated by waters downstream sulphide deposits mined for Cu and Zn.**

**The disease weakens bones and joints, making movements painful.**



Numero atomico

33

As

Arsenico  
74,9216

[Ar] 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>3</sup>

Configurazione  
elettronica

Simbolo atomico

Nome dell'elemento

Peso atomico

-3, 0, +3, +5

# Arsenic (curve type A)

Metalloid  
Calcophile

Natural sources: carboniferous shists, sulphides, sediments, volcanic and thermal springs

Minerals:

Arsenopirite (FeAsS), Pirite arseniosa (Fe(AsS)<sub>2</sub>), Realgar (AsS), Orpimento (As<sub>2</sub>S<sub>3</sub>)

Cu<sub>3</sub>AsS<sub>4</sub> -  
Enargite



AsS -  
Realgar



FeAsS - Arsenopirite



As<sub>2</sub>S<sub>3</sub> - Orpimento



Numero atomico	
33	
<b>As</b>	Simbolo atomico
Arsenico	Nome dell'elemento
<b>74,9216</b>	Peso atomico
[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>3</sup>	
Configurazione elettronica	
	-3, 0, +3, +5

## Anthropogenic sources:

Mining

Coal

Pesticides

Glass

microelectronics (semiconductors and laser, GaAs)

medicine (As<sub>2</sub>O<sub>3</sub> in leukemia)

As<sub>2</sub>S<sub>2</sub> painting

military toxic gas (lewisite)

**Toxicity:** Arsina (AsH<sub>3</sub>) > As<sup>3+</sup> inorg > As<sup>3+</sup> org > As<sup>5+</sup> inorg > As<sup>5+</sup> org > As<sup>0</sup>

## Exposure to As occurs via:

Ingestion

Inhalation

Dermal contact

Parenteral route



# Arsenic-Induced Skin Disorders



Hyperpigmentation



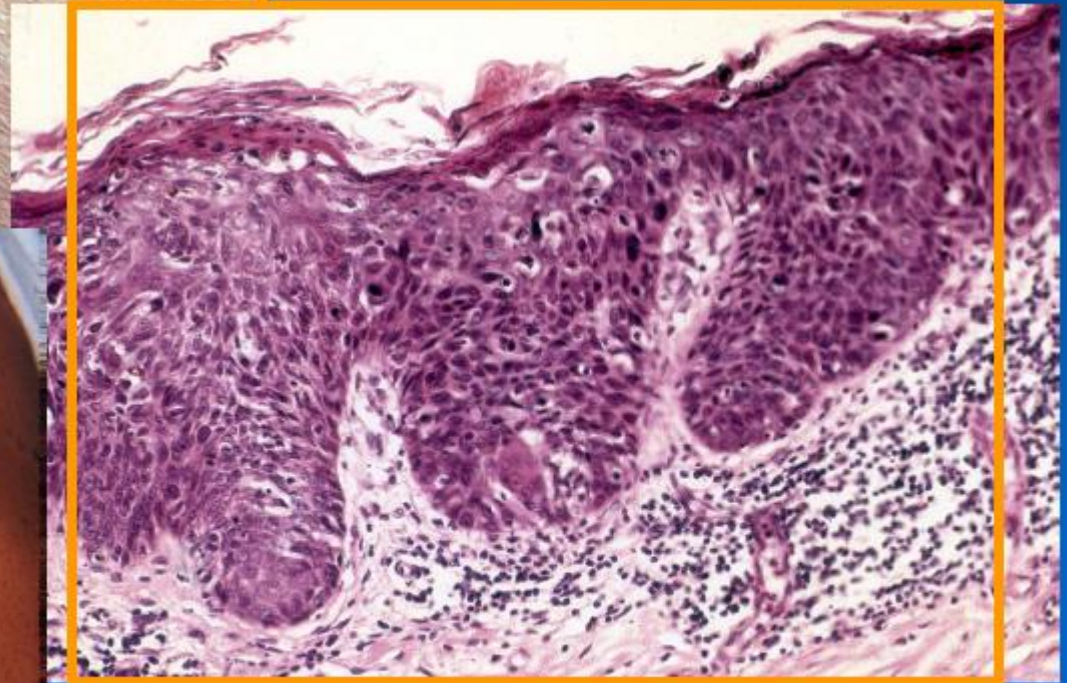
Hyperkeratosis



Photos: Courtesy of Prof. Baoshan Zheng, China and Prof. Arnulfo Portales, Mexico

# Arsenic-Induced Bowen's Disease

Carcinoma intraepidermico



Drinking water contaminated with As is a major public health problem!

Acute and chronic As exposure via drinking water has been reported all over the world



Freshwaters: 0.1-2.0  $\mu\text{g/l}$   
 Concentrations higher in geothermal and mining areas

Drinking water (WHO):  
 50  $\mu\text{g/l}$  (1942)  
 10  $\mu\text{g/l}$  (2002)

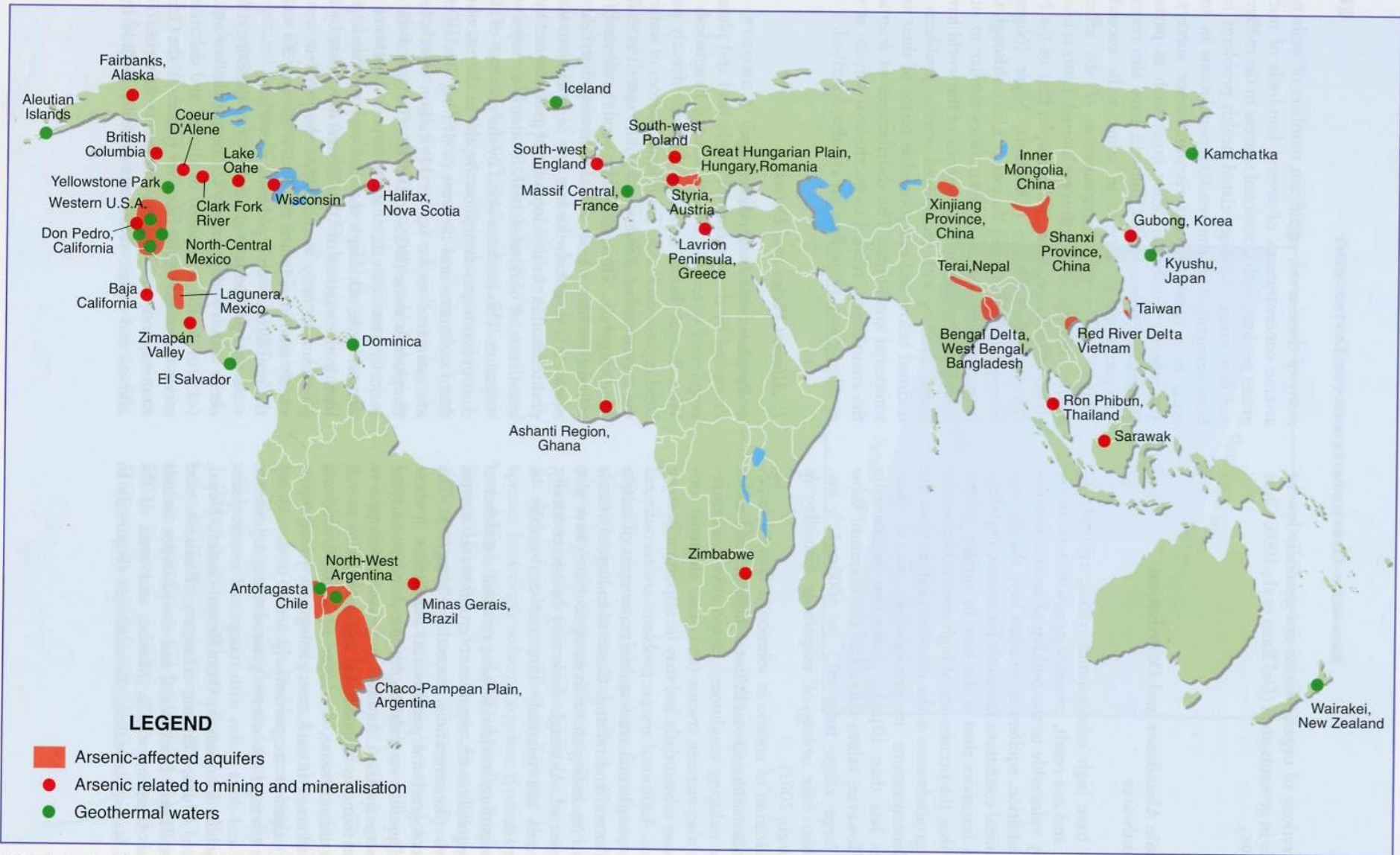
Sediments: 1-20 mg/Kg

### GLOBAL ARSENIC CONTAMINATION IN GROUND WATER

Country/region	Potential exposed population	Concentration ( $\mu\text{g/liter}$ )	Environmental conditions
Bangladesh	30,000,000	< 1 to 2,500	Natural; alluvial/deltaic sediments with high phosphate,* organics
West Bengal, India	6,000,000	< 10 to 3,200	Similar to Bangladesh
Vietnam	> 1,000,000	1 to 3,050	Natural; alluvial sediments
Thailand	15,000	1 to > 5,000	Anthropogenic; mining and dredged alluvium
Taiwan <sup>†</sup>	100,000 to 200,000	10 to 1,820	Natural; coastal zones, black shales
Inner Mongolia	100,000 to 600,000	< 1 to 2,400	Natural; alluvial and lake sediments; high alkalinity
Xinjiang, Shanxi	> 500	40 to 750	Natural; alluvial sediments
Argentina	2,000,000	< 1 to 9,900	Natural; loess and volcanic rocks, thermal springs; high alkalinity
Chile <sup>‡</sup>	400,000	100 to 1,000	Natural and anthropogenic; volcanogenic sediments; closed basin lakes, thermal springs, mining
Bolivia <sup>§</sup>	50,000	–	Natural; similar to Chile and parts of Argentina
Brazil <sup>  </sup>	–	0.4 to 350	Gold mining
Mexico	400,000	8 to 620	Natural and anthropogenic; volcanic sediments, mining
Germany	–	< 10 to 150	Natural; mineralized sandstone
Hungary, Romania	400,000	< 2 to 176	Natural; alluvial sediments; organics
Spain <sup>¶</sup>	> 50,000	< 1 to 100	Natural; alluvial sediments
Greece <sup>#</sup>	150,000	–	Natural and anthropogenic; thermal springs and mining
United Kingdom <sup>**</sup>	–	< 1 to 80	Mining; southwest England
Ghana	< 100,000	< 1 to 175	Anthropogenic and natural; gold mining
USA and Canada	–	< 1 to > 100,000	Natural and anthropogenic; mining, pesticides, As <sub>2</sub> O <sub>3</sub> stockpiles, thermal springs, alluvial, closed basin lakes, various rocks

\*These estimates [from (6) except where noted] are highly uncertain, difficult to obtain, and changing as new water sources or treatment are established. <sup>†</sup>Additional estimate from (15, 16). <sup>‡</sup>Installation of a new treatment plant has greatly decreased the exposed population. <sup>§</sup>Estimate from (16). <sup>||</sup>Source (17), no ground waters analyzed. <sup>¶</sup>Source (18). <sup>#</sup>Source (6) and (16). <sup>\*\*</sup>Source (19)

(from Smith et al., 2002)

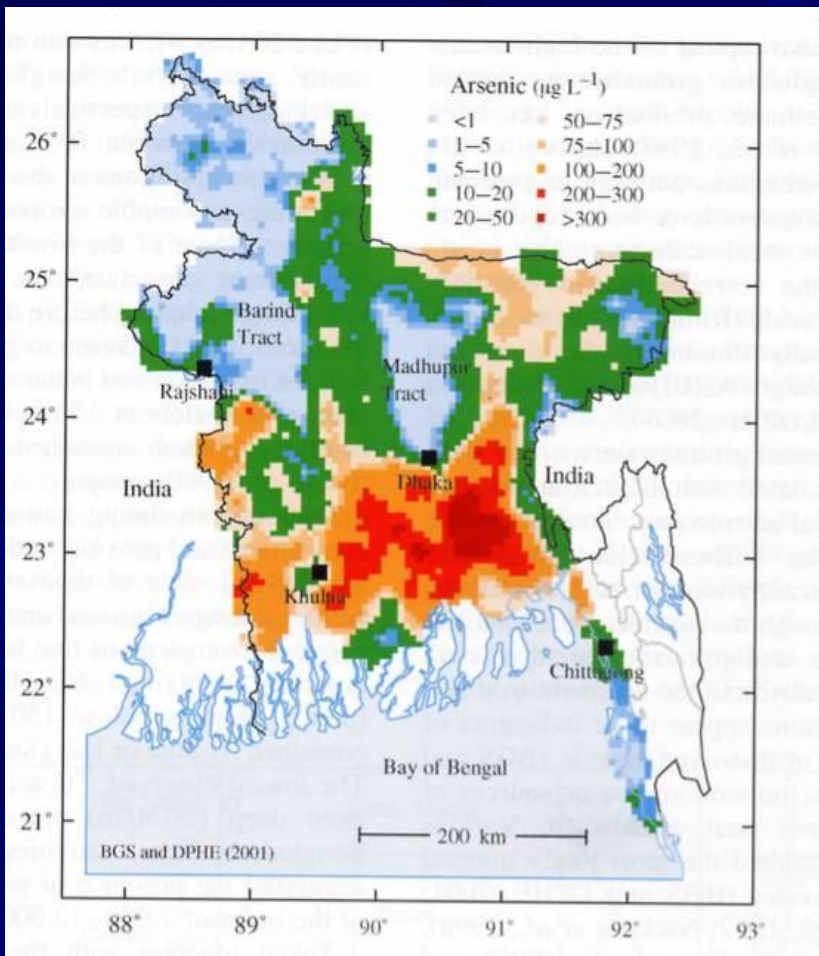


**FIGURE 2** Occurrence of documented arsenic problems in groundwater (arsenic  $>50\mu\text{gL}^{-1}$ ) in major aquifers and (Smedley and Kinniburgh, 2002). Related to mining and geothermal sources.

# Arsenic in groundwaters of Bangladesh

Need of drinking waters → surface freshwaters polluted from bacteriological point of view → groundwaters as alternative hydrological resource

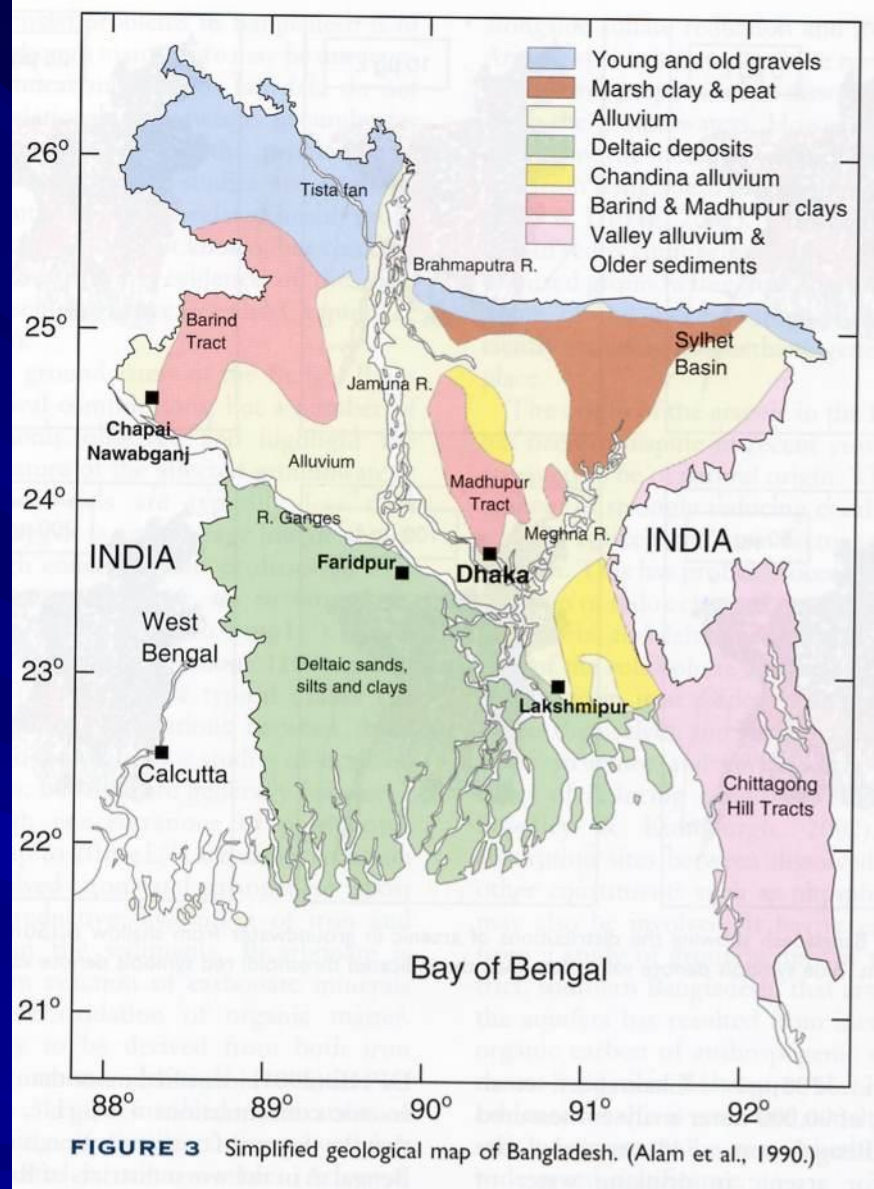
- 1993: first evidence of poisoning
- As in groundwaters: <math>0.50-3200\ \mu\text{g/l}</math>
- 2 millions of wells for drinking water supply
- 130 millions of inhabitants → 30 (80?) millions at risk
- 200.000 cronical affected: hyperpigmentation, arsenicosis and cancer of lung, skin, liver, urinary bladder, kidney and colon
- social problems



Usual concentrations in groundwaters  $< 10\ \mu\text{g/l}$   
(range  $<0.5\text{-}5000\ \mu\text{g/l}$ )

Common features in groundwaters:

- Eh  $< 100\ \text{mV}$
- Dissolved  $\text{O}_2$  low ( $< 1\ \text{mg/l}$  or absent)
- High dissolved Fe (up to  $60\ \text{mg/l}$ )
- High concentrations of P (up to  $20\ \text{mg/l}$ )
- Low nitrate and sulfate concentrations



- FIGURE 3** Simplified geological map of Bangladesh. (Alam et al., 1990.)
- Upper fan deposits, coarse (sand/gravel)
  - Middle region: meanders, backswamps, abandoned channels
  - Lower region: marsh and tidal flat deposits (silt-clay and sandy layer, occasionally with peat horizons)

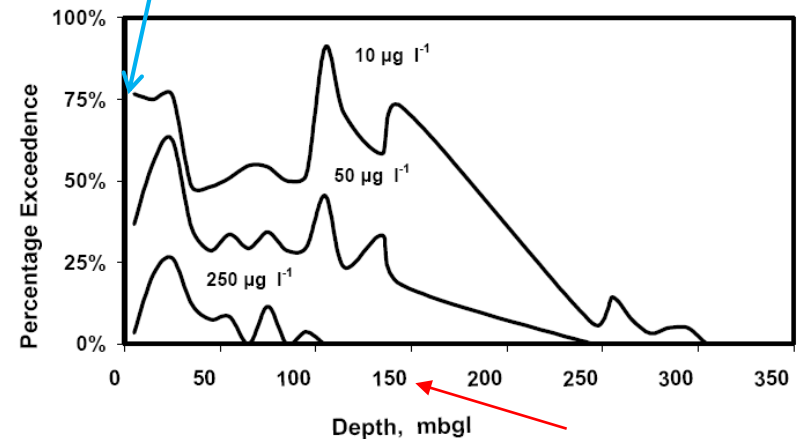
# Arsenic in groundwaters of Bangladesh: Groundwater contamination due to anthropogenic factors or “natural” process?

Local source: 1-30 mg/kg of As alluvial sediments (quartz-feldspatic sands) as aquifers

Regional source: sulphides deposits in the hydrographical basin of Gange-Brahmaputra (Himalaya and Precambrian basement of Bengala)

- 2.000.000 wells, 25 % with As > 50  $\mu\text{g/l}$  (WHO)
- Up to 60 % wells contaminated in the south-east of the country (25 % with As > 300  $\mu\text{g/l}$ )

Hand-dug wells are mostly < 5 m deep and usually unpolluted by arsenic



Main aquifers: 35-46 m e 70-150 m

Fig. 2. Percentage of wells in Bangladesh exceeding specified arsenic concentrations, shown as a function of depth (data from Regional Survey, DPHE 1999).

# What is the mechanism for As release in groundwaters?



- 1) Oxidation of arsenopyrite (FeAsS) in groundwaters and release of As  
$$4FeAsS + 13O_2 + 6H_2O \rightarrow 4Fe^{2+} + AsO_4^{3-} + 4SO_4^{2-} + 12H^+$$
- 2) “Competitiveness” among anions: adsorbed As is released in solution in favour of phosphates (organic matter, fertilizers ?)

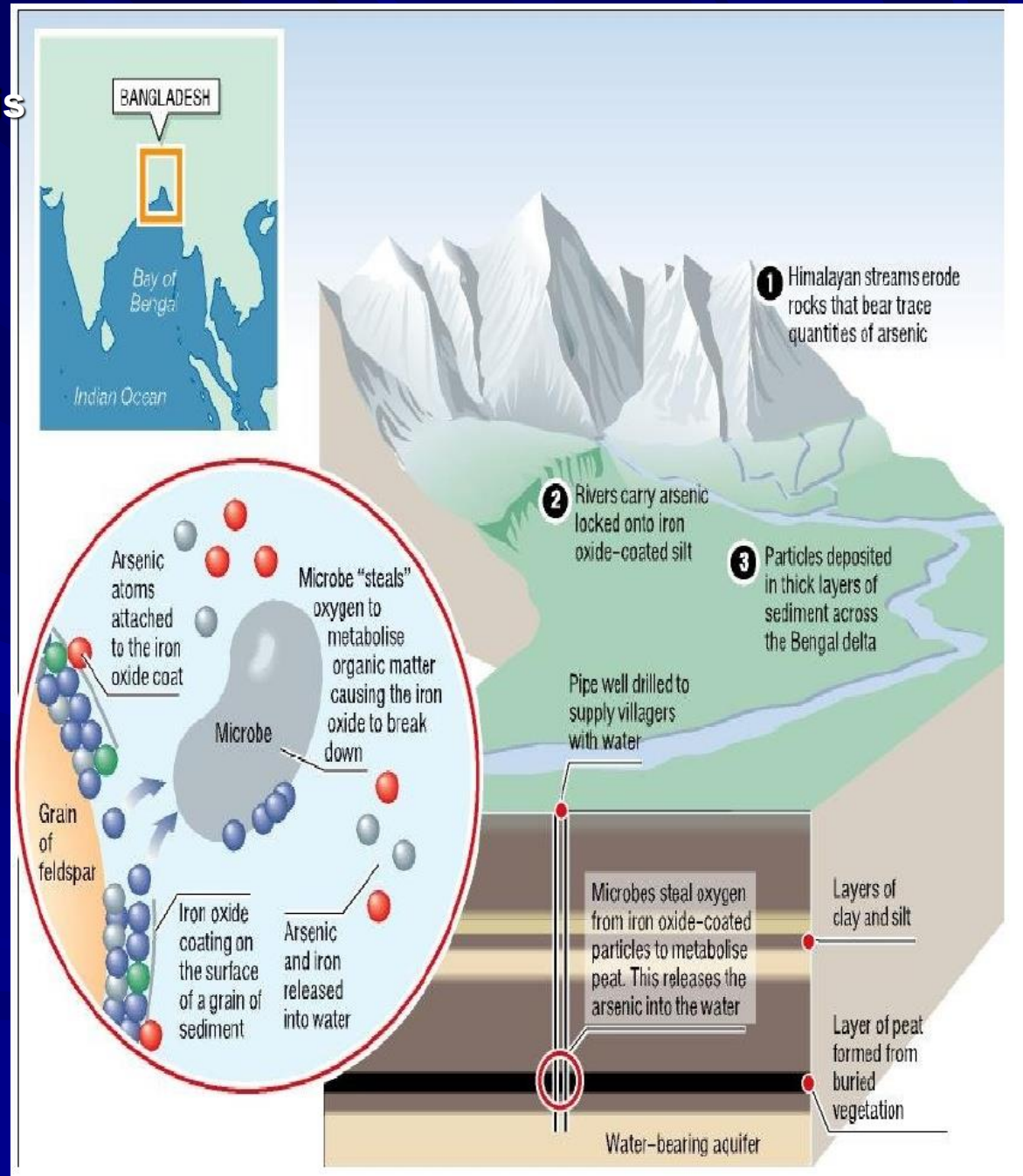
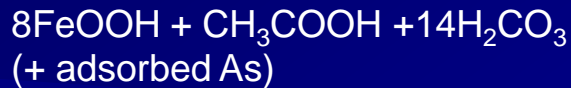


### 3) the most reliable hypothesis

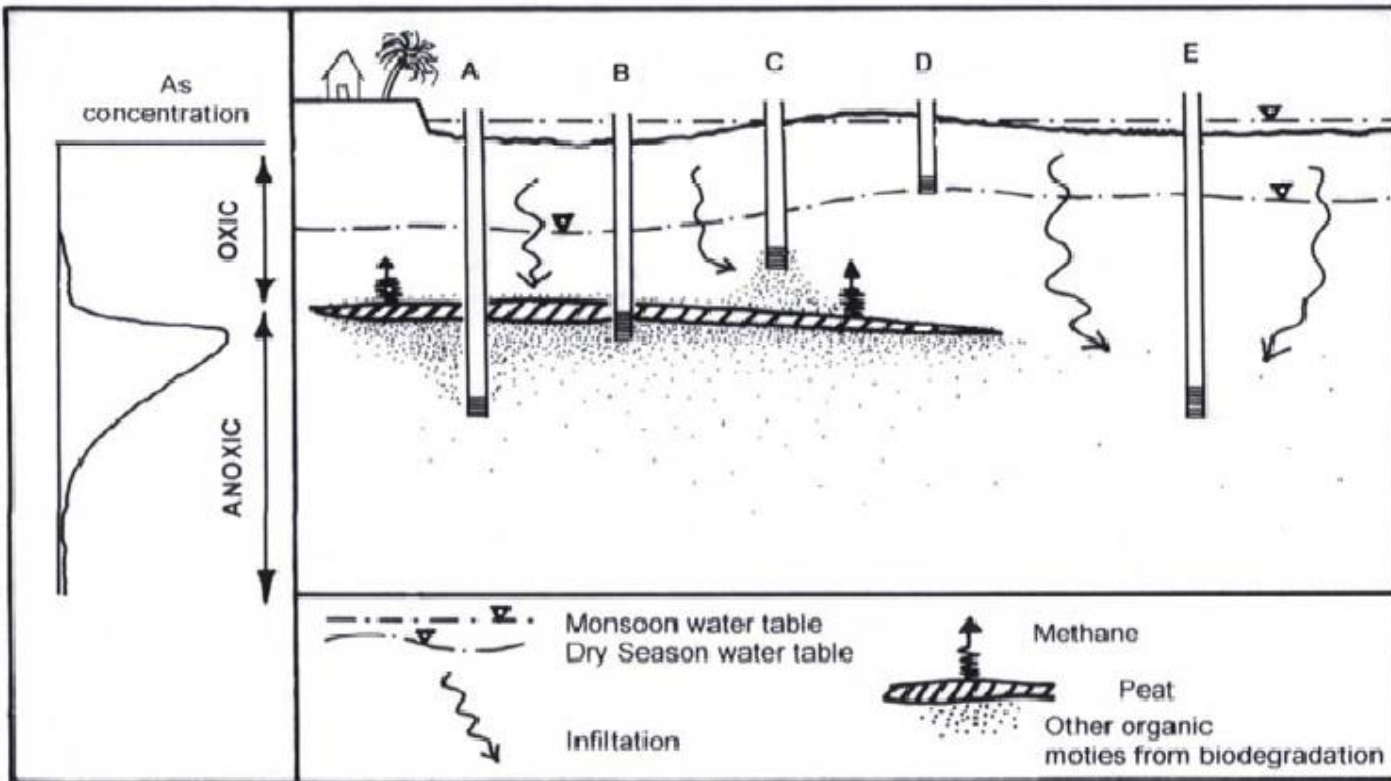
Decomposition of peat levels (Holocene optimum climatico, 6000 BP) mediated by bacteria



Release of Arsenic from hydrates Fe-oxides in groundwaters



## What does contamination degree depend on?

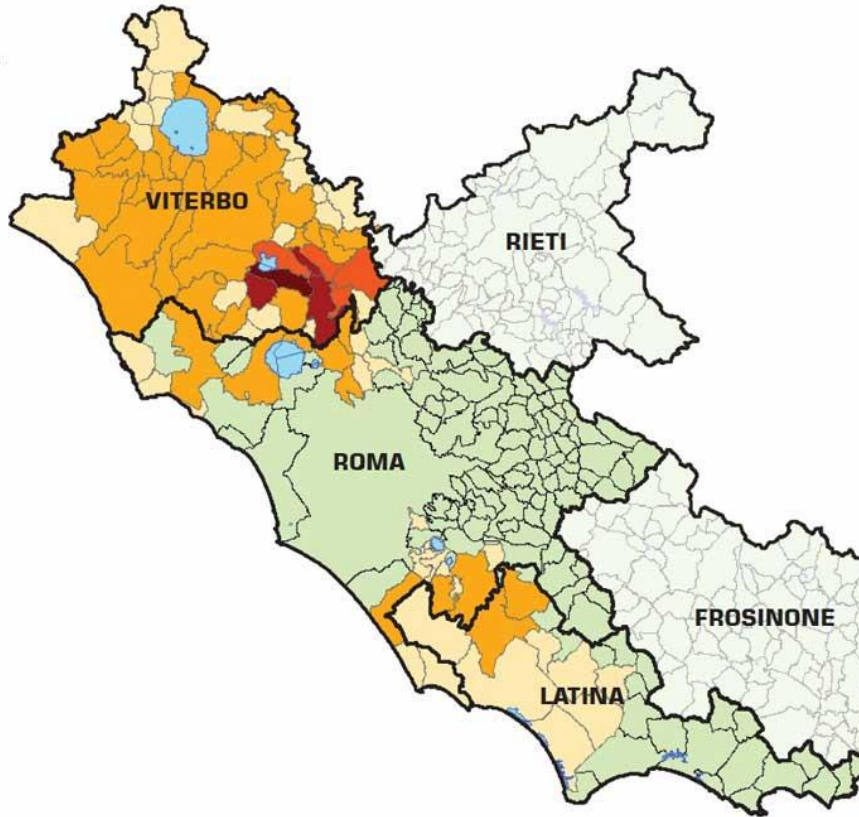


From Ravenscroft et al. (2001). In: *Arsenic Exposure and Health Effects IV*. W.R. Chappell, C.O. et al. (Eds), 53-77, Elsevier Science Ltd., Oxford.

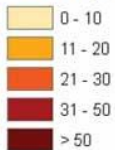
- A) low organic matter, peat level distant, less FeOOH reduction, low As content released
- B) high organic matter, peat level, high FeOOH reduction and As release
- C) migration of As and organic matter due to pumping, FeOOH reduction
- D) lower depth well, oxidized zone, no As release
- E) Contamination depends on mobility of organic matter before being consumed by FeOOH reduction and mobility of As

# Arsenic in groundwaters in Italy

Kilometers  
0 4 8 16 24 32



As (mean µg/L)



## L'arsenico nell'acqua

Limite imposto  
dalla **direttiva Ue del 1998**  
sulla sicurezza delle acque  
destinate al consumo

**10**

Limite massimo  
**derogabile**  
(solo per brevi periodi)  
secondo l'Oms

**20**

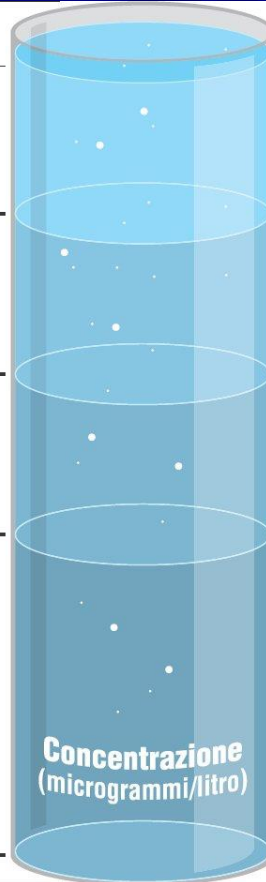
Oltre questo valore  
insorgono rischi di **malattie**  
quali forme particolari  
di cancro

**30**

Limite autorizzato  
in Italia da una **deroga**  
(scaduta il primo di gennaio)  
e raggiunto in **43 comuni**  
in provincia di Viterbo

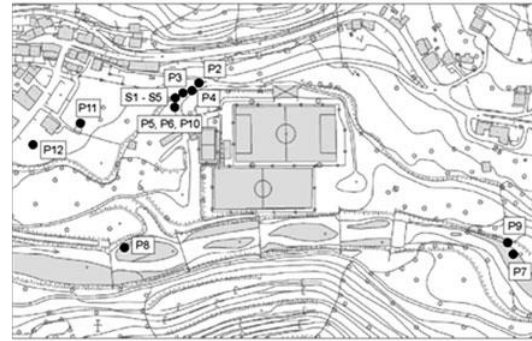
**50**

ANSA-CENTIMETRI

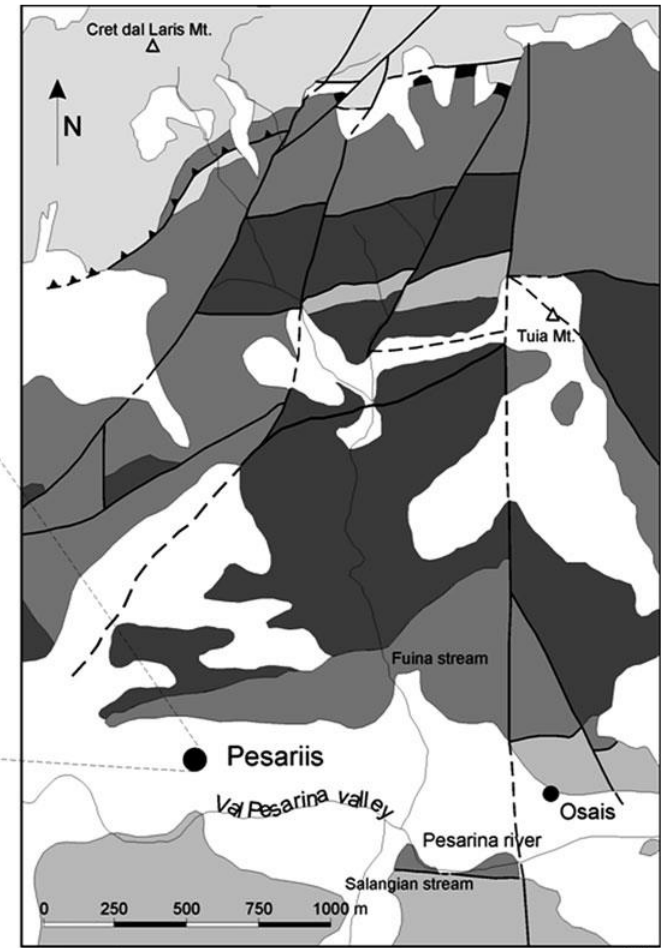


Arsenic in the drinking waters: warning at Rome and in the nearby Region - 7 aqueducts and 500 users in the Capital. On the whole, 90 villages in the Region!









# Natural arsenic contamination in waters from the Pesariis village, NE Italy



(B)



(A)

-  Alluvial and slope deposits - Quaternary
-  Schlern Dolomite - Middle Triassic
-  Buchenstein Formation - Lower Triassic
-  Serla Formation - Lower Triassic
-  Werfen Formation - Lower Triassic
-  Bellerophon Formation - Upper Permian
-  Thrusts
-  Faults





**Sorgente sulfurea**

**As = 728  $\mu\text{g/l}$**



**Scolo sorgente sulfurea  
As = 778  $\mu\text{g/l}$**



All substances are poisons... there is none which is not a poison.

The right dose differentiates a poison and a remedy..... *Paracelsus (1493-1541)*