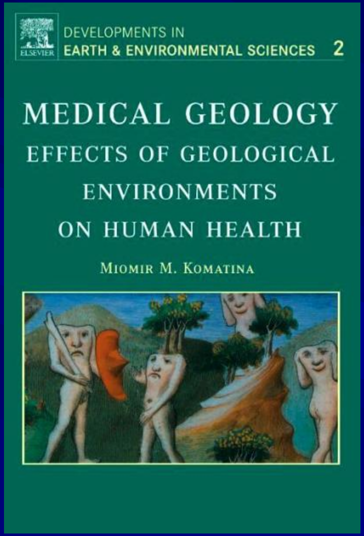
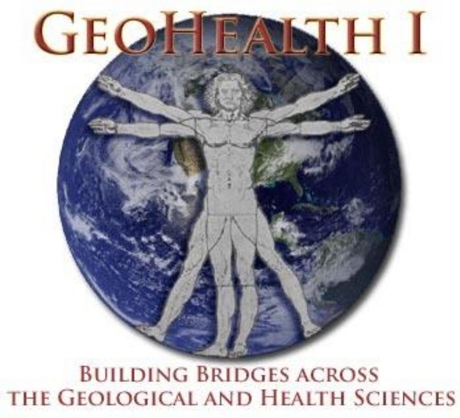
What is Medical Geology ?

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

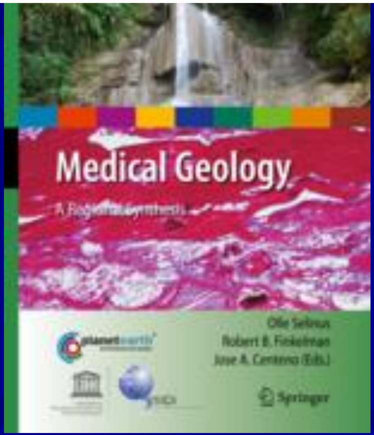

DEVELOPMENTS IN
EARTH & ENVIRONMENTAL SCIENCES 2

MEDICAL GEOLOGY
EFFECTS OF GEOLOGICAL ENVIRONMENTS ON HUMAN HEALTH

MIOMIR M. KOMATINA

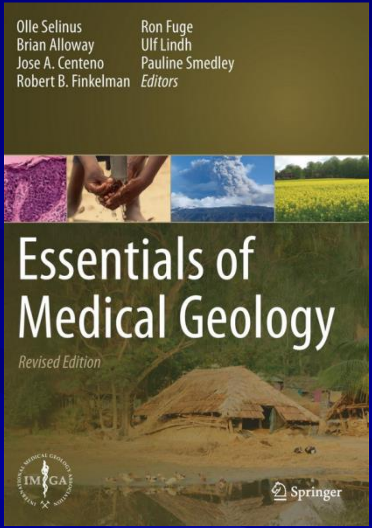

GEOHEALTH I

BUILDING BRIDGES ACROSS
THE GEOLOGICAL AND HEALTH SCIENCES


Medical Geology
A Regional Synthesis

Olle Selinus
Robert B. Finkelman
Jose A. Centeno (Eds.)

Springer


Olle Selinus
Brian Alloway
Jose A. Centeno
Robert B. Finkelman
Ron Fuge
Ulf Lindh
Pauline Smedley
Editors

Essentials of
Medical Geology
Revised Edition

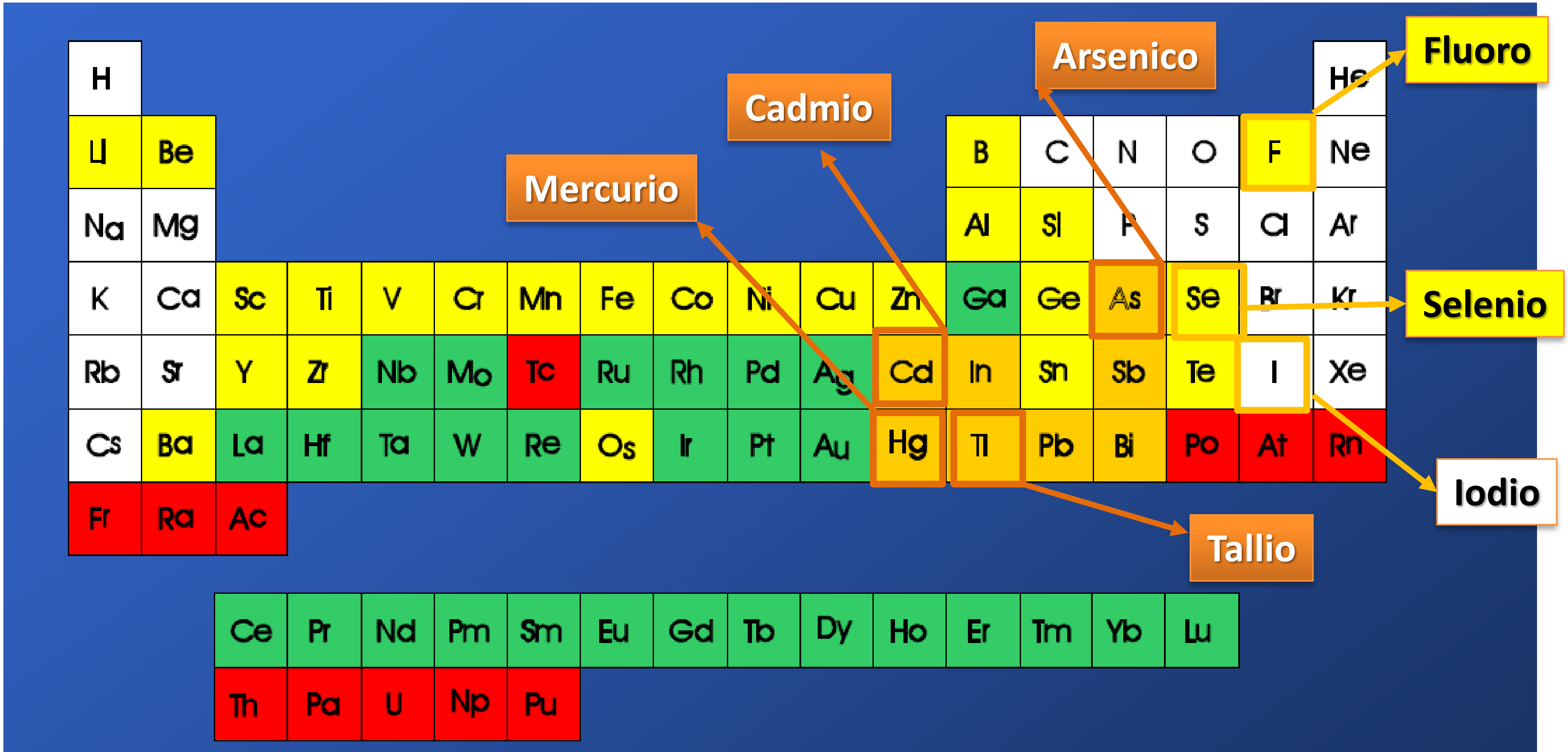
Springer

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

Aspetti ambientali della tavola periodica degli elementi



⬜ 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

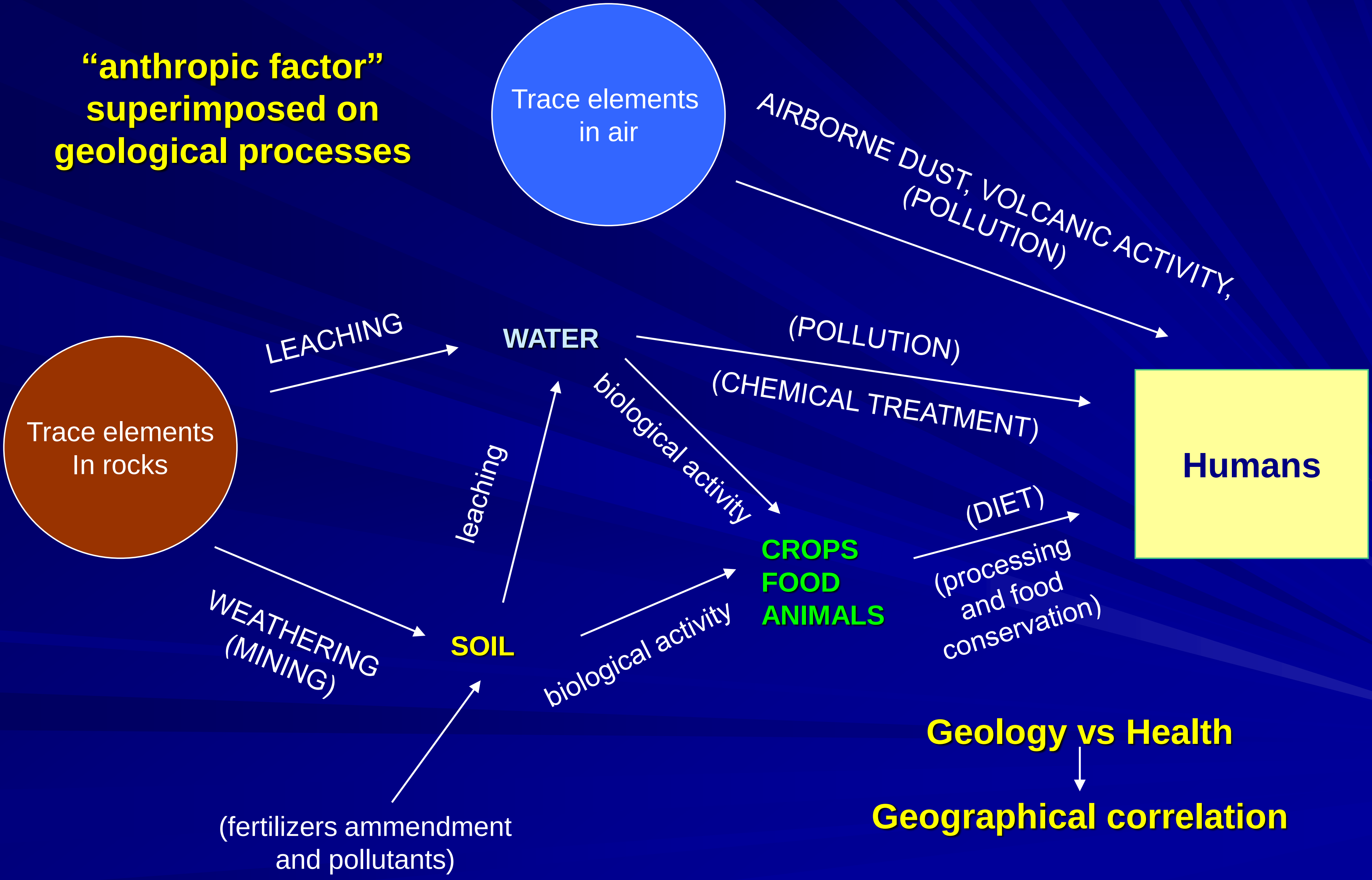
🟧 Elementi tossici

🟨 Elementi potenzialmente tossici

🟥 Elementi tossici e radioattivi

Pathways through which trace elements enter the body

“anthropic factor” superimposed on geological processes



Trace elements in air

AIRBORNE DUST, VOLCANIC ACTIVITY, (POLLUTION)

Trace elements In rocks

LEACHING

WATER

(POLLUTION)

(CHEMICAL TREATMENT)

Humans

leaching

biological activity

CRAPS

WEATHERING (MINING)

SOIL

biological activity

CROPS
FOOD
ANIMALS

(DIET)

(processing and food conservation)

(fertilizers ammendment and pollutants)

Geology vs Health

↓

Geographical correlation

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.

Diseases Due to Trace Elements

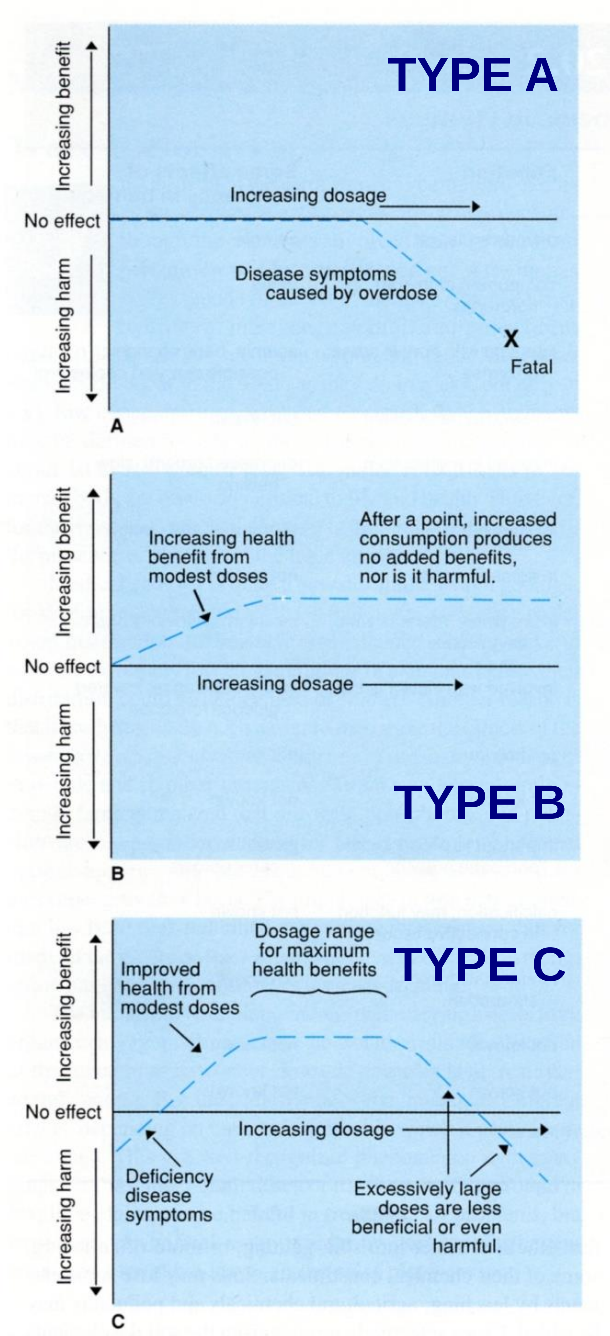
Endemic diseases due to trace element deficiency

- Iodine
- Selenium

Cronical exposure to essential and non-essential elements

- Fluorine
- Cadmium
- Arsenic
- Thallium
- Mercury

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



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

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

Diseases due to trace element deficiency as well as excess (ex. Cu, Mo, Mn)

Iodine (curve type C)

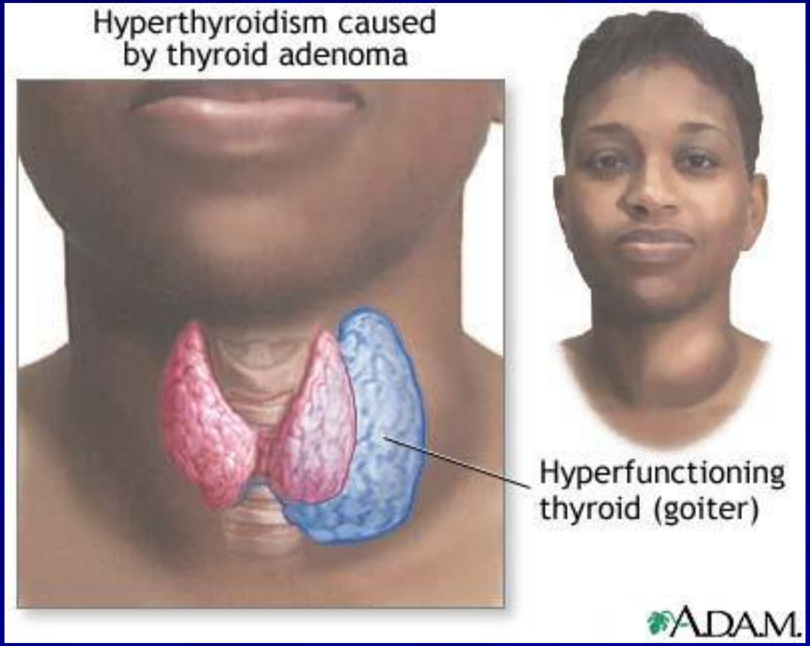
First element recognized as being essential to humans

Discovered accidentally in 1811 by *Bernard Courtois*

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

Goitrogens (Sulfur-containing compounds) inhibit Iodine uptake by thyroid and formation of hormones

The endemic disease was the first to be related to environmental geochemistry



At risk: 30 % worldwide population and 50-100 million people in Europe

Iodine (curve type C)

Geochemistry

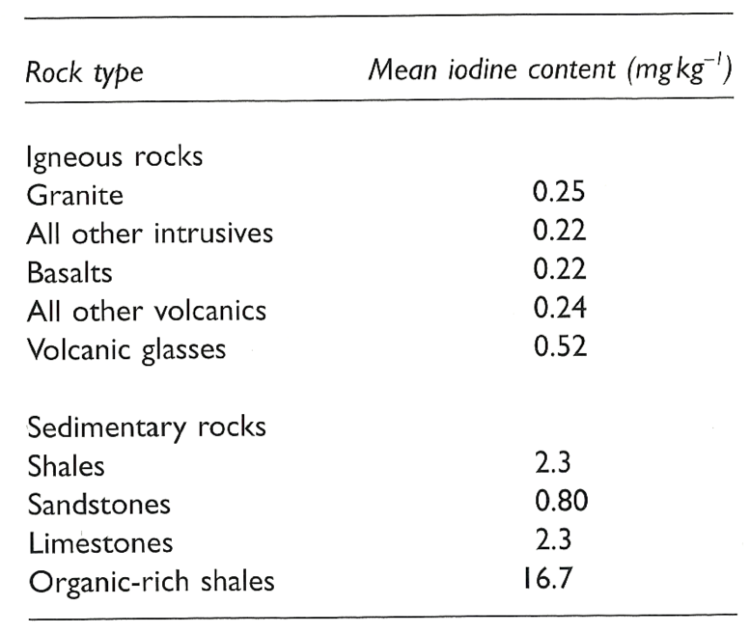
Hydrophile, biophile, atmophile and chalcophile element

Abundance in the lithosphere: 0.25 mg/kg

Enriched in volcanic glasses but low concentrations in igneous rocks

Sedimentary rocks show a greater range of Iodine content

The highest concentrations in organic-rich shales



Rock type	*Mean iodine content* ($mg\,kg^{-1}$)
Igneous rocks	
Granite	0.25
All other intrusives	0.22
Basalts	0.22
All other volcanics	0.24
Volcanic glasses	0.52
Sedimentary rocks	
Shales	2.3
Sandstones	0.80
Limestones	2.3
Organic-rich shales	16.7

(Fuge, 2005)

Iodine (curve type C)

Geochemistry

Seawater is the biggest reservoir (avg. 60 µg/l)

Iodine is depleted in surface waters due to uptake from the organisms

Two inorganic forms:

- **Iodide anion I^- → surface and shallow shelf waters → biological activity**
- **Iodate anion IO_3^- → stable in oxygenated, alkaline seawater**

Organic form:

- **Methyl-iodide (CH_3I) → due to its volatility may transfer Iodine from oceans to the atmosphere**
- **Brown algae (*Fucus vescicolous*) along with red and green algae and phytoplankton concentrate Iodine**

Iodine (curve type C)

Main geochemical processes in the sea

Transfer of Iodine from the oceans to the atmosphere governs its distribution in the terrestrial environment

Iodine as seawater spray is the major mechanism of transfer

Iodide ion can be converted to elemental iodine (I_2) by photochemical oxidation

Iodine (curve type C)

Geochemistry of Iodine in soils (<0.1-150 mg/kg)

Higher content in soils than parent material

The majority of the Iodine in soils is derived from atmosphere and marine environment.

Two main factors:

1) **The proximity of the soil to the sea**

2) **The element can be strongly absorbed by soil component (water soluble content generally < 10 % of the total)**

N.B! the only exception ^{129}I from nuclear reprocessing plant (22-49%)

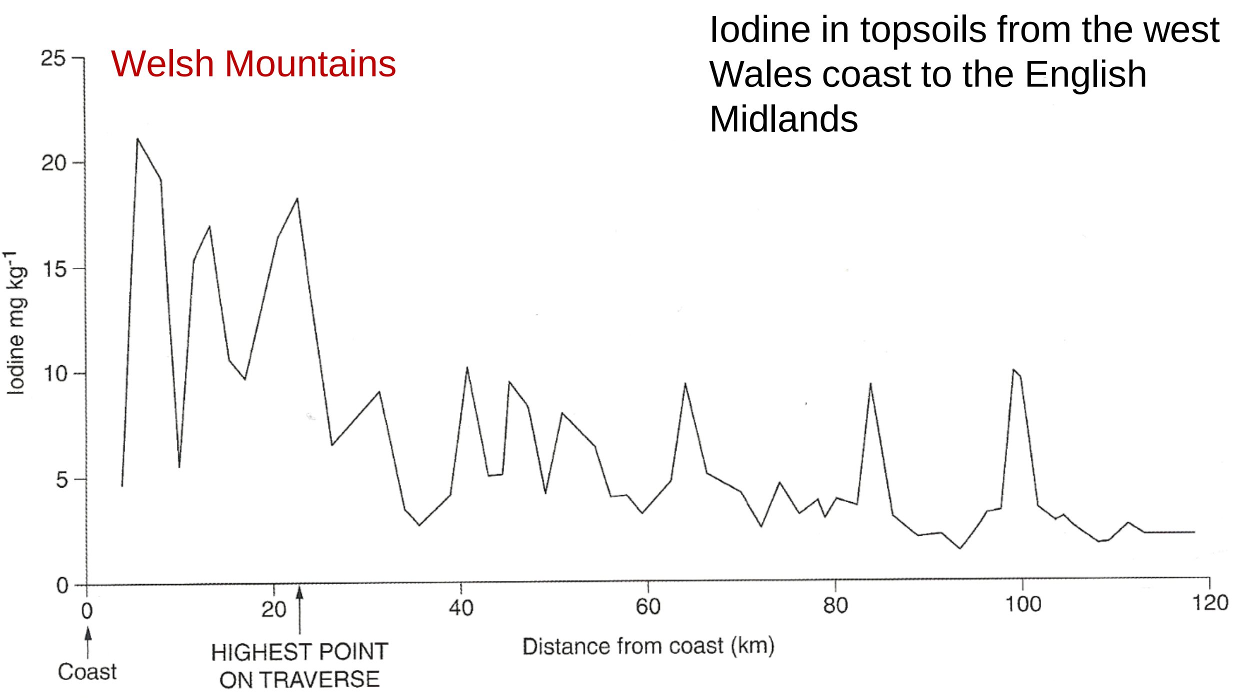
↓

High incidence of childhood thyroid cancer following the nuclear accident in Chernobyl (UKR)

Iodine (curve type C)

The relationship soil enriched in Iodine vs distance from the coast is not obvious !

Influence of topography; washout of atmospheric Iodine due to greater precipitation; upland soils are rich in organic matter



(Fuge, 1996)

Fe and Al oxides also play an important role in soil Iodine retention strongly dependent on soil pH: high sorption in acidic conditions

Iodine (curve type C)

Where Iodine is solubilized in soils at greatest rates?

It is strongly desorbed in waterlogged soils, in reducing conditions typical of rice paddies.

Acid soils: predominance of anion I$^-$

Alkaline soils: anion IO_3^- is dominant

↓

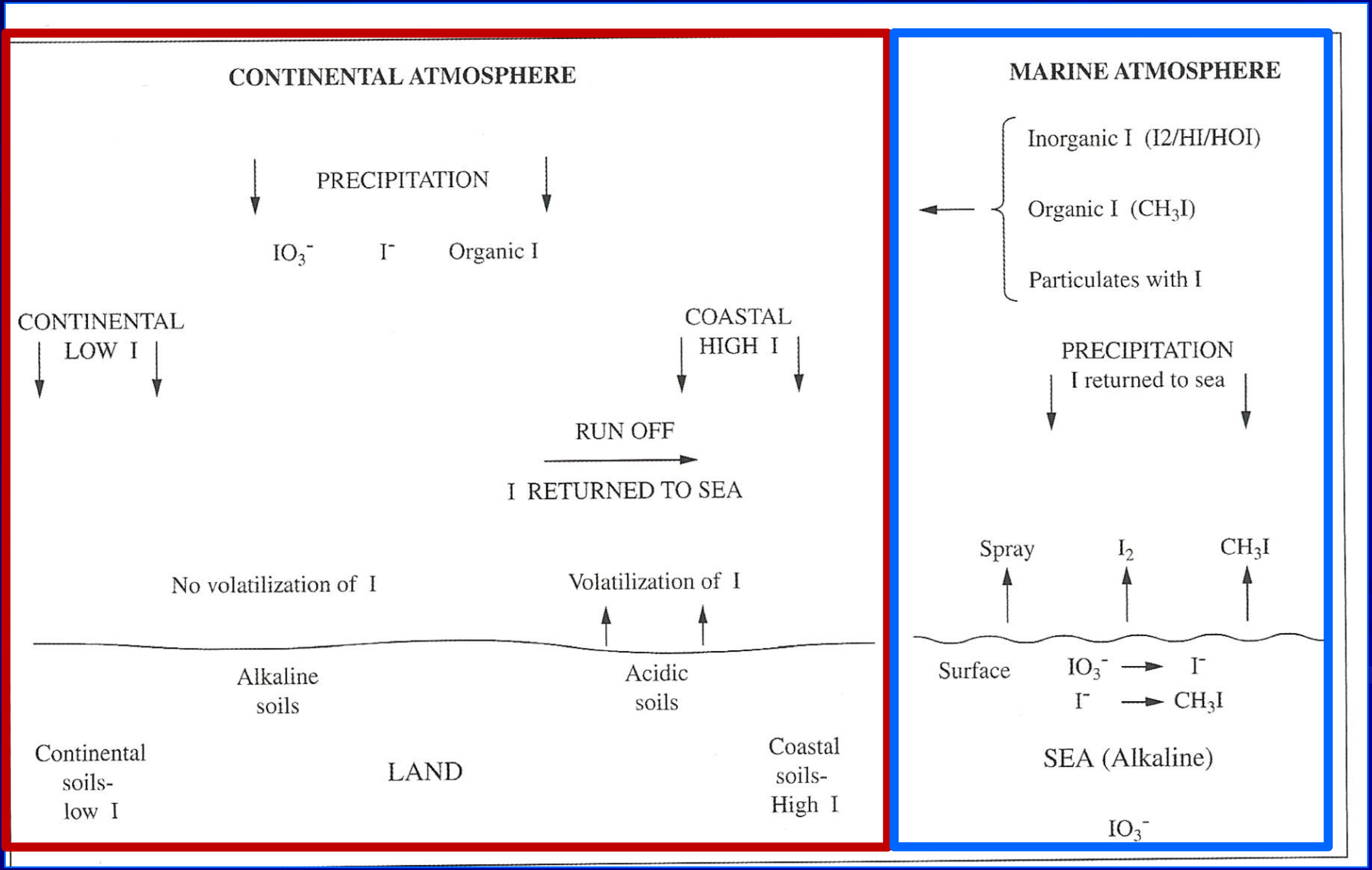
Bioavailability ?

Volatility ?

In the case of soils derived from sand-rich parent material, sandy soils have little ability to trap Iodine which is found in low concentrations

Iodine (curve type C)

Geochemical cycling



(Fuge, 2005)

Iodine (curve type C)

Transfer from soil to plant

No direct correlation between Iodine in soil and plants on it.

Iodide ion more than Iodate ion can be easily uptaken by the root system

Little translocation from the root to the aerial parts of the plant

↓

The most important pathway for the uptake is from atmosphere through leaves

Iodine (curve type C)

The traditional view: humans derive Iodine from consumption of crops and vegetables.

Seafood is also a rich source of Iodine (excess of the element in the diet in Japan and Iceland) → decrease of thyroid hormone production

In the developed countries, the major source is from dairy products (addition of Iodine to cattle feed, Iodine disinfectants in the dairy industry)

Possible uptake of Iodine by inhalation and by drinking water (not more than 10 % of the daily requirement)

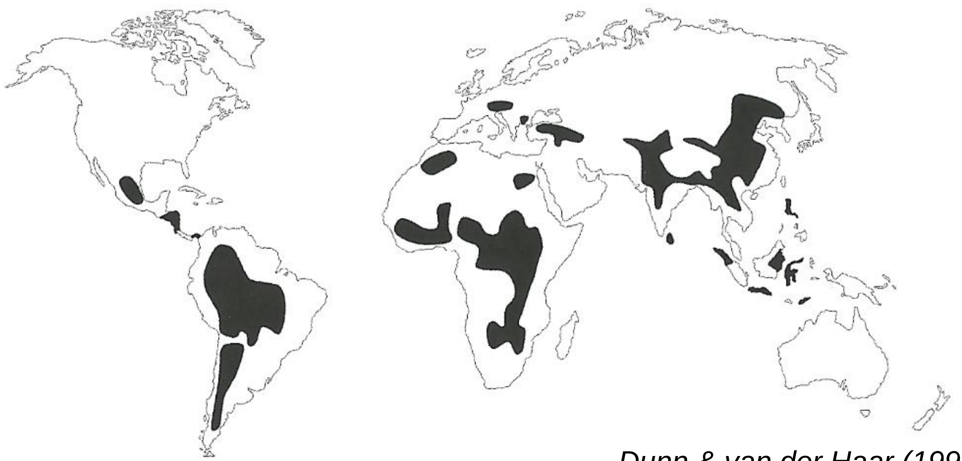
Iodine Deficiency Disorders (IDD)

Before 1950 in every country in the world….solution to IDD?

Addition of Iodine to the diet (iodized salt, bread, oil, irrigation waters) in many countries.

From 1970s: endemic goiter in poor countries!

In the 1990s, Iodine deficiency seems to go back to western Europe: as a result of dietary changes?



Dunn & van der Haar (1990)

Remote areas: Himalaya, Alps, the Andean Chain, continental Africa and China

Iodine Deficiency Disorders (IDD)

Endemias are not always esplicable with vicinity of the countries to the sea

Involvement of sulfur-containing goitrogens from geological sources and incorporated into drinking water and food or naturally occurring in vegetables.

Genus Brassica

Cassava

Causes of IDD problems are due to the geochemistry of Iodine and its bioavailabilty

Ex. Atmosperic Iodine added to sandy soils in coastal areas of China are leached very rapidly → little Iodine available for plants and crops → no Iodine for livestock and humans

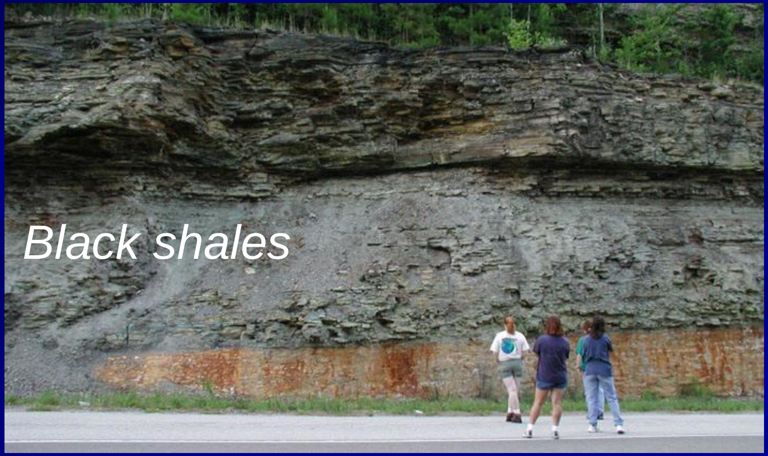
Selenium (curve type C)

Essential at low concentrations (antioxidant protective functions) but harmful in excess !

Dietary deficiency (<40 µg/day) and toxic levels (>400 µg/day)

Geology controls on concentration of Se in soils and the food chain

Phosphatic rocks



Black shales

Coal

The assessment of Se-related health risks may be achieved by understanding the biogeochemical controls on the distribution and mobility of Se in the environment.

Health outcomes are not only dependent of total Se content in rocks!

Selenium (curve type C)

1817: it was identified by the Swedish chemist J.J. *Berzelius*

A consistent daily intake of elevated Selenium levels will lead to a chronic condition known as “alkali disease”.

- 13th century: Marco Polo noticed hoof disease in horses travelling to China

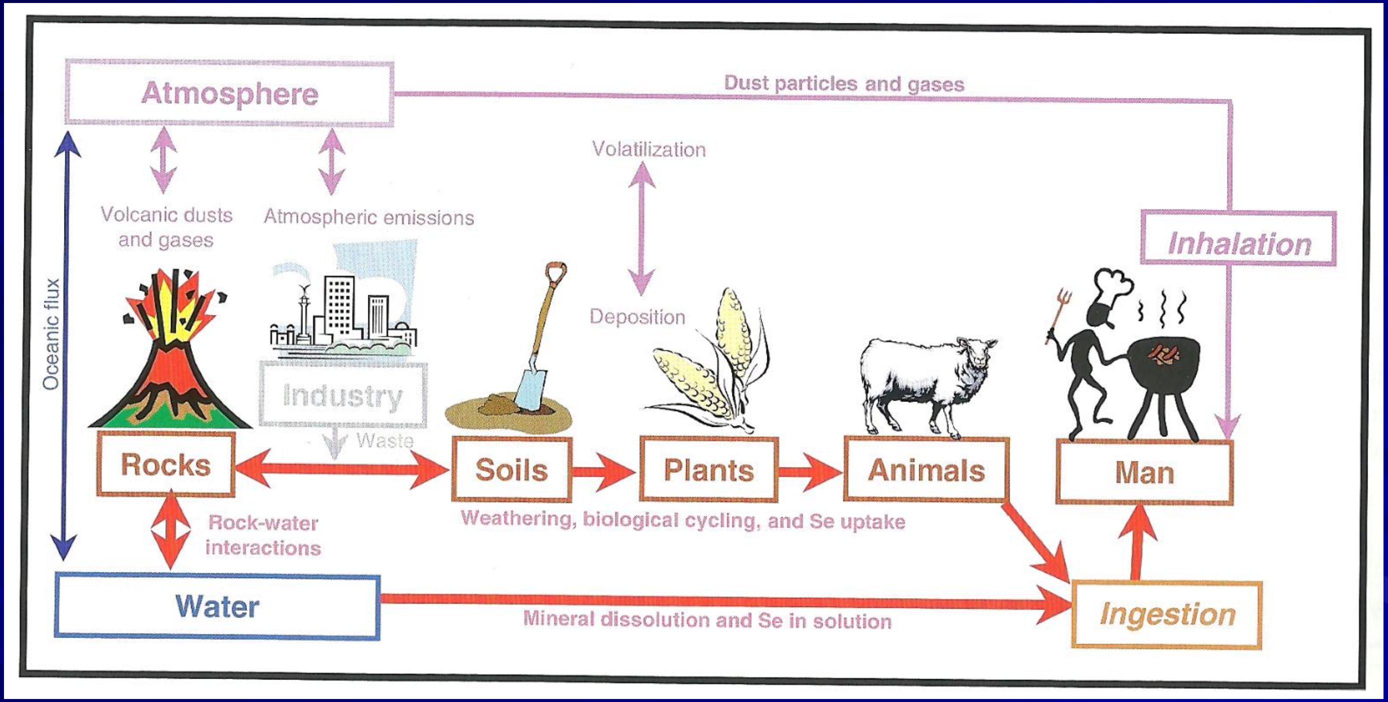
- 1931: Selenosis (Se toxicosis) was Identified (hair and nail loss in humans and hoof loss in animals)

- Se deficiency in crops and livestock have been reported all over the world

Se supplementation has become a common practice in agriculture

Selenium (curve type C)

Se is dispersed from the **rocks (primary source)** through the **food chain** via complex **biogeochemical cycling processes** including **weathering** to form soils, **rock-water interactions** and **biological activity.**

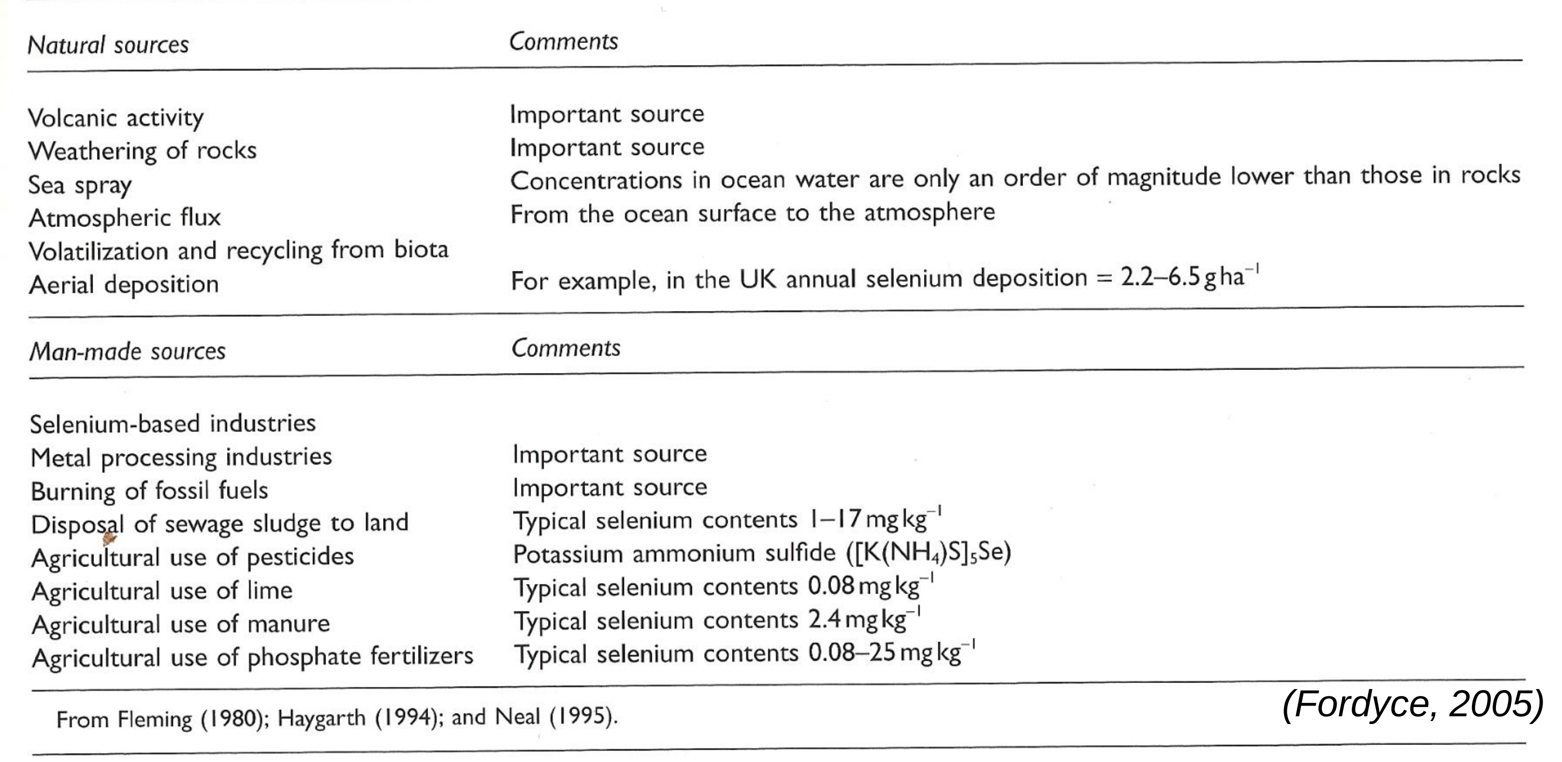


(Fordyce, 2005)

Significant is also Se **cycling through the atmosphere** because of rapid transport

Selenium (curve type C)

Main sources of Selenium in the Environment



Natural sources	*Comments*
Volcanic activity	Important source
Weathering of rocks	Important source
Sea spray	Concentrations in ocean water are only an order of magnitude lower than those in rocks
Atmospheric flux	From the ocean surface to the atmosphere
Volatilization and recycling from biota	
Aerial deposition	For example, in the UK annual selenium deposition = 2.2–6.5 g ha^{-1}
Man-made sources	*Comments*
Selenium-based industries	
Metal processing industries	Important source
Burning of fossil fuels	Important source
Disposal of sewage sludge to land	Typical selenium contents 1–17 mg kg^{-1}
Agricultural use of pesticides	Potassium ammonium sulfide ($[K(NH_4)S]_5Se$)
Agricultural use of lime	Typical selenium contents 0.08 mg kg^{-1}
Agricultural use of manure	Typical selenium contents 2.4 mg kg^{-1}
Agricultural use of phosphate fertilizers	Typical selenium contents 0.08–25 mg kg^{-1}

From Fleming (1980); Haygarth (1994); and Neal (1995).

(Fordyce, 2005)

Mining mineral deposits specifically for Se is not economical.
The element is recovered from the electrolytic refining of Cu and Pb and from sludge in sulfuric acid plants.

Man-mad sources have a major impact upon Se cycle

Selenium (curve type C)

Rocks

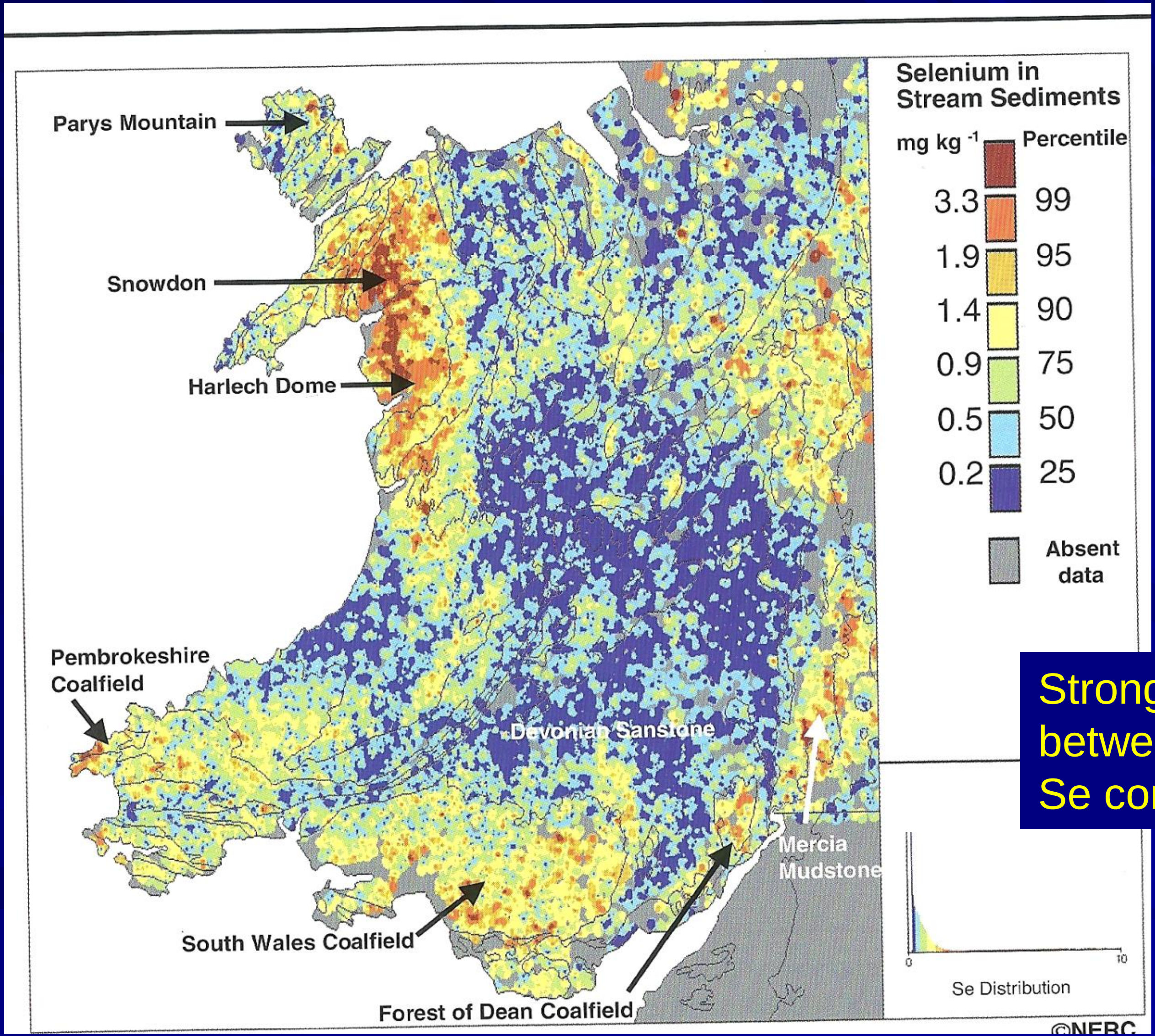
Crustal abundances very low (0.05 – 0.09 mg/kg)

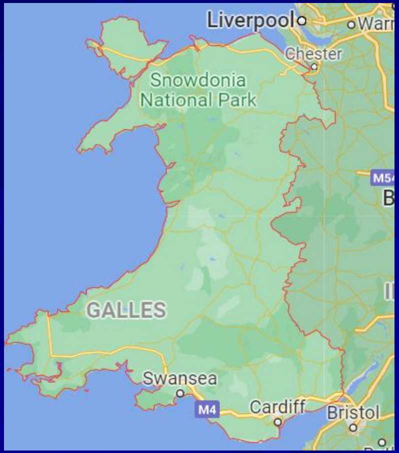
Ash and gas from volcanoes can contain significant amount of Se (6-15 mg/kg) but volcanic rocks (basalts and rhyolites) are usually poor in Se.

Sedimentary rocks contain greater Se concentrations (0.1 mg/kg) than igneous rocks.

Very high concentrations (≤ 300 mg/kg) in phosphatic rocks due to similarity between phosphate and selenite anions; high concentrations (1-20 mg/kg) also in coal and organic-rich deposits.

Selenium (curve type C)



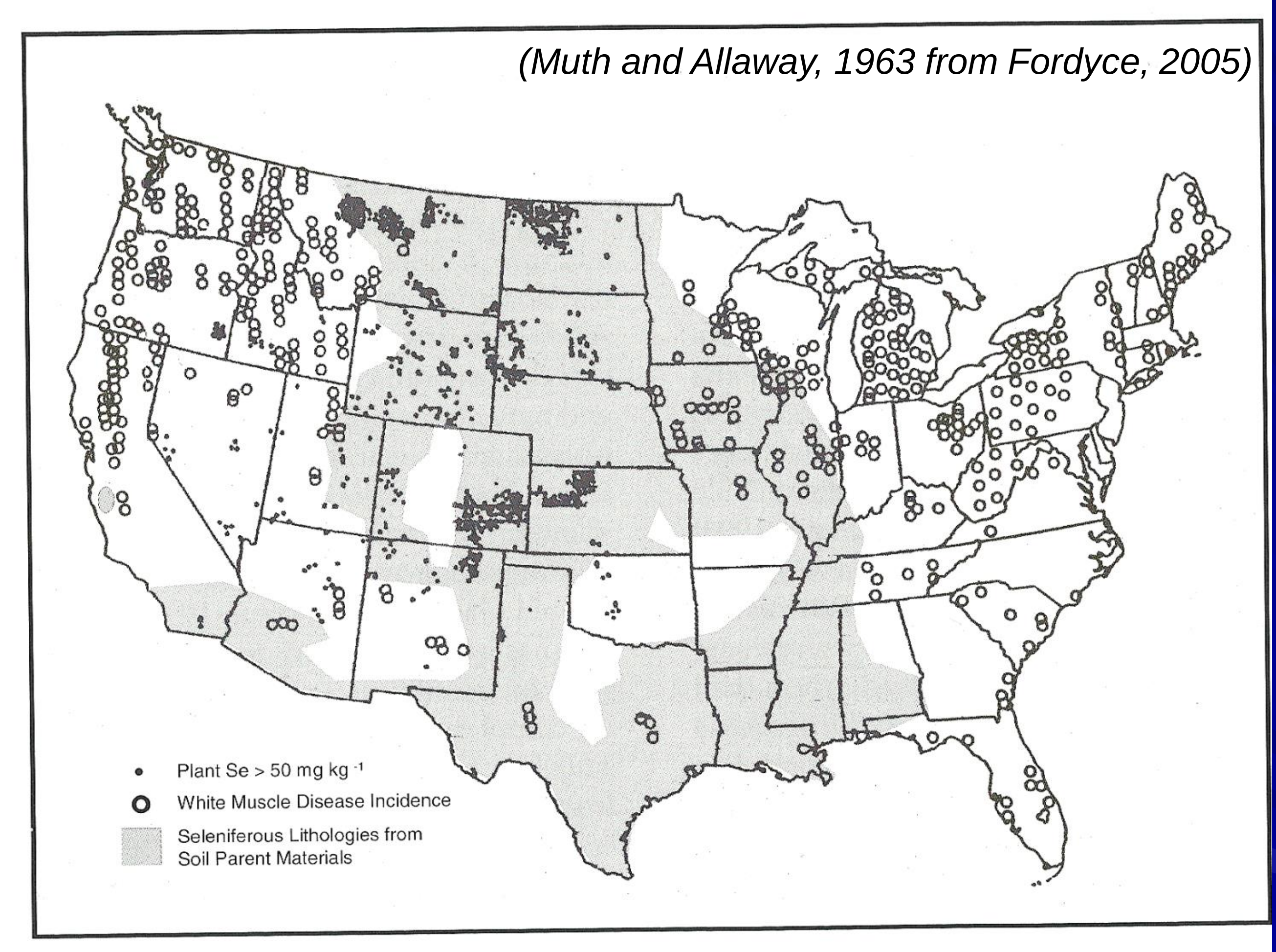


Strong relationship between geology and Se concentrations

(BGS, 2000 from Fordyce, 2005)

Selenium (curve type C)

Soil



(Muth and Allaway, 1963 from Fordyce, 2005)

Soils capable of producing **Se-rich vegetation toxic to livestock** were reported over black shale and sandstone deposits of the Great Plain (USA)

Selenium (curve type C)

Soil geochemsitry

Factors affecting bioavailability:

pH,

redox,

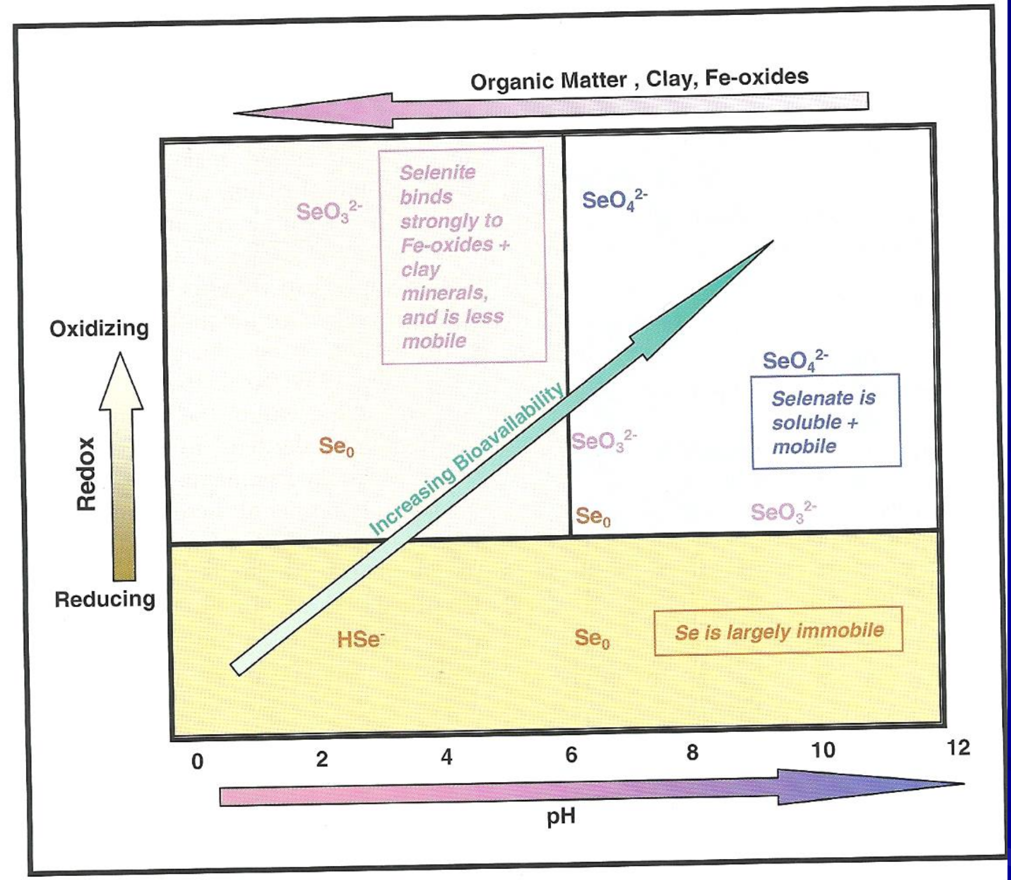
speciation,

texture,

mineralogy,

organic matter,

competitive ions



(Fordyce, 2005)

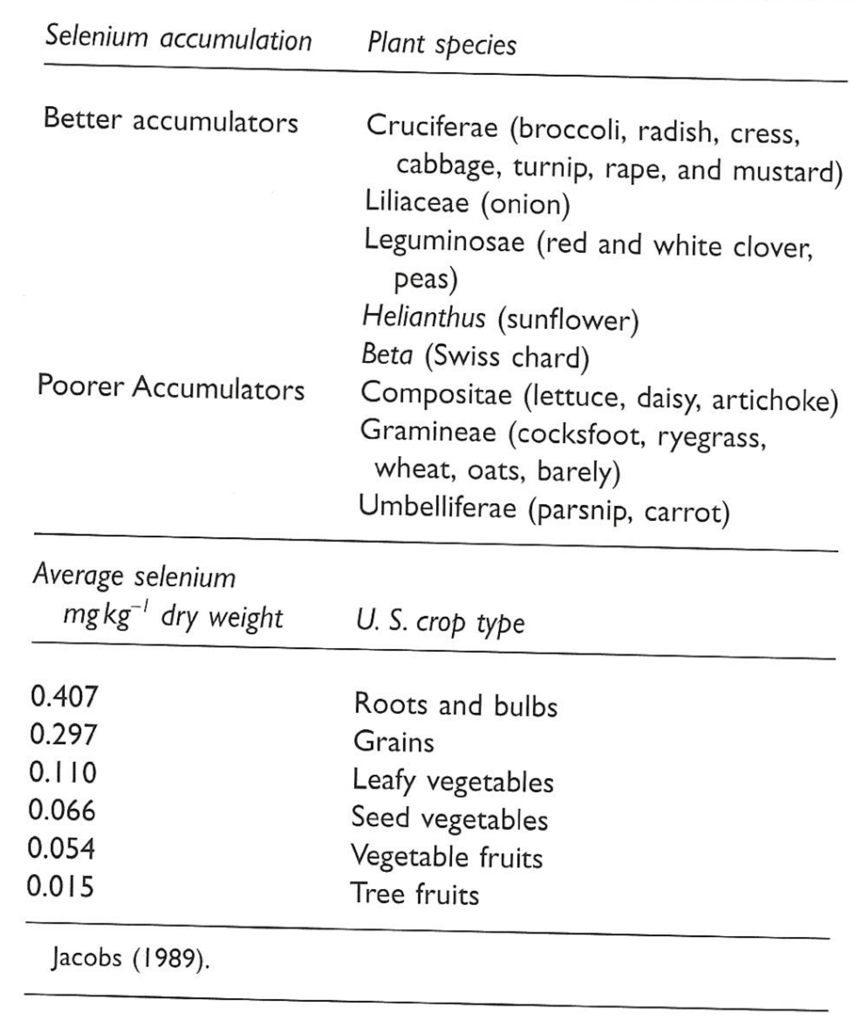
Selenate (Se^{6+}) is more mobile, soluble and less well absorbed by Selinite (Se^{4+}), thus, Selenium is much more bioavailable under oxydizing alkaline conditions and much less bioavailable in reducing acid conditions

Selenium (curve type C)

Plants

Food crops tend to have relatively low tolerance to Selenium toxicity, and most crops have the potential to accumulate the element in quantities that are toxic to animal and humans.

In general, root crops contain higher Se than plant leaves



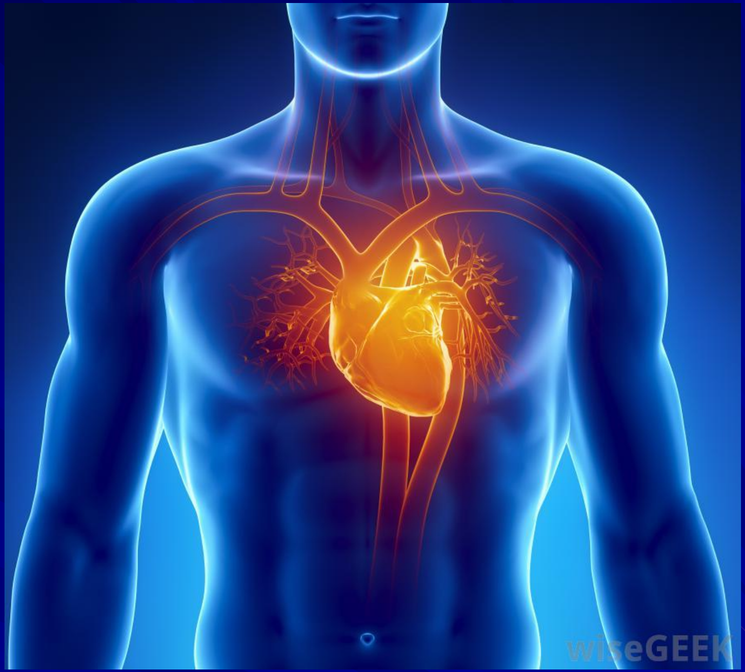
Selenium accumulation	*Plant species*
Better accumulators	Cruciferae (broccoli, radish, cress, cabbage, turnip, rape, and mustard)
	Liliaceae (onion)
	Leguminosae (red and white clover, peas)
	Helianthus (sunflower)
	Beta (Swiss chard)
Poorer Accumulators	Compositae (lettuce, daisy, artichoke)
	Gramineae (cocksfoot, ryegrass, wheat, oats, barely)
	Umbelliferae (parsnip, carrot)

Average selenium mg kg^{-1} dry weight	*U. S. crop type*
0.407	Roots and bulbs
0.297	Grains
0.110	Leafy vegetables
0.066	Seed vegetables
0.054	Vegetable fruits
0.015	Tree fruits

Jacobs (1989).

(Fordyce, 2005)

Selenium deficiency (curve type C)

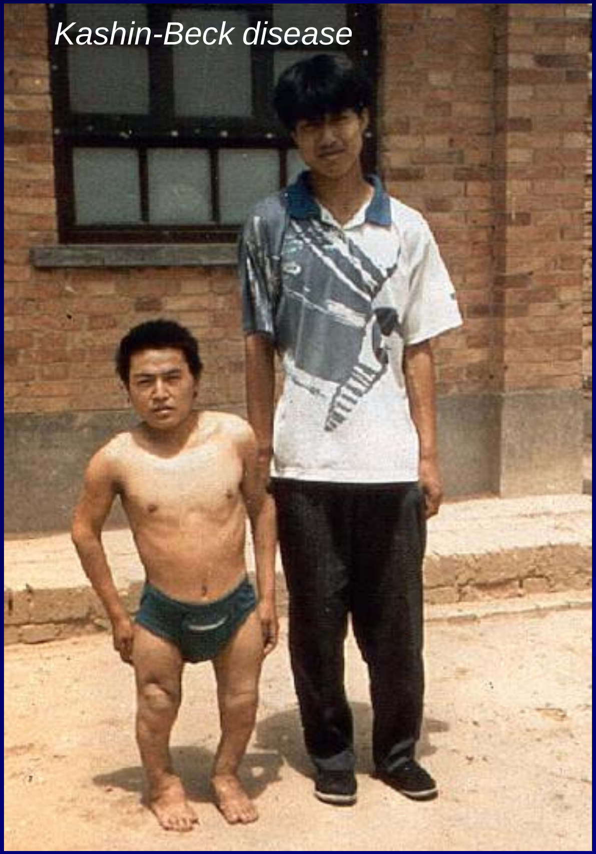


(Tan, 1989 from Fordyce, 2005)

Keshan disease juvenile cardiomyopathy affecting women and children: acute insufficiency of the heart function or as a chronic moderate-to-severe enlargement of the heart.

Remote areas in China where Se in soils and crops (<0.04 mg/kg) was very low

Selenium deficiency (curve type C)



In Siberia, China, South Korea and Africa

Kashin-Beck* disease endemic osteoartopathy causing deformity of the affected joints

Impairment of movement in the extremities is commonly followed by bone development disturbances such as schortened fingers and toe and, in more extremes cases, dwarfism

Se deficiency also adversely affects thyroid hormone metabolism

* The Russian scientists who first described it (1861-1899)

Selenium toxicity (curve type C)

Hydrogen Selenide (HSe^-) is the most toxic compound by inhalation.
Sodium selenite (Na_2SeO_3) is the most toxic via ingestion
Elemental Se in the diet has low toxicity as it is insoluble

Figure 2: Clubbing, onychomadesis, onycholysis, nail bed erythema, and granulation

Hair and nail loss were the prime symptoms of the disease in China in the 1960s, but disorders of the nervous system, skin, poor dental health, garlic breath and paralysis were also reported.

Fluorine (curve type C)

In natural waters (0.1 – 10 mg/L where 1 mg/L is optimal !)
WHO guidelines for drinking waters: 1.5 mg/L

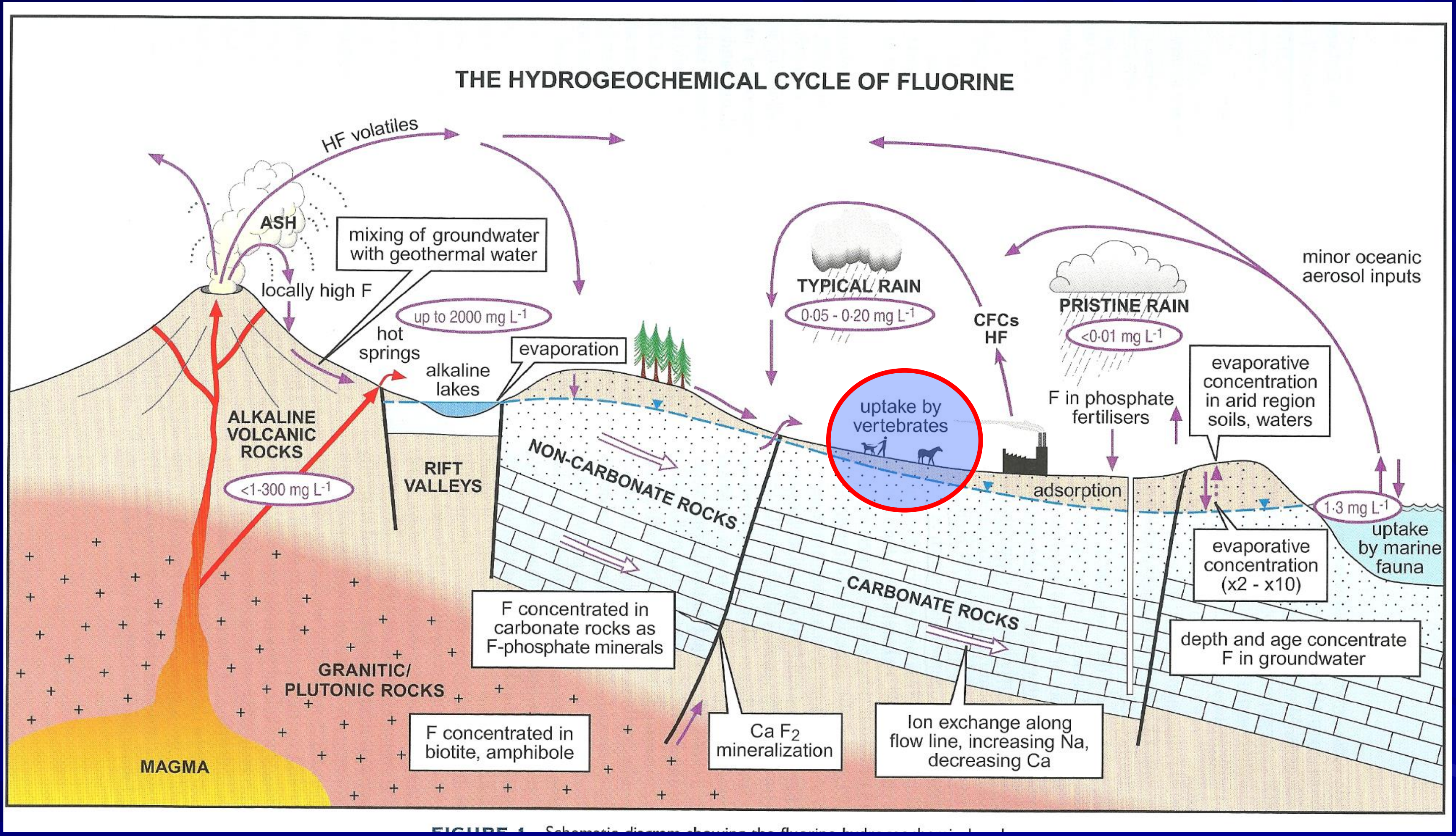
0.3-5 mg/day → intake on dietary basis → soils
Important in osteosclerosis reduction

19° Century: first potential association between Fluorine and health

20° Century:
Clear association between Fluorine in water supplies and dental health was established.
Recogniton of defined patterns for dental caries and dental fluorosis with geology and groundwaters.
Fluoridation of fluoride-deficient water supplies in England and USA.

Exposure to fluoride from drinking waters and food is an important even today due to industrial sources.

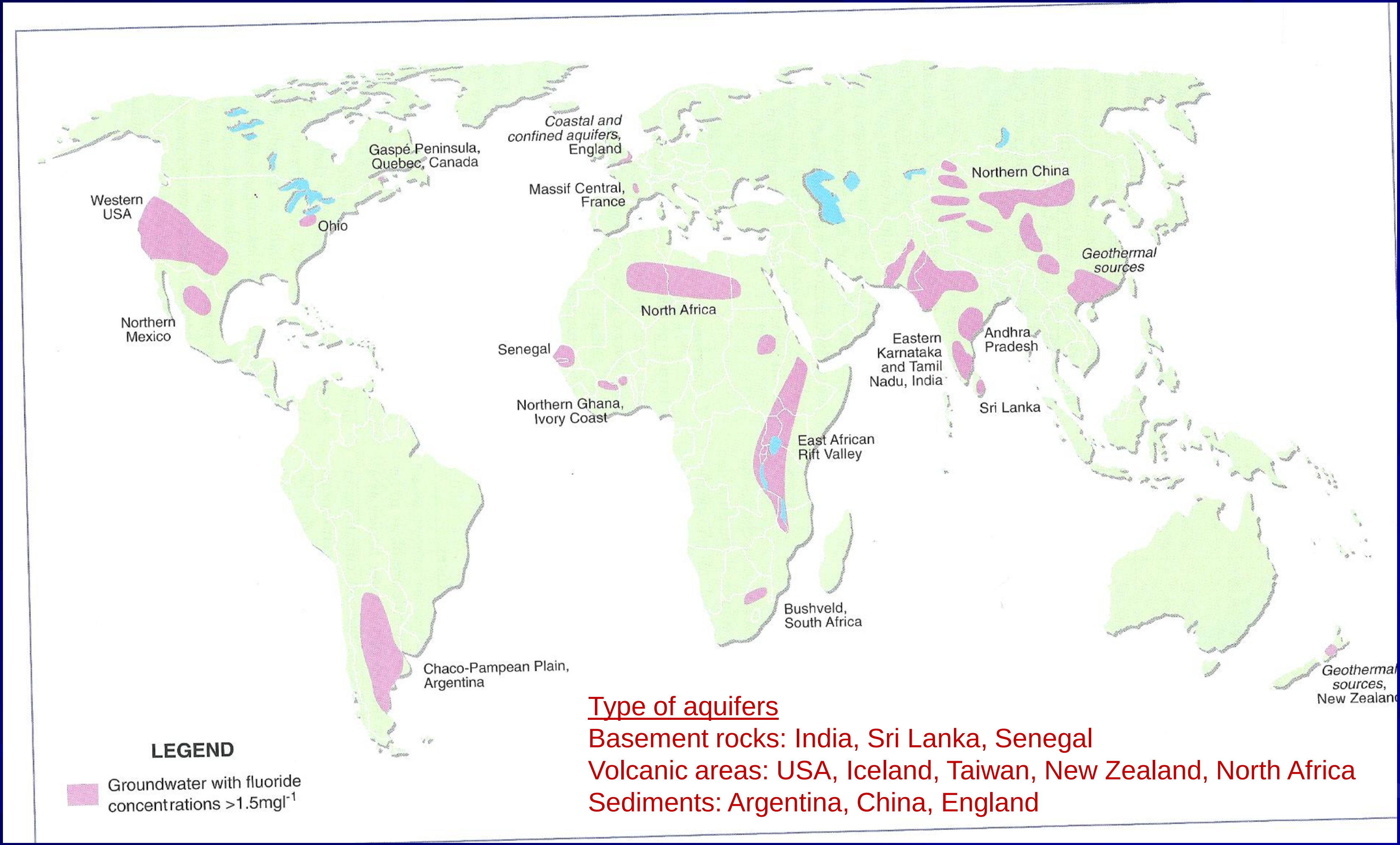
Fluorine (curve type C)



(Edmunds & Smedley, 2005)

Fluorine (curve type C)

High-fluoride groundwaters



Type of aquifers

Basement rocks: India, Sri Lanka, Senegal

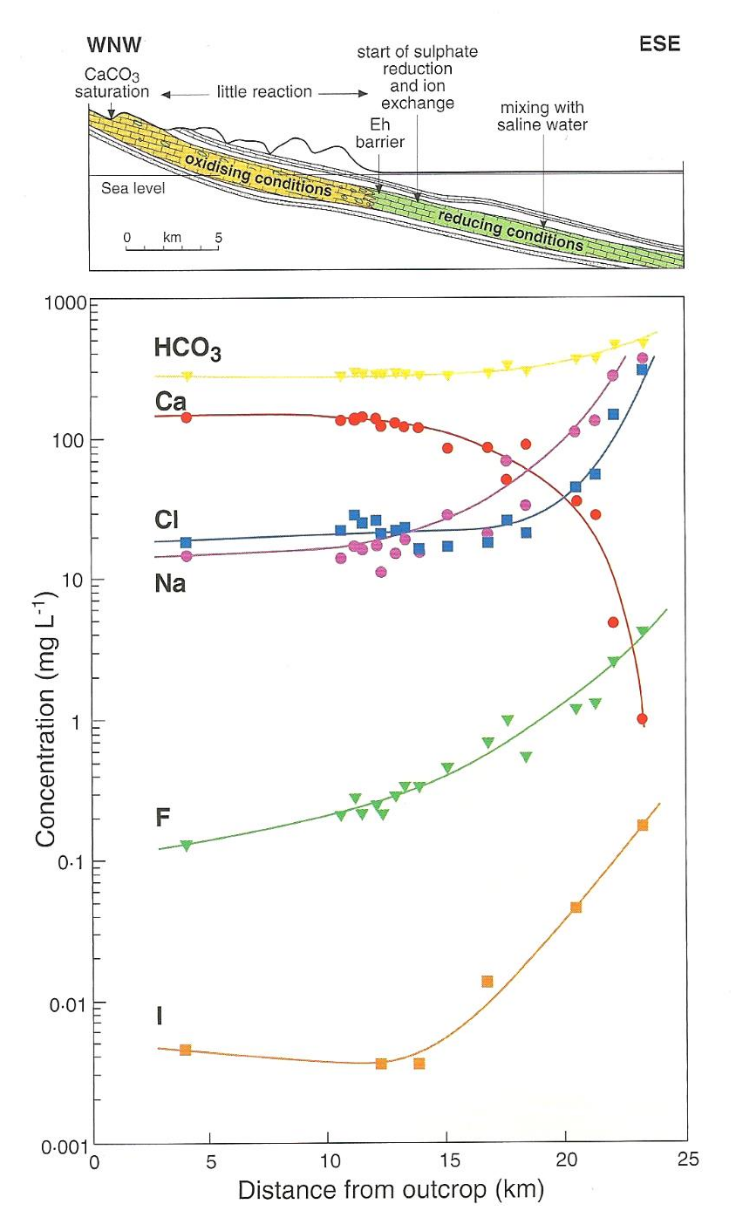
Volcanic areas: USA, Iceland, Taiwan, New Zealand, North Africa

Sediments: Argentina, China, England

(Edmunds & Smedley, 2005)

Endemic Fluorisis is a problem for million of people where F^- > WHO guideline value for drinking water (1.5 mg/L)

Fluorine (curve type C)



(The UK Lincolnshire Limestone – Downgradient Evolution)

In sedimentary aquifer Fluoride concentrations can increase along flow lines and with residence time in response to mineral dissolution and ion-exchange reactions.

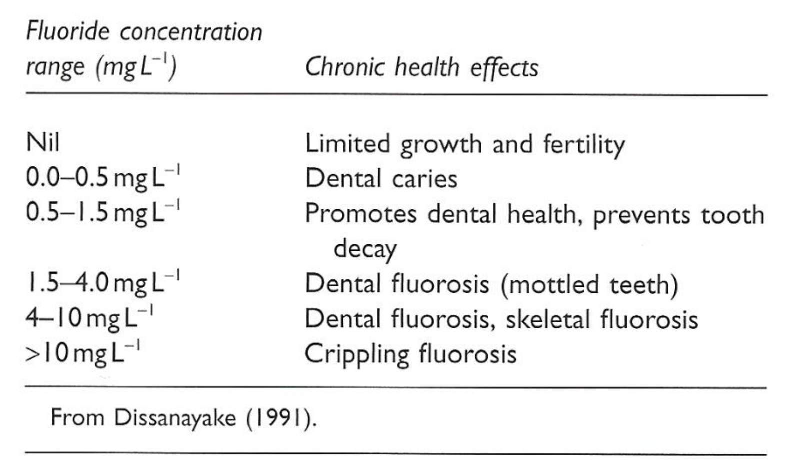
Sodium for Calcium exchange takes place and groundwaters evolves from Ca-HCO_3 to Na-HCO_3 types.

Under low Ca concentrations in old groundwaters, Fluoride contents may increase to excessive concentrations, Where Ca is abundant, Fluoride concentrations are limited by saturation with the mineral fluorite (CaF_2)

(Edmunds & Walton, 1983)

Fluorine (curve type C)

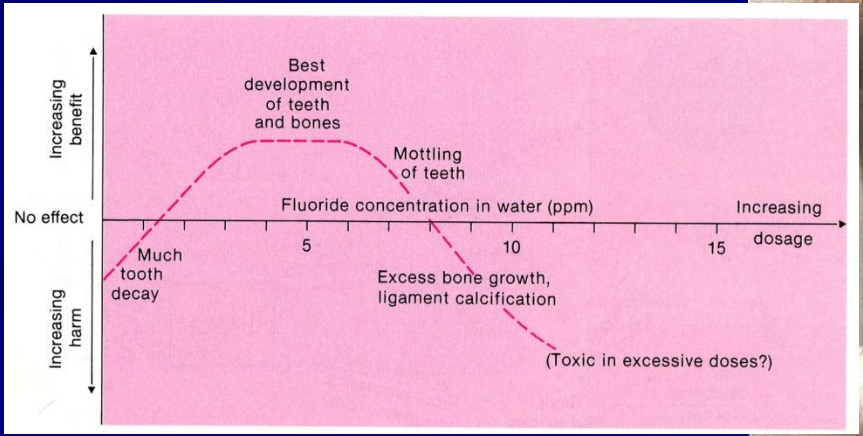
Health effects of Fluoride concentrations in Drinking Water



Fluoride concentration range ($mg\,L^{-1}$)	*Chronic health effects*
Nil	Limited growth and fertility
0.0–0.5 $mg\,L^{-1}$	Dental caries
0.5–1.5 $mg\,L^{-1}$	Promotes dental health, prevents tooth decay
1.5–4.0 $mg\,L^{-1}$	Dental fluorosis (mottled teeth)
4–10 $mg\,L^{-1}$	Dental fluorosis, skeletal fluorosis
>10 $mg\,L^{-1}$	Crippling fluorosis

From Dissanayake (1991).

(Edmunds & Smedley, 2005)



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

Cadmium (curve type A)

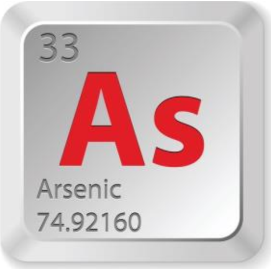
- Incorporated in trace amounts in Zn minerals (ZnS) and separated as by product of mining operations.
- Uses: to prevent corrosion, Ni-Cd batteries.
- The expense of mining and refining Cd has encouraged recycling.

- 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



Metalloide
Calcofilo

Sorgenti naturali: scisti carboniferi, sulfuri, sedimenti, sorgenti vulcaniche e termali.

Minerali:
Arsenopirite (FeAsS), Pirite arseniosa ($Fe(AsS)_2$),
Realgar (AsS), Orpimento (As_2S_3)

Realgar e Orpimento

Sorgenti antropogeniche:

Attività mineraria
Carbone
Pesticidi
Industria del vetro
Microelettronica
(semiconduttori, laser, GaAs)
Medicina (As_2O_3 →leucemia)
As_2S_2 → pigmenti
Gas tossici militari (lewisite)

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

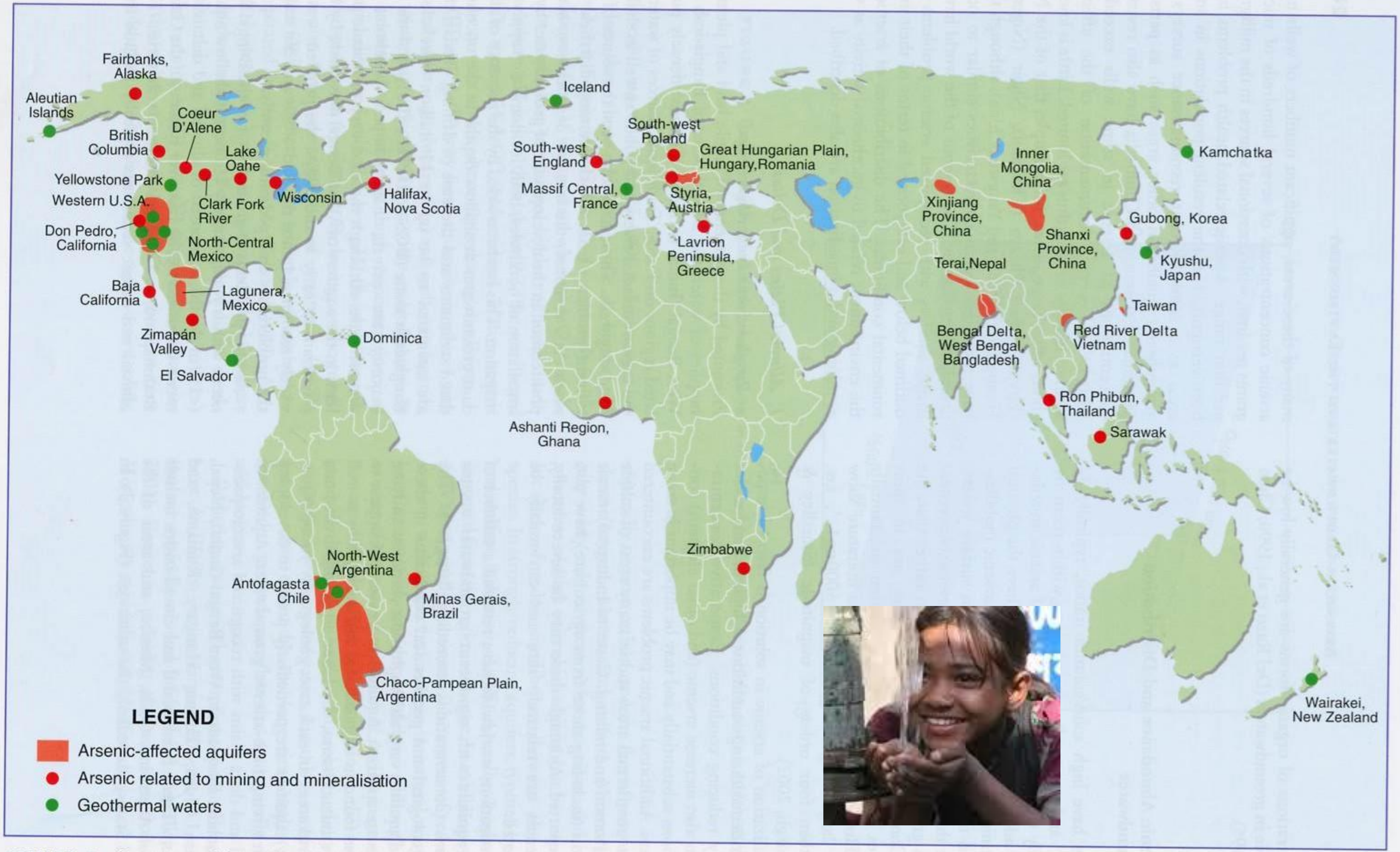
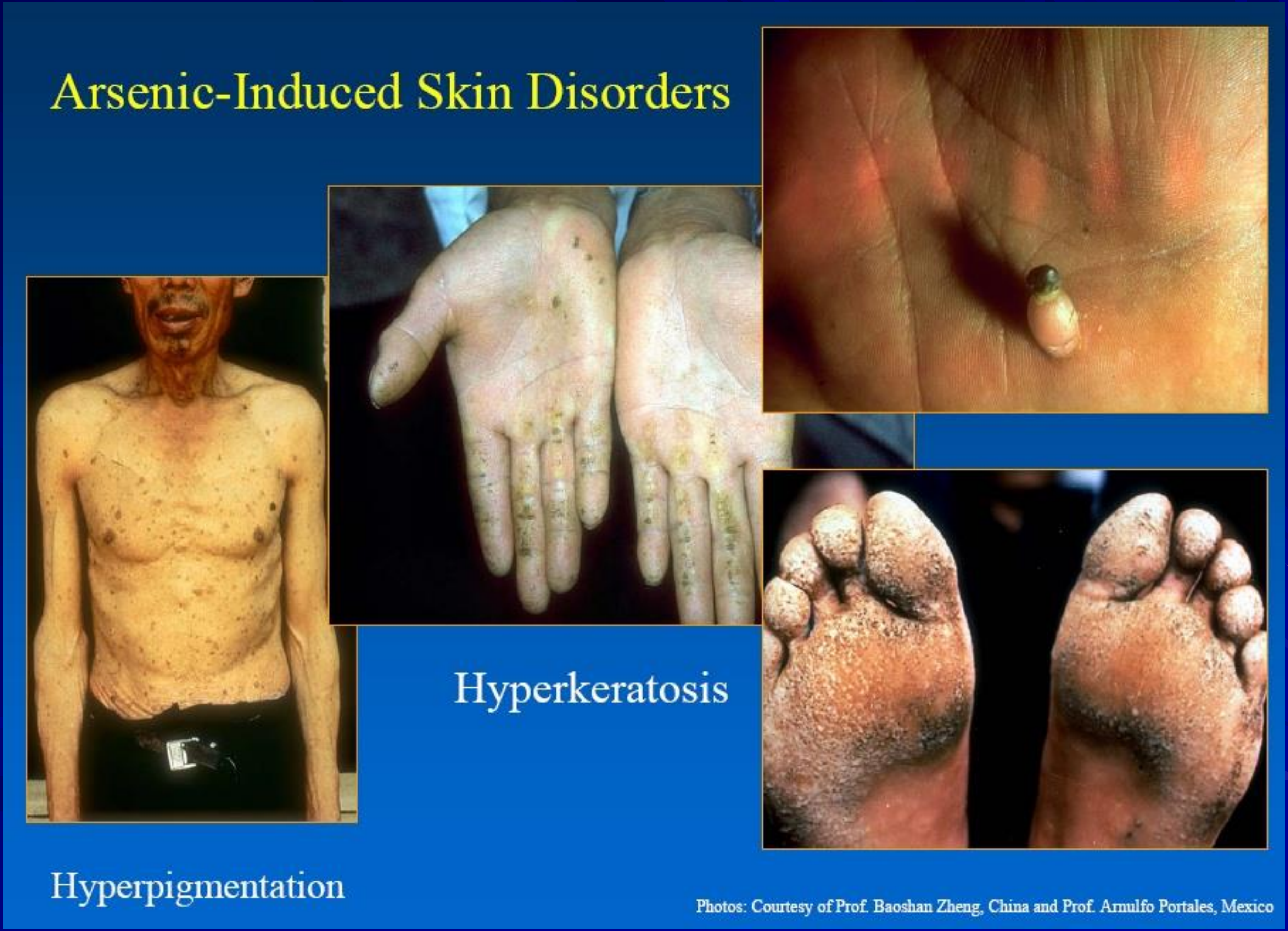


FIGURE 2 Occurrence of documented arsenic problems in groundwater (arsenic >50 μg L^{-1}) in major aquifers and (Smedley and Kinniburgh, 2002). Related to mining and geothermal sources.

Drinking water (WHO): 50 μg/l (1942); 10 μg/l (2002)

Smedley & Kinninburgh, 2005 - BGS



Arsenic-Induced Skin Disorders

Hyperkeratosis

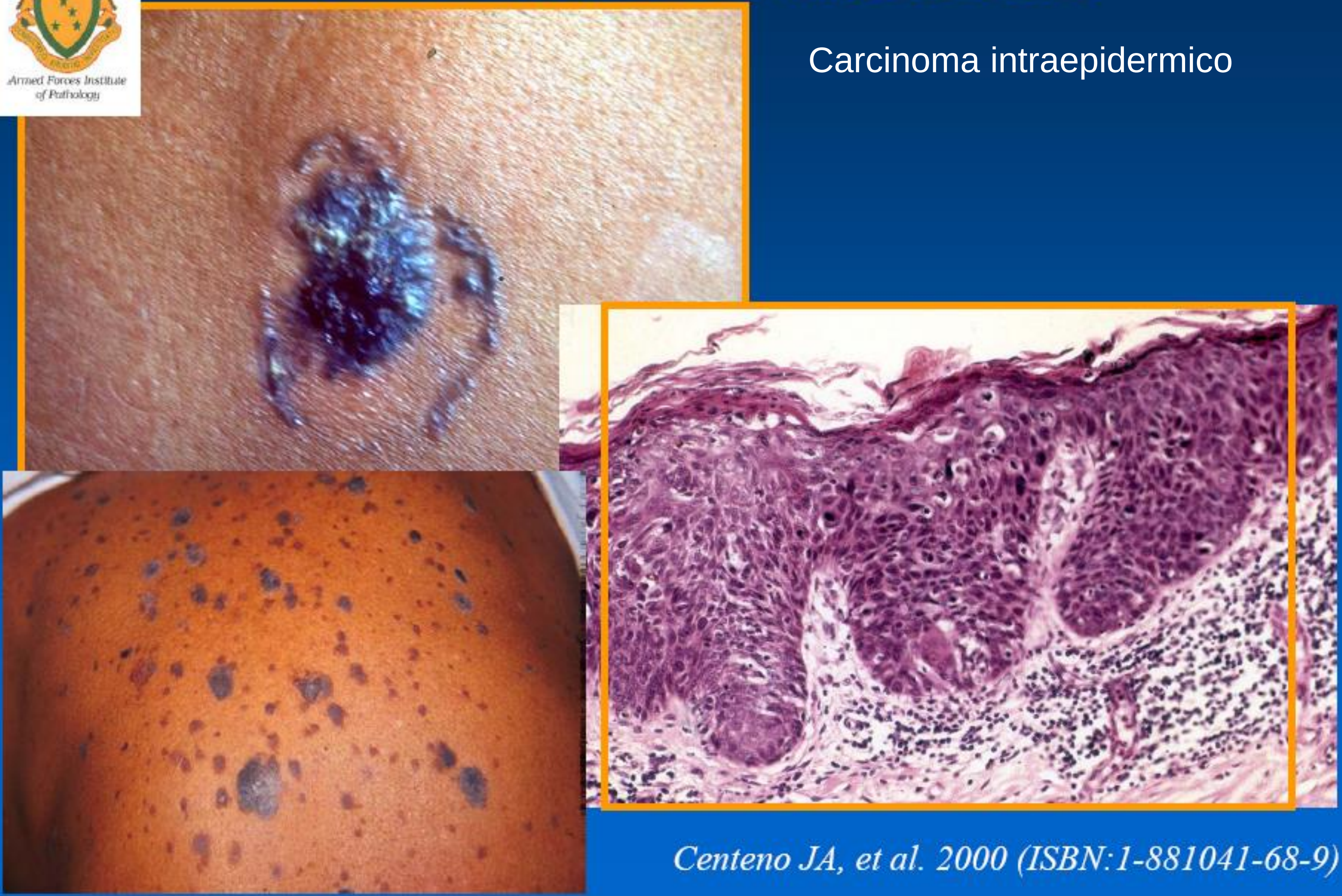
Hyperpigmentation

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

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

Arsenic-Induced Bowen's Disease

Carcinoma intraepidermico



Centeno JA, et al. 2000 (ISBN:1-881041-68-9)

Arsenic in groundwaters of Bangladesh

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

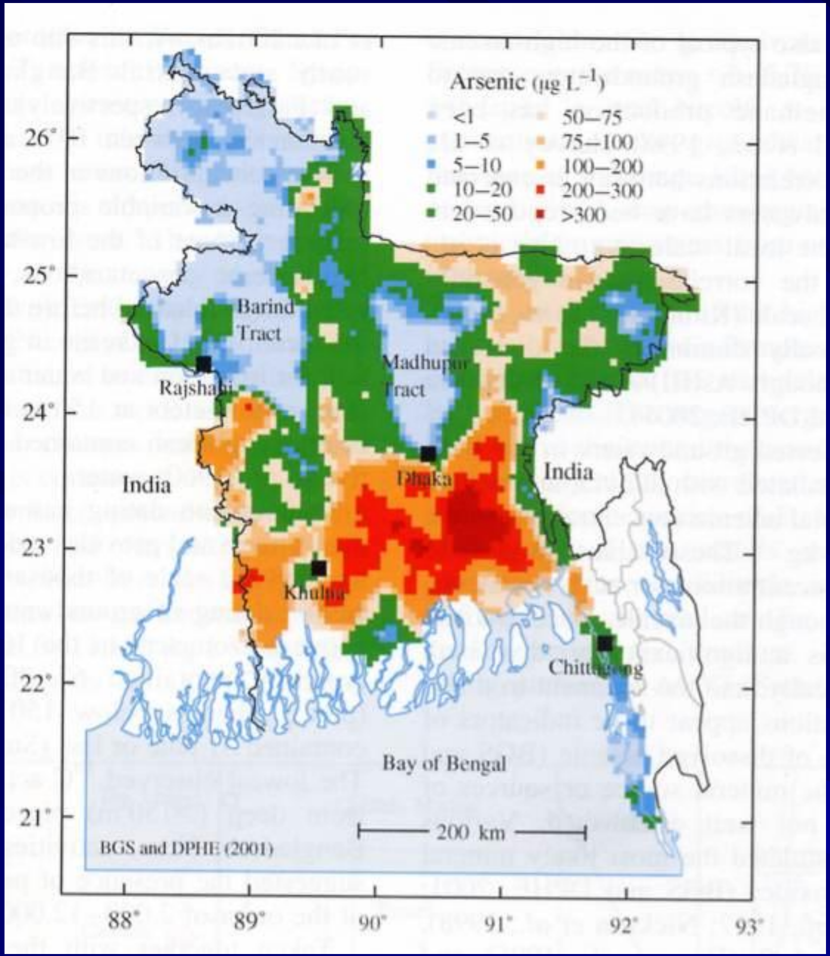
- 1993: first evidence of poisoning
- As in groundwaters: <0.50-3200 µg/l

- 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

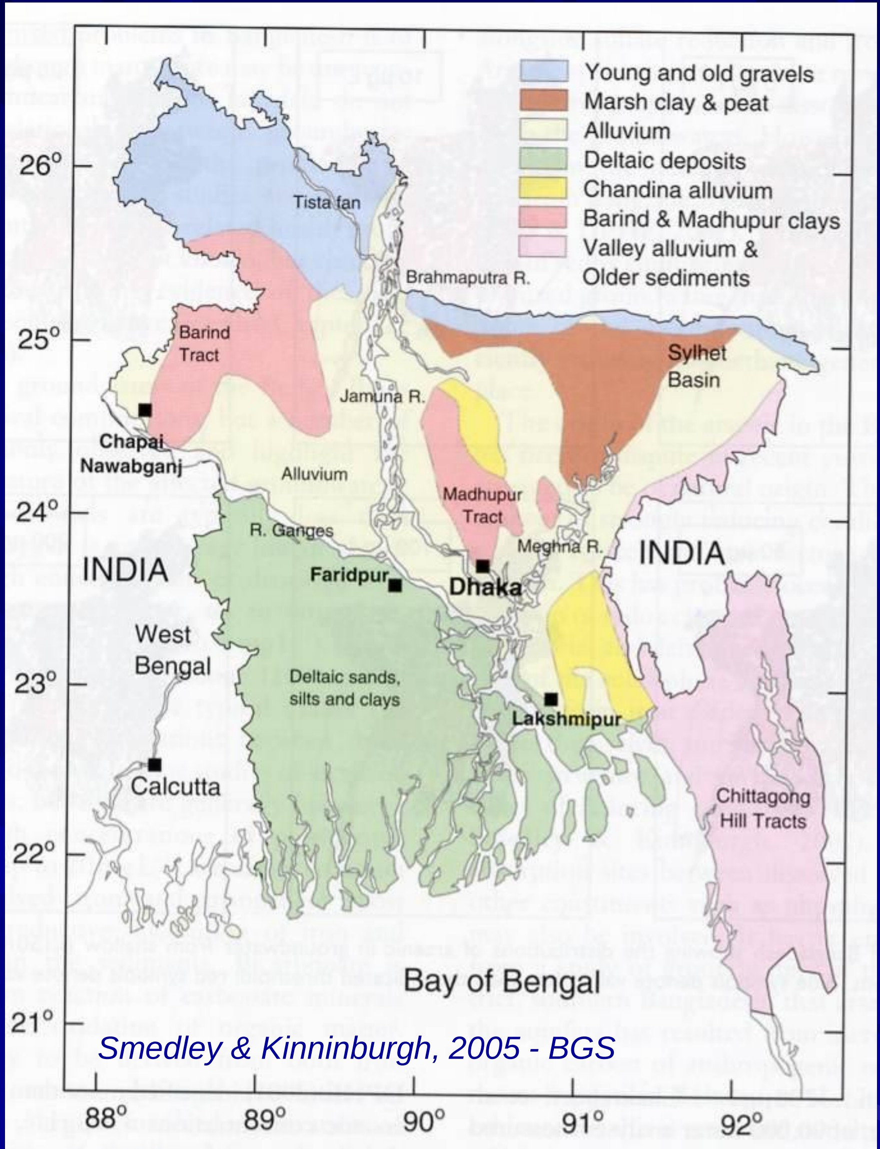
Anthropogenic factors or “natural” processes?



Usual concentrations in groundwaters < 10 µg/l (range <0.5-5000 µg/l)

Common features in groundwaters:

Eh < 100 mV
Dissolved O_2 low (< 1 mg/l or absent)
High dissolved Fe (up to 60 mg/l)
High concentrations of P (up to 20 mg/l)
Low nitrate and sulfate concentrations



Smedley & Kinninburgh, 2005 - BGS

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, occasionaly with peat horizons

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

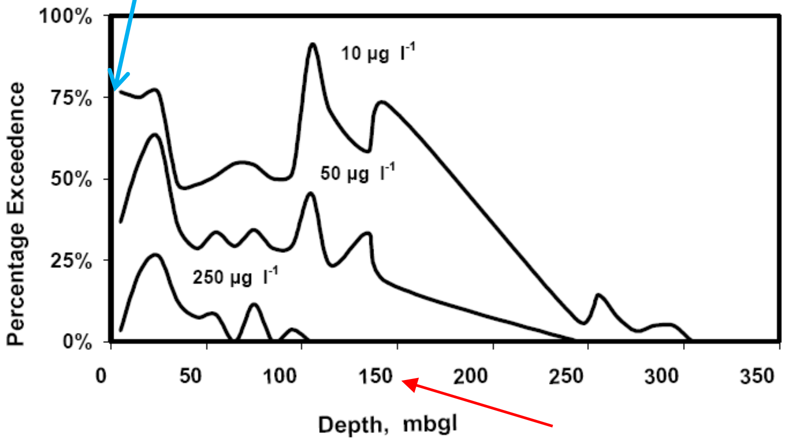
<u>Local source:</u> 1-30 mg/kg of As alluvial sediments (quartz-feldspatic sands) as aquifers

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

➢ 2.000.000 wells, 25 % with As > 50 µg/l (WHO)

➢ Up to 60 % wells contaminated in the south-east of the country (25 % with As > 300 µg/l)

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



Main acquifers: 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

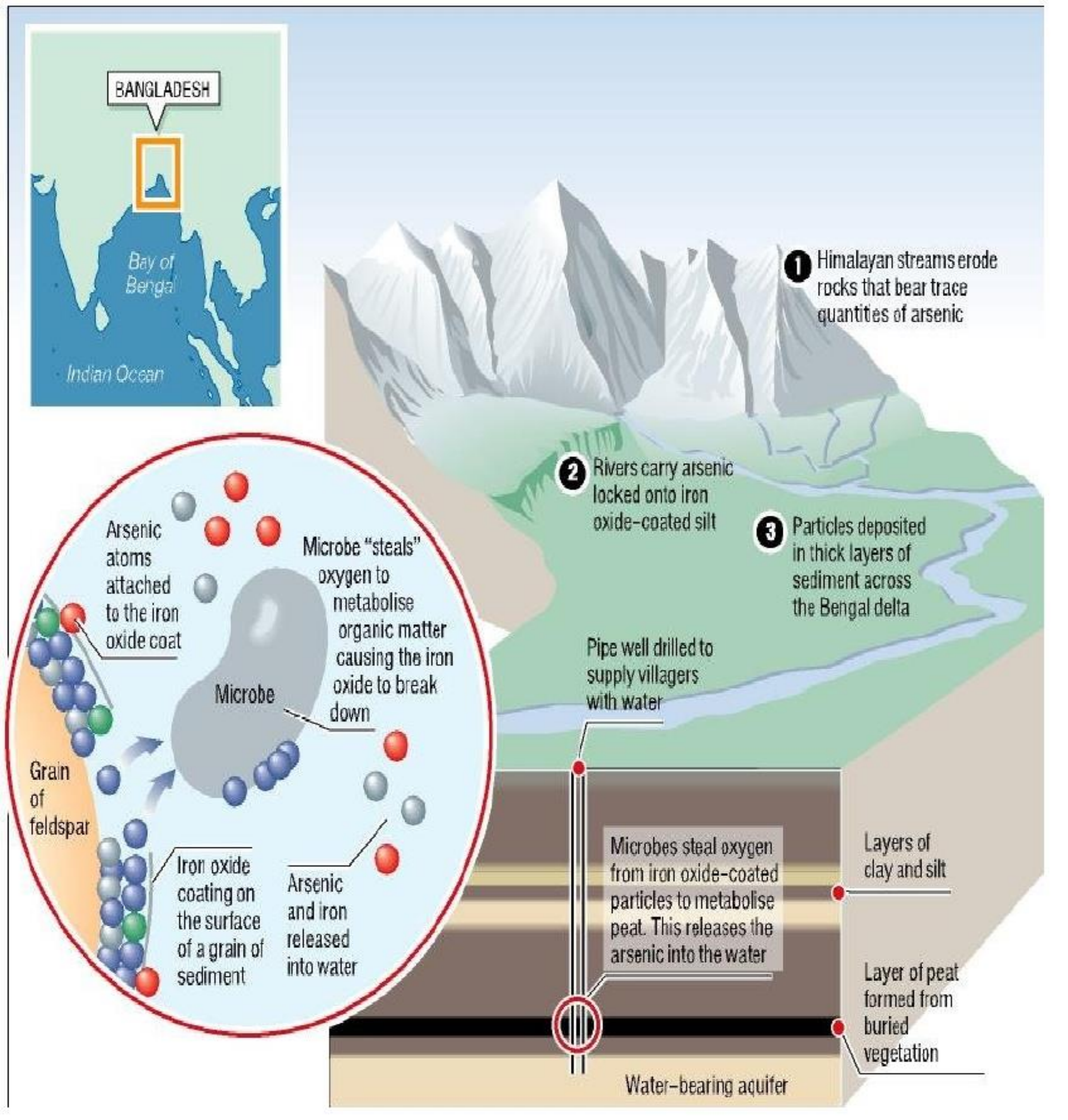
Decomposition of peat levels (Holocene *optimum climatico, 6000 BP*) mediated by bacteria

↓

Release of Arsenic from hydrates Fe-oxides in groundwaters

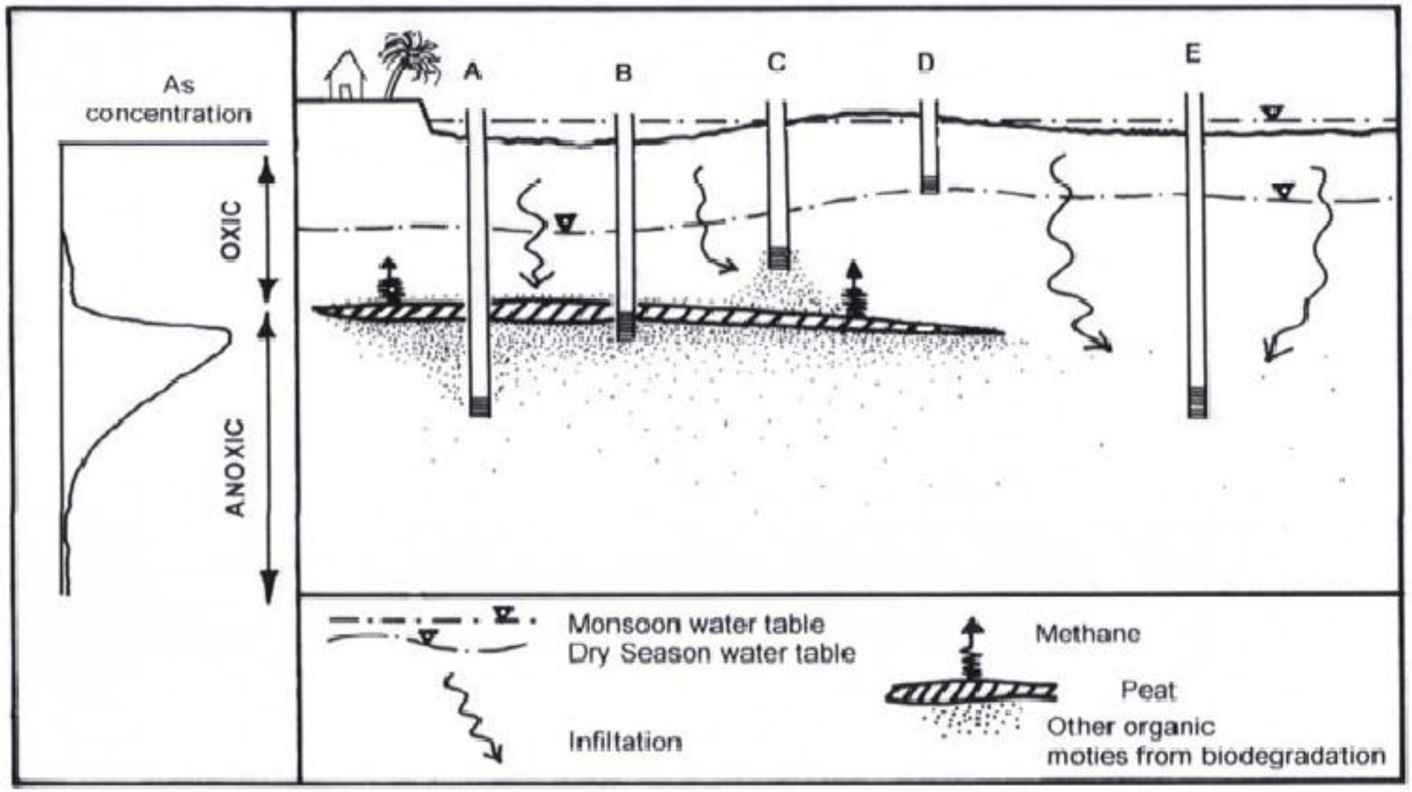
$8FeOOH + CH_3COOH + 14H_2CO_3$
(+ adsorbed As)

$\rightarrow 8Fe^{2+} + 16HCO_3^- + 12H_2O$
(+ dissolved As)



(McArthur et al., 2001)

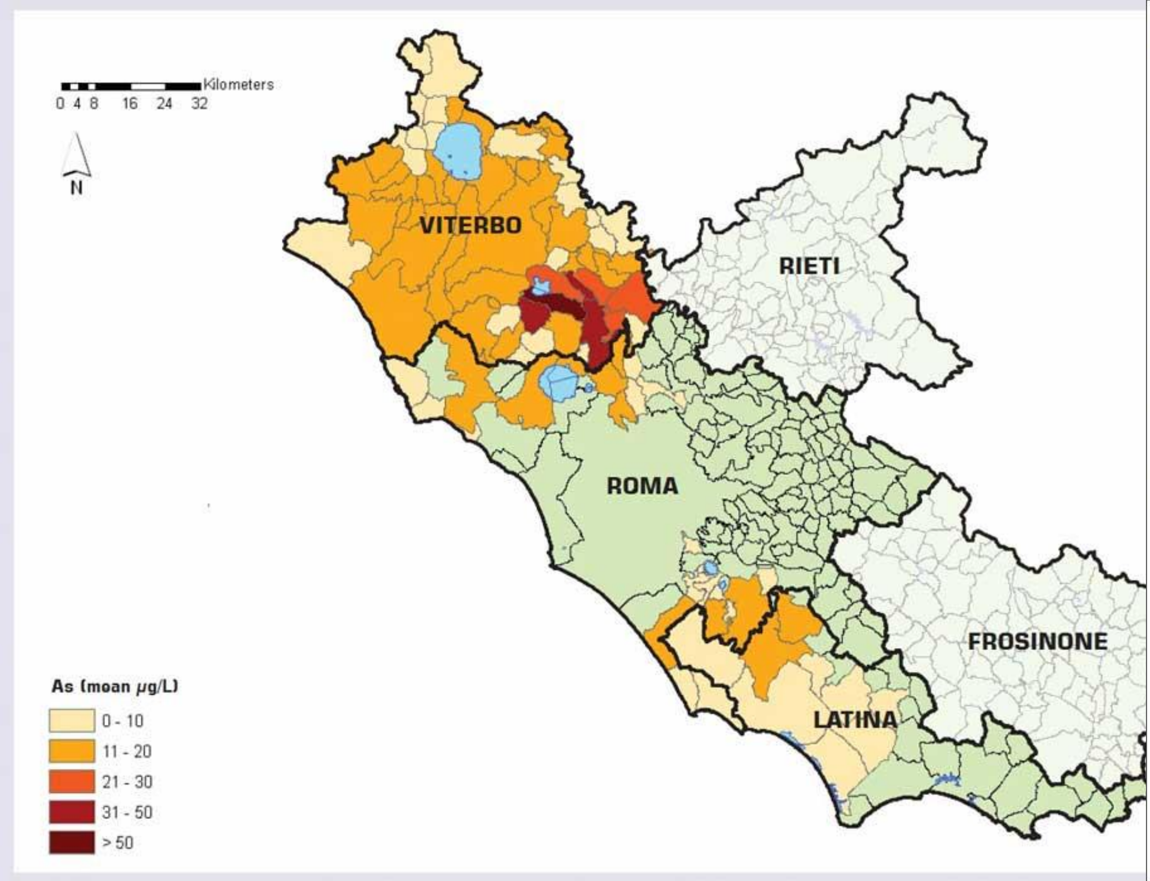
What does contamination degree depend on?



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



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**

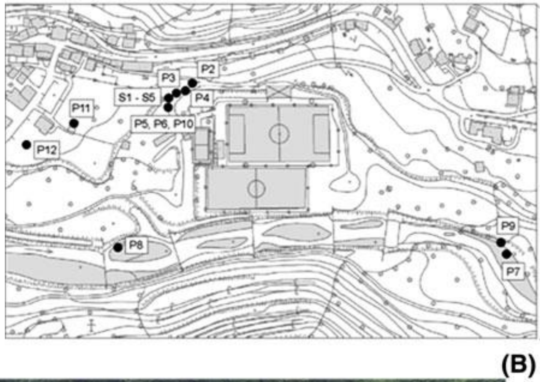
Limite autorizzato in Italia da una **deroga** (scaduta il primo di gennaio) e raggiunto in **43 comuni** in provincia di Viterbo **50**

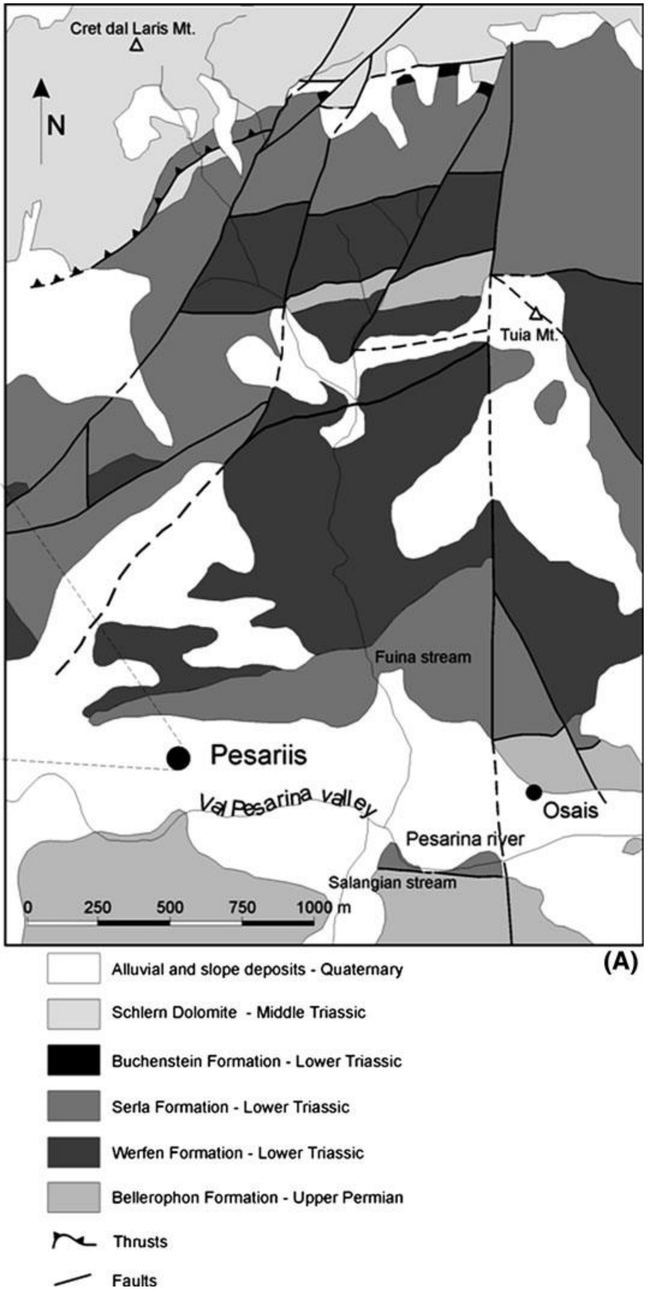
Concentrazione (microgrammi/litro)

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





Petrini et al. (2011) Env. Earth Sci.

Scolo sorgente sulfurea
As = 778 µg/l

Sorgente sulfurea

As = 728 µg/l