Chapter 18

Natural Aerosolic Mineral Dusts and Human Health

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Earth 281

Main reference: Chapter 18 from Selinus O., Alloway B., Centeno J.A., Finkelman R.B, Fuge R., Lindh U., and Smedley P., 2005. *Essentials Of Medical Geology: Impacts Of The Natural Environment On Public Health.* p.832. Academic Press.

Aerosols and Dust

- **Dust**: Consists of fine mineral grains – organic detritus and pathogens (hitchhikers).

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- *Normally we worry about anthropogenic sources and ignore natural sources.*

Materials

a) minerals – asbestos, silica, coal, natural weathering – anthropogenic
b) volcanic ash and gases
c) soils → dust, metals, organics, pathogens
d) by-products of mining
e) construction materials, fiberglass, gypsum (gyp) rock
f) demolition (e.g. The dramatic destruction and demolition of the World Trade Centre – New York)

Volumes of each natural vs. anthropogenic

Natural sources of dust

a) Sahara (Scirrocco)
b) North American “dust bowl” of 30’s
c) China – Mongolia (Hexi)
d) Australia – pictures

....and volcanoes

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What is in these dust storms?

....minerals (60% silica) – salt – sulphate and chlorides

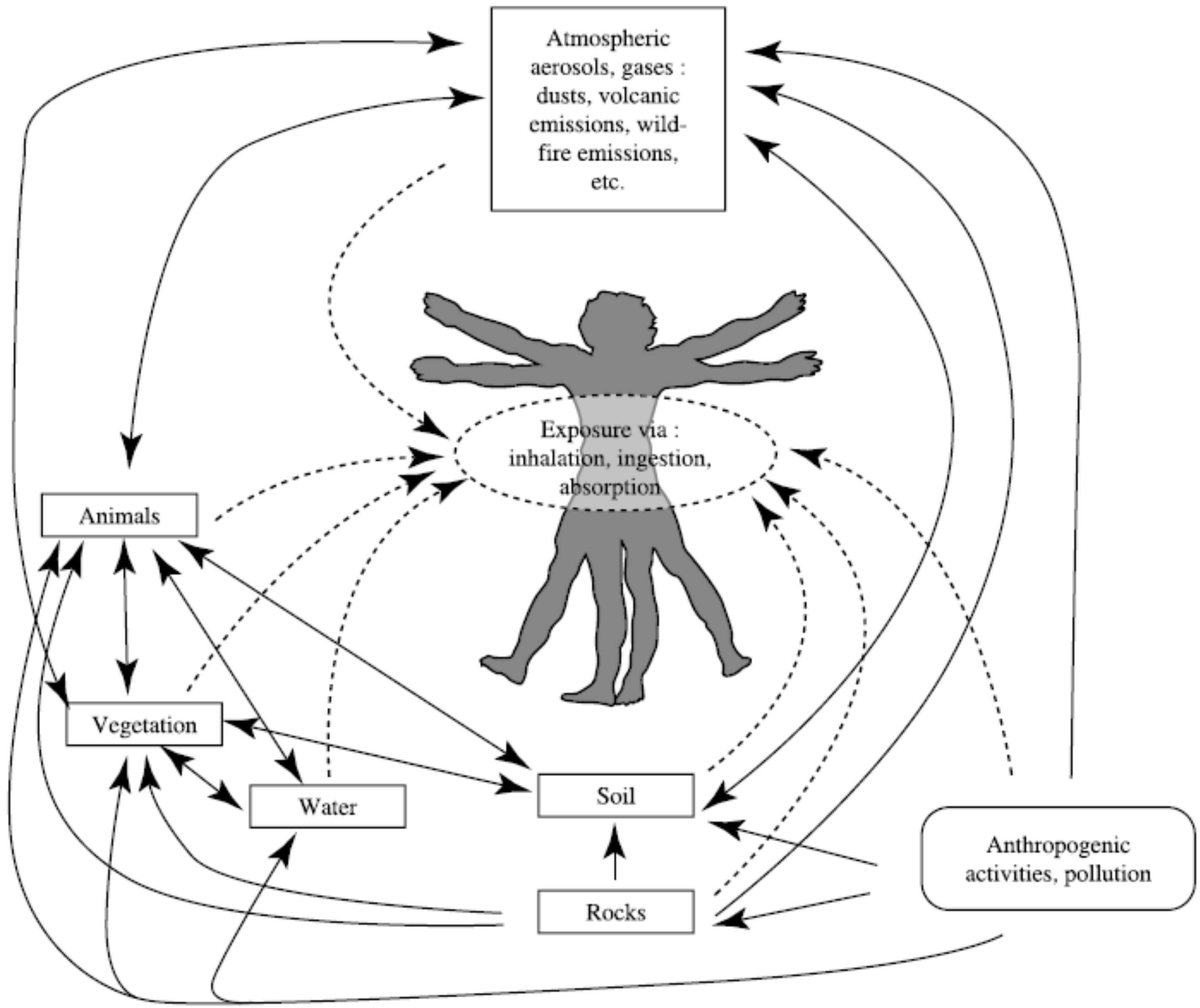

Figure 1 Potential human exposure routes within the earth's geochemical cycle can come from a wide variety of both natural and anthropogenic sources.

From Plumlee and Ziegler (2005) *in* Vol. 9 *Treatise on Geochemistry*

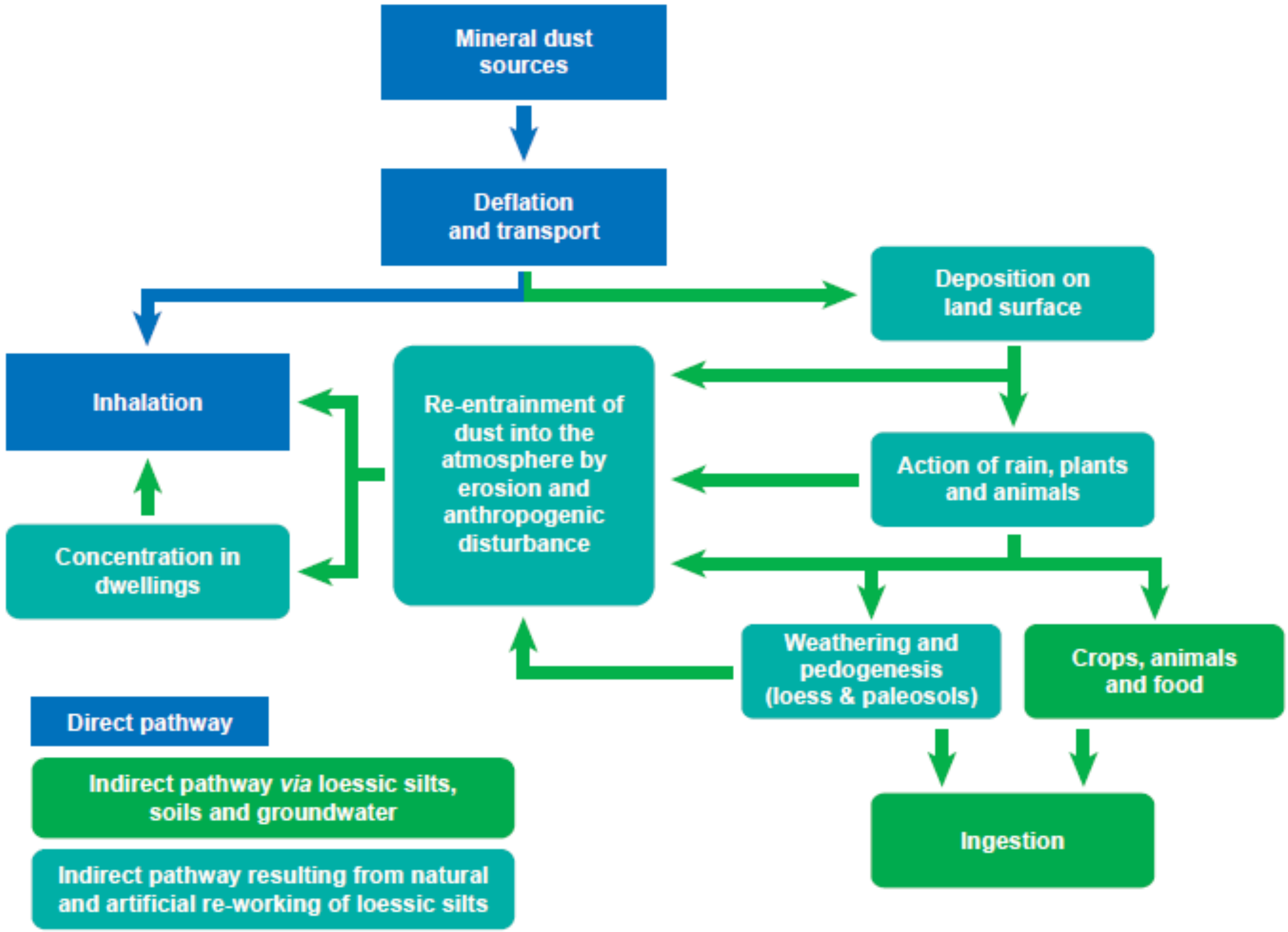

FIGURE 1 Some essential links in the direct and indirect pathways from dust sources to human inhalation and ingestion. Note: The wind-lain and variously weathered sediment known as loess commonly contains buried soils (paleosols) marking phases of relatively stable former land surfaces during the accumulation of the loess.

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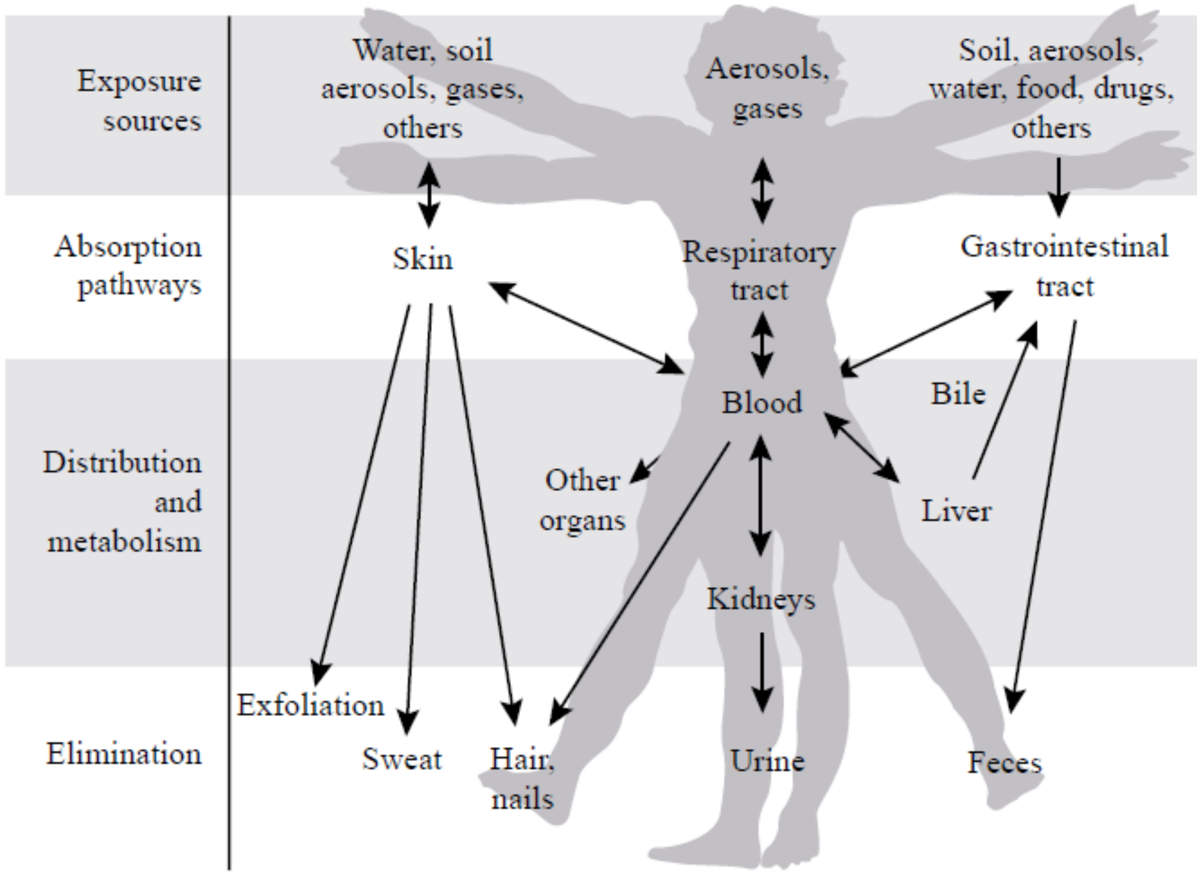

Figure 2 This schematic diagram shows the absorption pathways and systems of distribution, metabolism, and elimination for potential toxins. "Aerosols" include dusts, other solid particulates (such as smoke), and liquid droplets (such as fog, mists, etc.). Distribution may involve deposition of a toxin within a target organ and/or metabolism with or without excretion of the toxin by the target organ (after Goyer and Clarkson, 2001).

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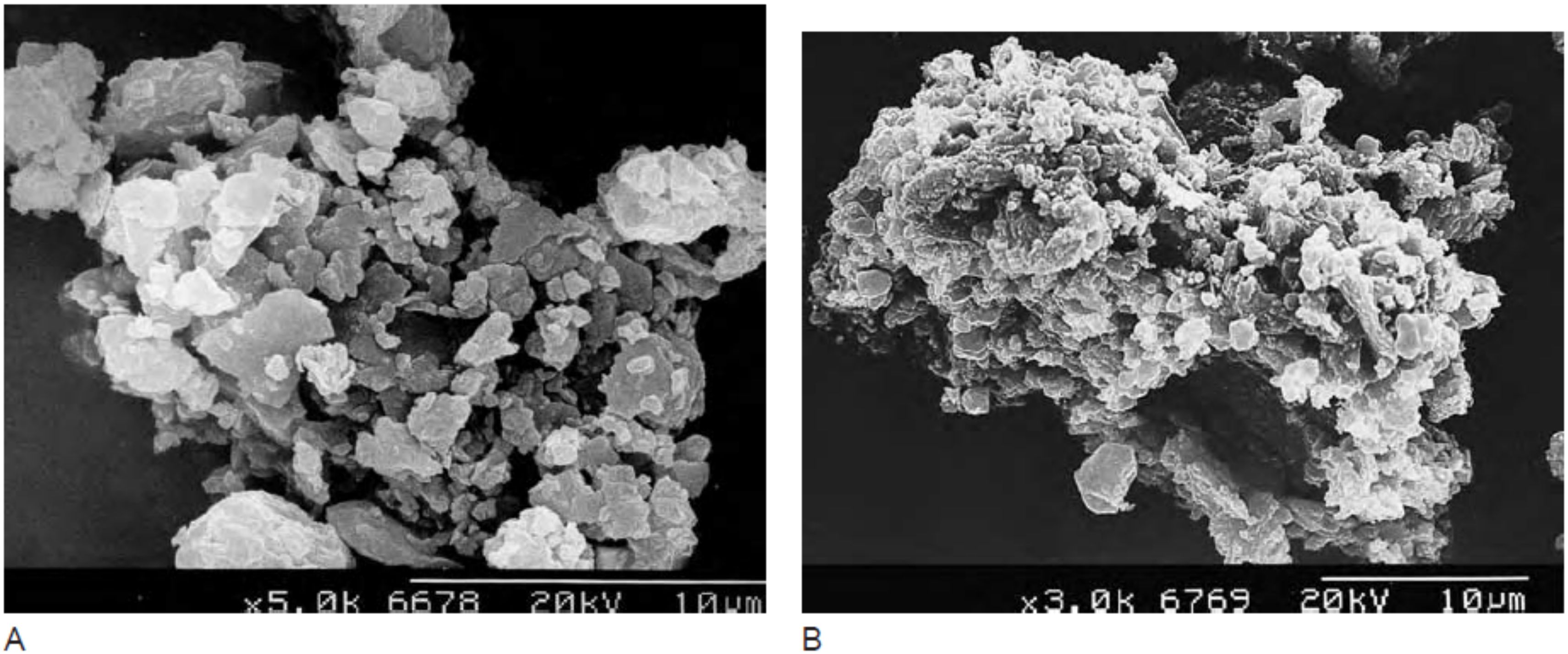

FIGURE 4 Scanning electron micrographs of windblown dust aggregates. (A): Silt size aggregate made up of clay-grade mineral particles, as commonly found in the young (Last Glacial) loess deposits of central and eastern Asia. (B): Silt size aggregate taken from the dust on a house beam in Ladakh. Elemental composition of such beam dust is dominated by silica, with lesser amounts of oxygen, aluminum, sulfur, potassium, calcium, and iron. Both scale bars = $10\,\mu m$.

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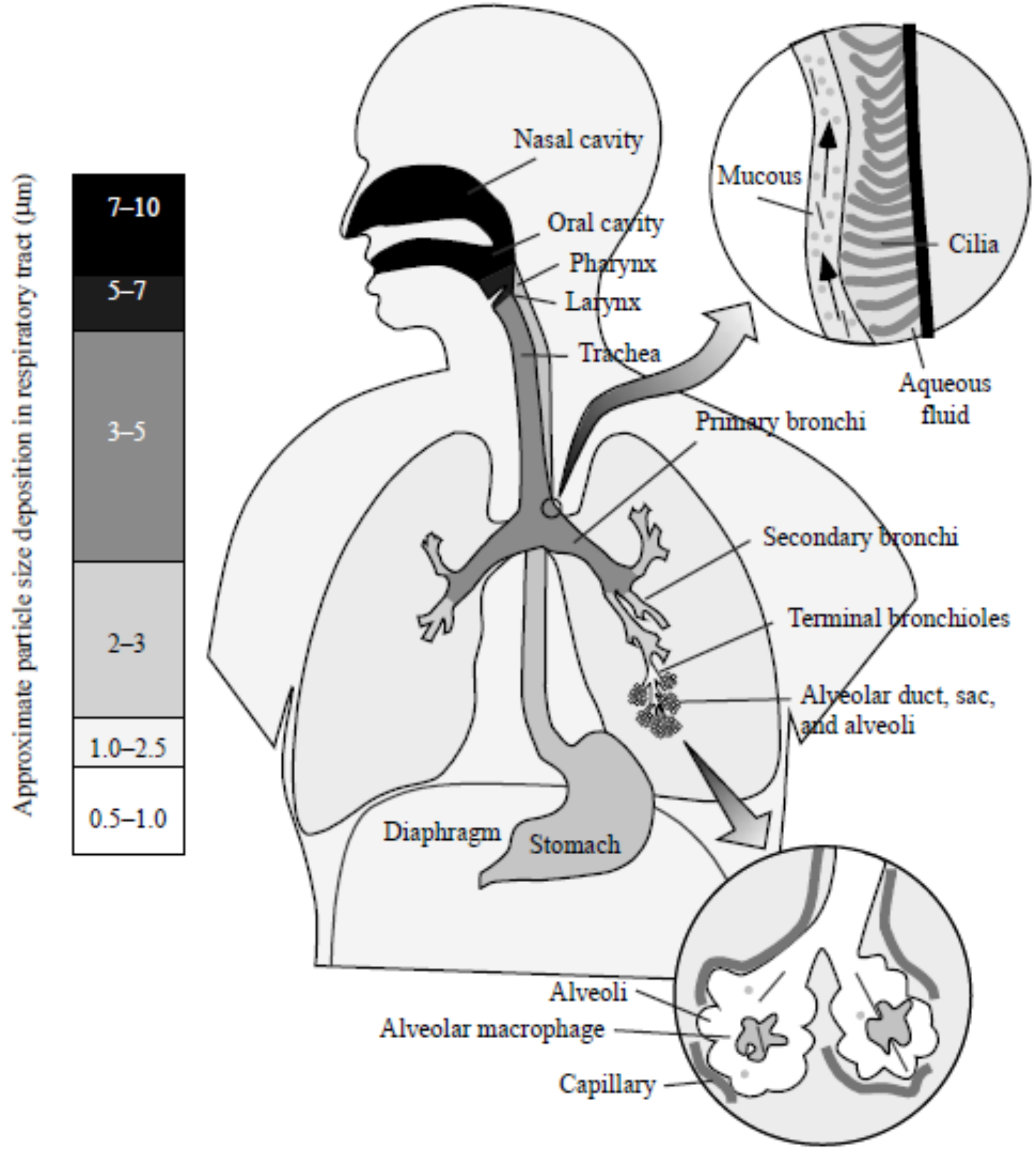

Figure 3 A schematic diagram of the respiratory system shows the fractionation of particle sizes that occurs with progressive depth in the system (after Newman, 2001).

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Dust and time

- Many periods in the Earth's history where dust would have been more severe, e.g. after each

University of Waterloo Greenland Project

Ice sheets – loess (what are the underlying rocks? e.g. ultramafic rich = asbestos vs granite = silica)

Photos courtesy of E. Henkemens

Dust and transport:

- Particle size decreases with distance from source

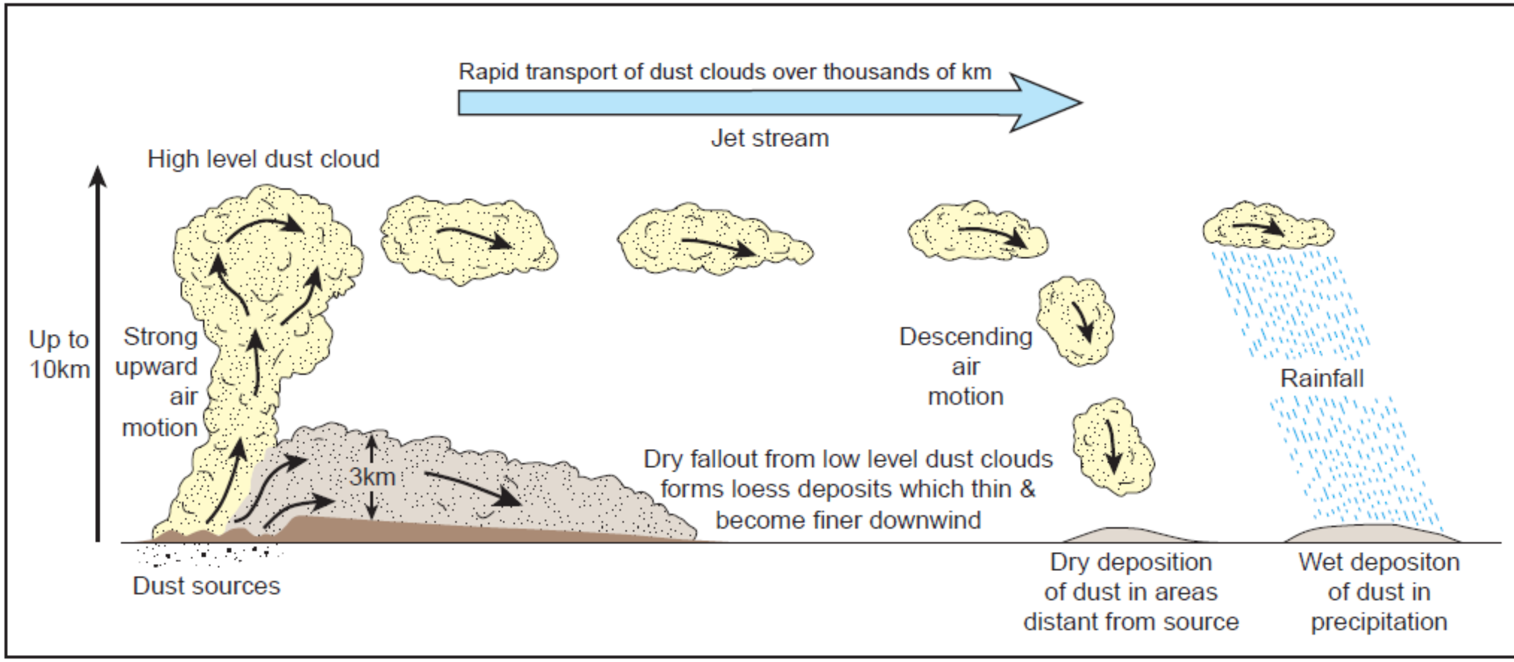

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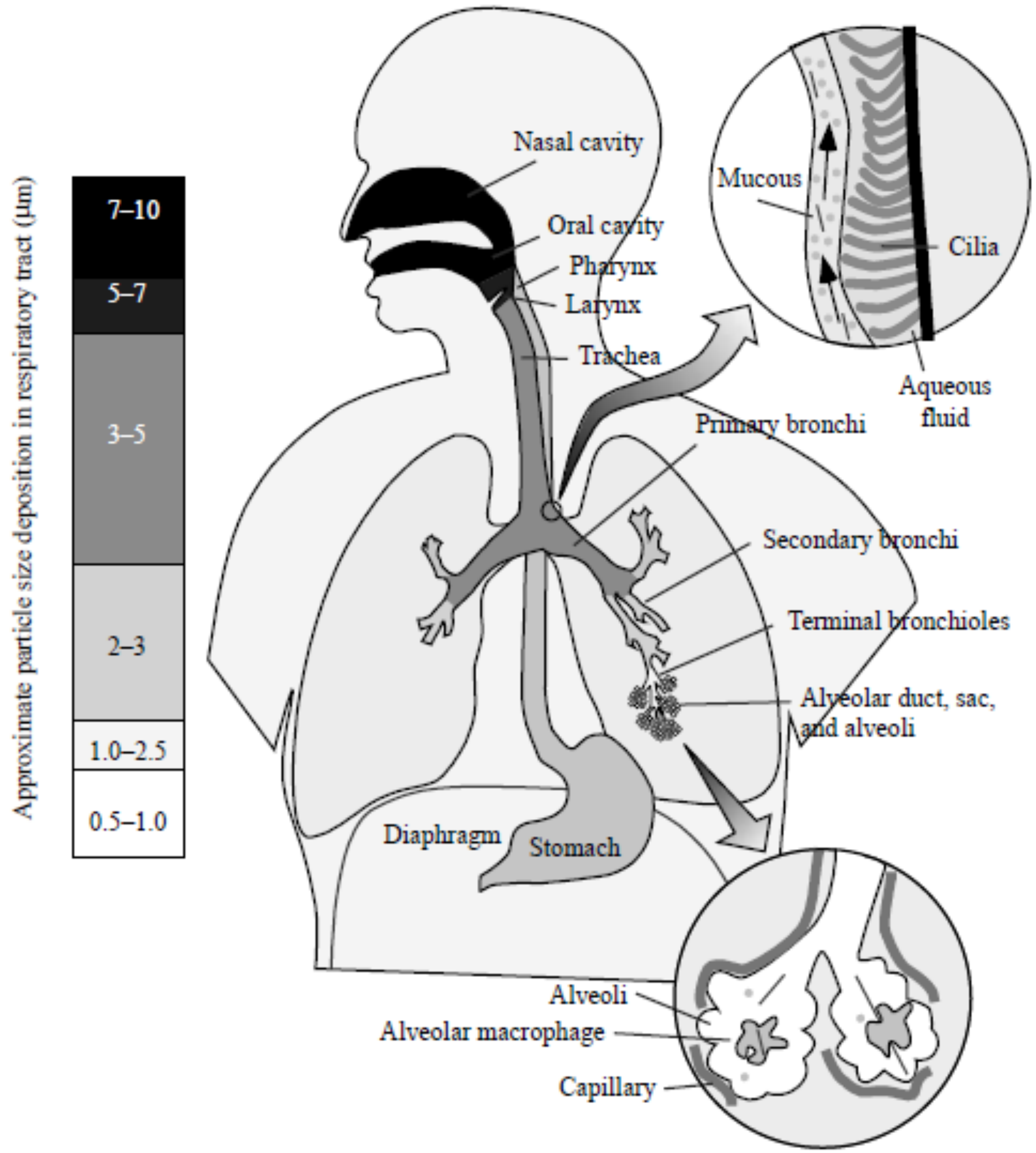
FIGURE 5 Sketch showing the two principal modes of aeolian dust transport and deposition, based on a transect from the Chinese drylands to the Loess Plateau and the North Pacific Ocean. Re-drafted from Pye and Zhou (1989).

a) Near the dust source – more mass, coarser grains – can result in “pneumoconiosis” and/or “desert lung” (lungs scar and stiffen)
b) With transport the fraction inhaled (< 10μm) increases and chance for the fine dust to get deeper into your lungs increases.



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Dust and climate change

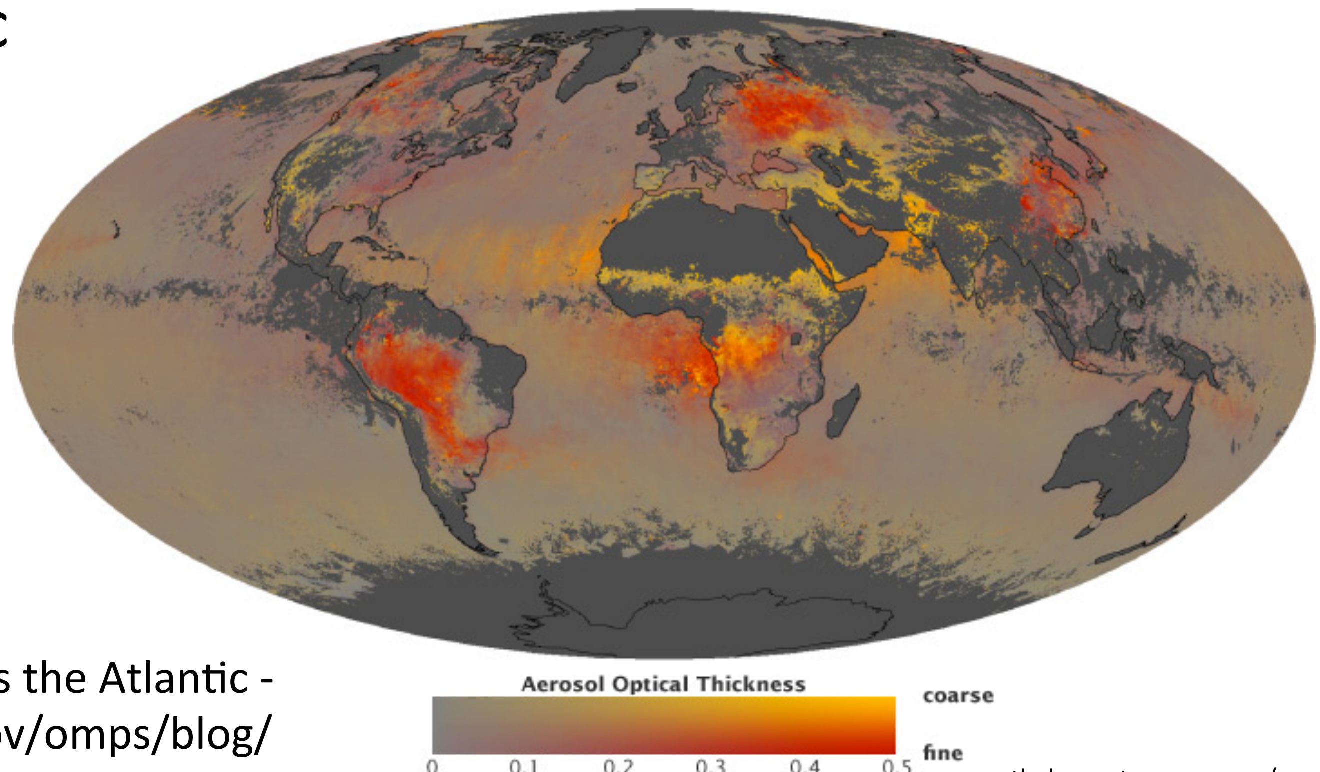
- Obviously aerosol loadings in the atmosphere reflect and impede sunlight – can lower temperature; also affect atmospheric chemistry and ozone; add chemicals to the ocean, etc.

Saharan Dust impacts:

a) Europe to South America
b) increased in the last 2000 years (man's influence – cut down forests)
c) asthma cases (increases are in the 1000's)
d) Dust settles on coral reefs of the Caribbean

Dust storms

1. Ingredients – dry desert like conditions, e.g. Saharan or Mongolian/Gobi types
   a) local course-medium material
   b) tropospheric fines – in winter north easterlies cross the Atlantic
   c) Also fires



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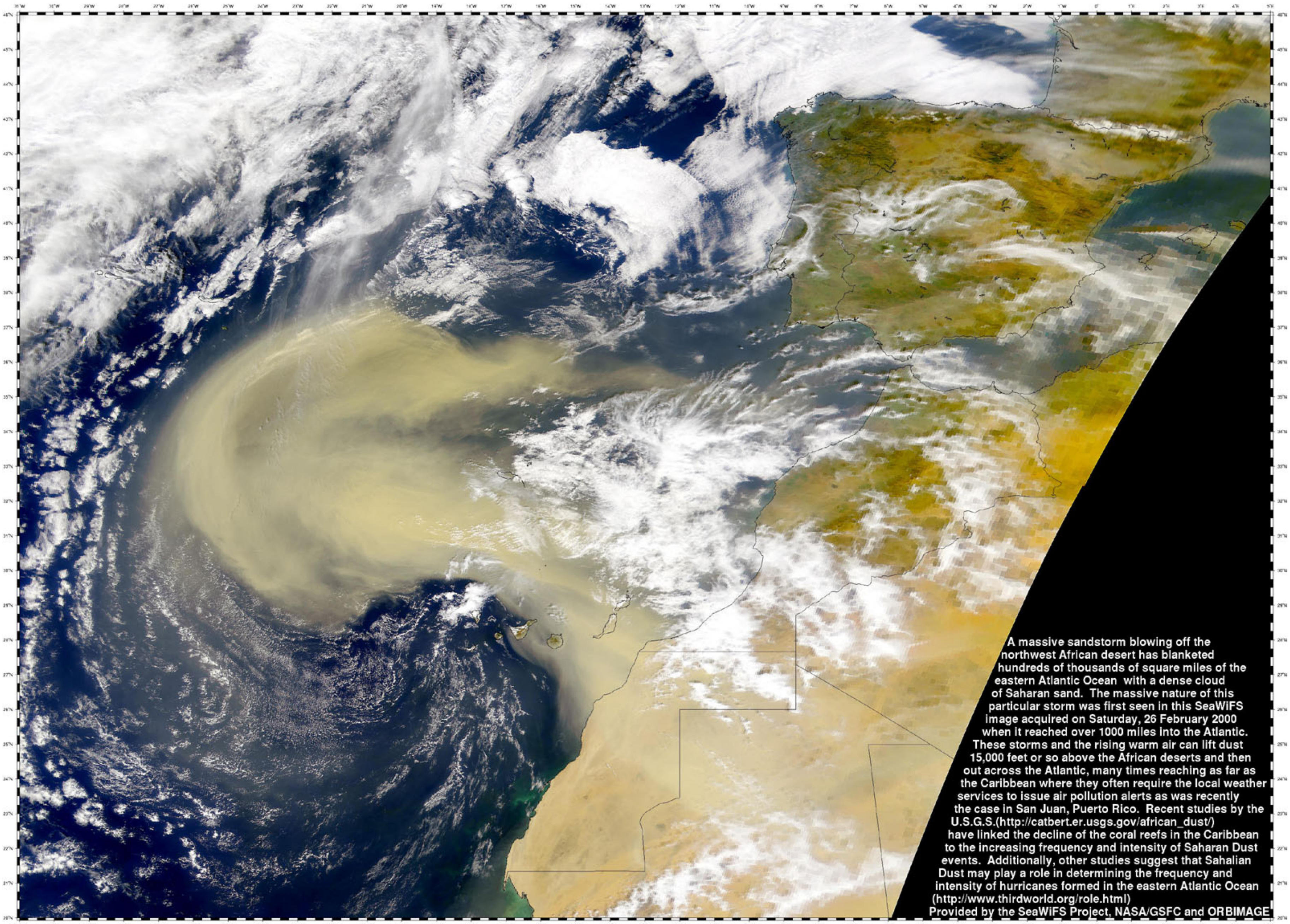
Watch the dust travel across the Atlantic - http://ozoneaq.gsfc.nasa.gov/omps/blog/2013/08/saharan-dust-transport-animated-



www.noaanews.noaa.gov/

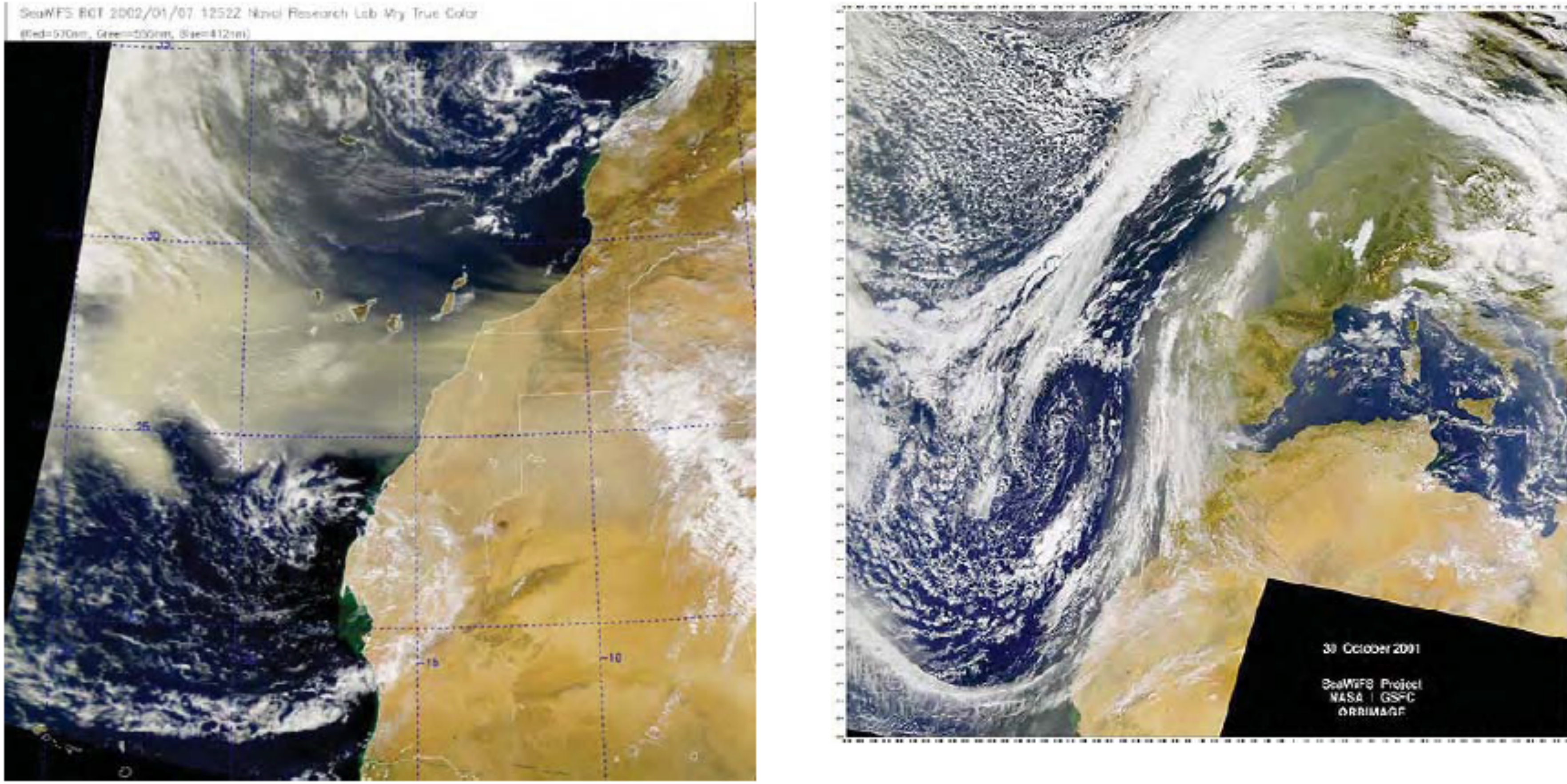


FIGURE 6 (Left): Outbreak of Saharan dust across the North Atlantic, January 2002. High pressure over and north of Morocco, with a depression centered off the West Sahara-Mauritania coast, indicates a strong easterly flow across the African coast and the Canary islands (center) and into the mid-Atlantic. A dense pall of dust, about 500 km wide, reduced visibility and enhanced sunset colors for several days in the southern Canaries and deposited red dust. (Right): African dust over western Europe, October 2001. High pressure over the Mediterranean basin and an extensive and vigorous depression west of North Africa and Spain (centered close to the island of Madeira) induced strong southerlies from Mauritania to Scandinavia. A high-level dust pall can be clearly seen running from off the Moroccan coast across western Iberia, the Bay of Biscay, western and central France, southern and central Great Britain, the Low Countries, North Germany, and Denmark. Both are NASA SeaWiFS images.

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Dust storms

2. Mongolian-Chinese corridor-- here we have mountains
   a) fine "loess soils" result of glacial dust (Loess Plateau is greater than 400,000 km^2 and more than 100m thick)

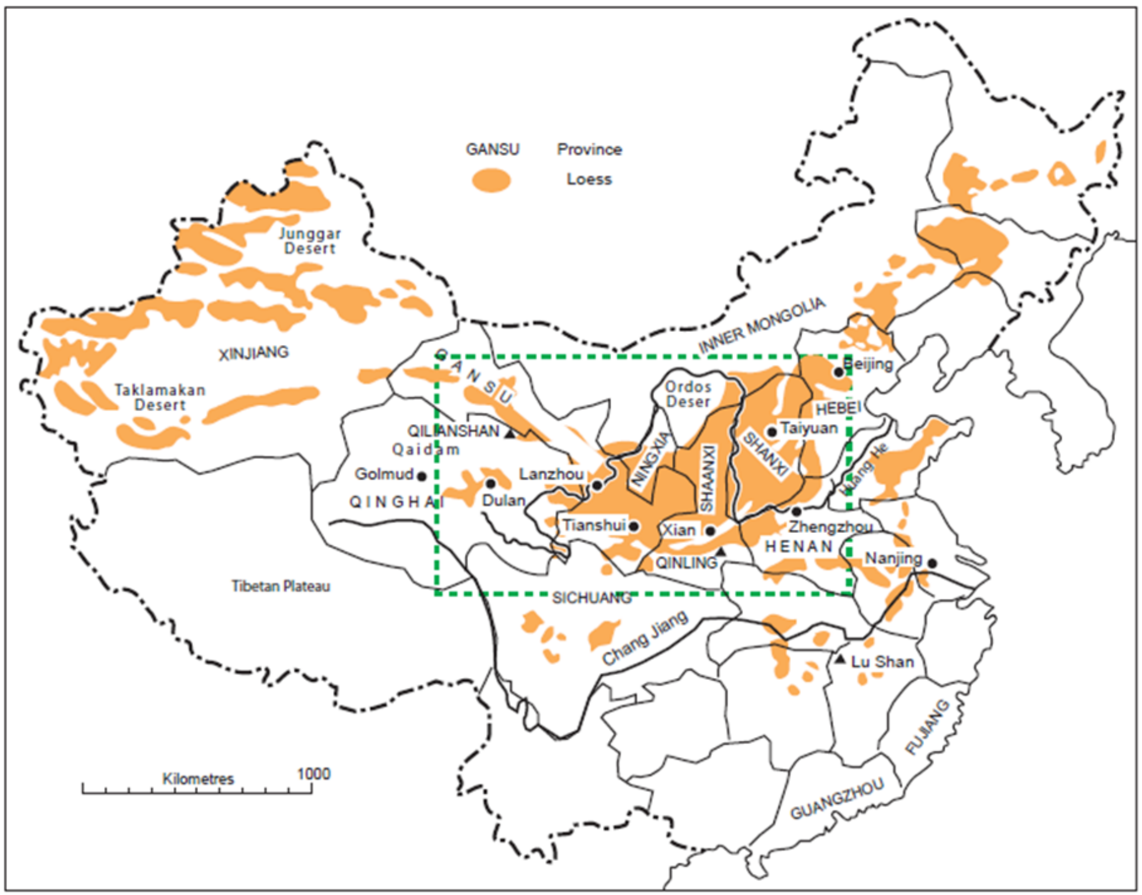

FIGURE 7 Upper: The Loess Plateau of North China in relation to the Hwang He (Yellow River) and the principal deserts. The box indicates area covered in lower half of the figure. Lower: Part of northern China, showing the Loess Plateau and the Hexi Corridor. See text. Re-drawn from Derbyshire et al. (1998).

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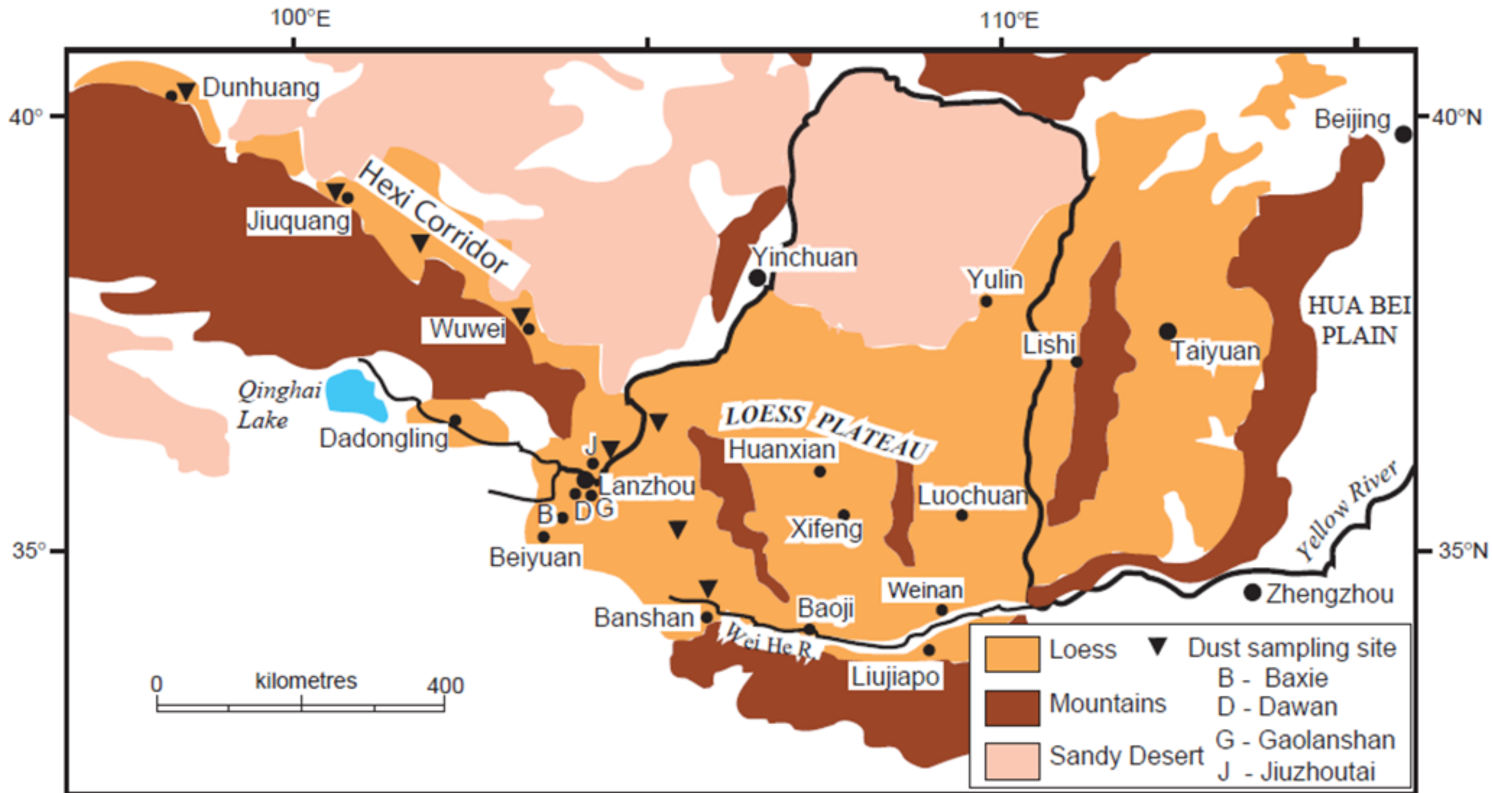
Dust storms

2. Mongolian-Chinese corridor here we have mountains
    b) A tremendous HIGH Pressure in the URAL Mtns. of Russia creates a cold front that moved south in May 1993



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Dust storms

2. Mongolian-Chinese corridor here we have mountains
   c) The front gets constricted between two mountain ranges ,the air is funnelled to the east
   d) The funnelling results in sustained winds of high velocity across the narrow corridor

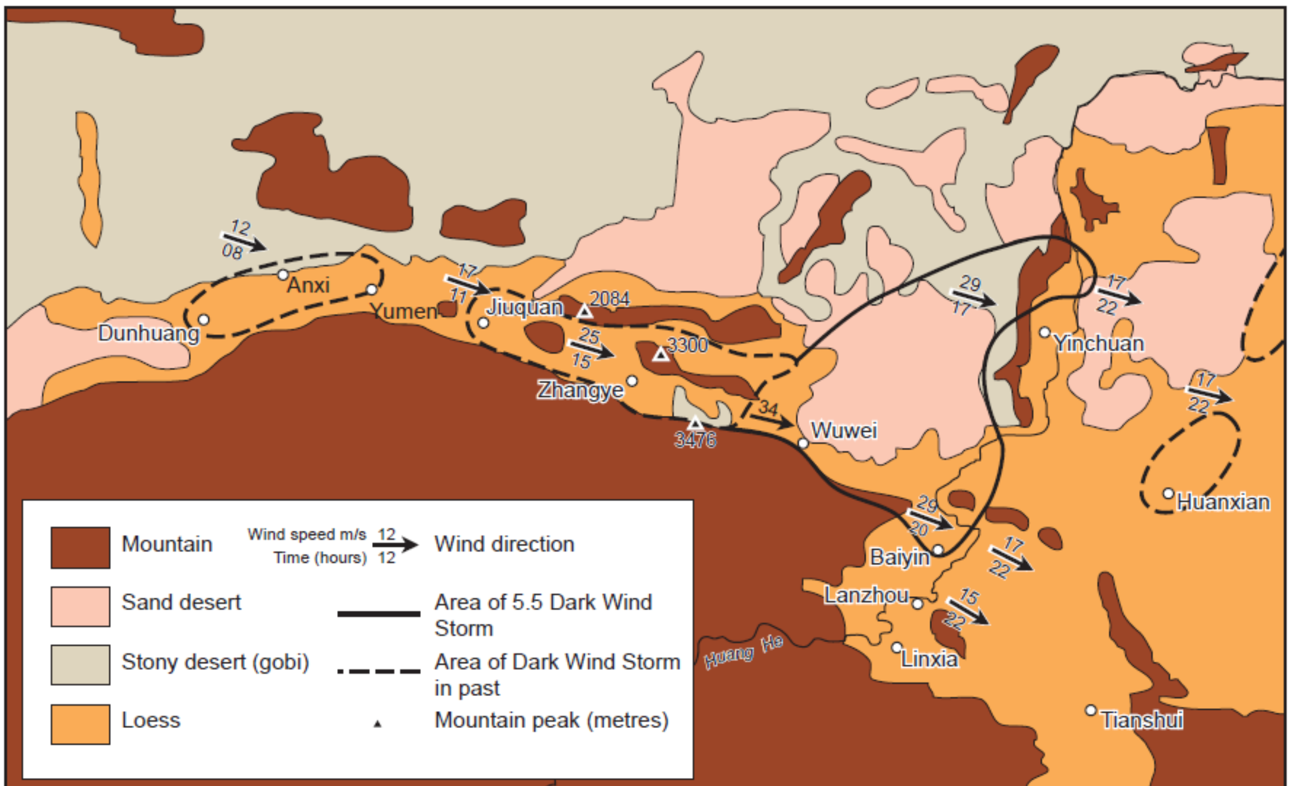

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FIGURE 8 Terrain sediment cover types, dust storm zones, wind velocities, and timing (in hours) of the "dark storm" of May 5, 1993, in the Hexi Corridor and the western Loess Plateau, China. Data provided by the State Meteorological Service of China, and the Meteorological Bureau of Gansu Province. Re-drawn from Derbyshire et al. (1998).

Dust storms

2. Mongolian-Chinese corridor

e) Result - tons of sand and coarse dust fall to the east (Figure 9) BUT, also incredible

f) amounts of fines move further east

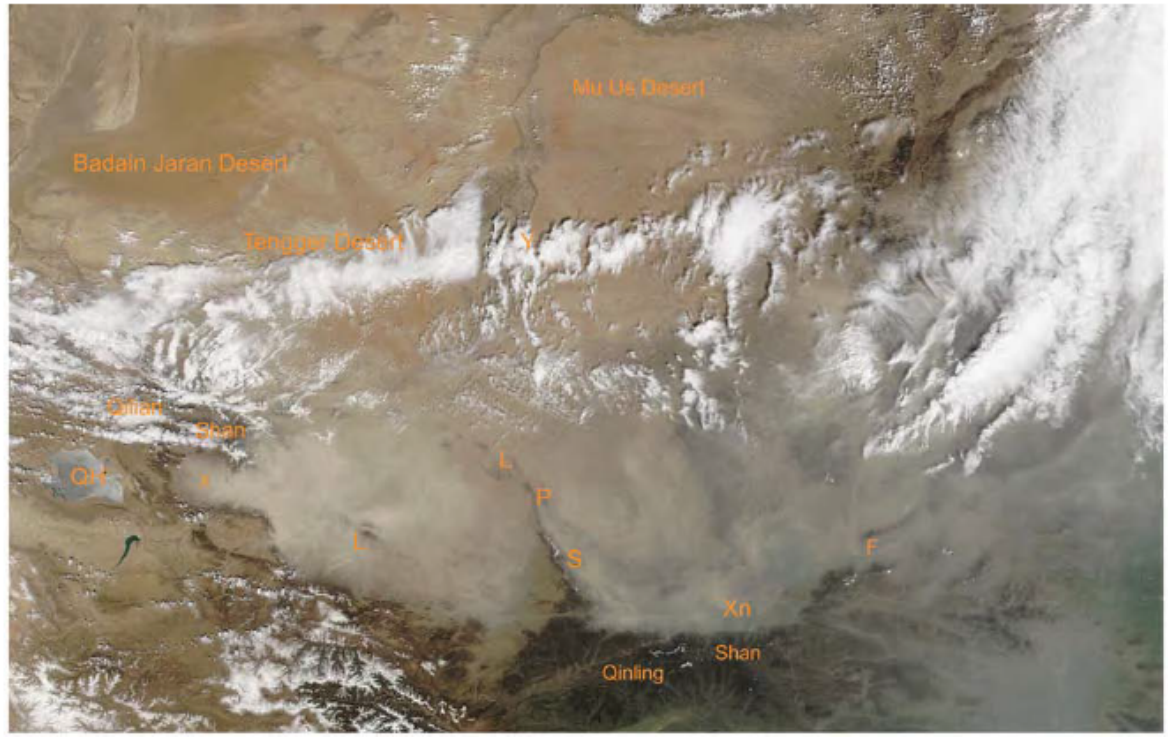

FIGURE 9 Part of a Terra Satellite image, using the MODIS sensor, taken on March 29, 2002, and showing a dust storm generated by winds from the west-northwest over northwest China. (For comparative location, compare with Figures 7 and 8). The air over the Badain Jaran and Tengger deserts is clear of dust, as it is over the Mu Us Desert (to the north of which can be seen the big bend of the Yellow River). However, the dust thickens rapidly with proximity to the cold-weather-front and the alluvial-fan-covered Hexi Corridor on the northern side of the Qilian Shan. The Xining Basin (X = city of Xining, just to the east of Qinghai Lake; QH) generates its own pulse of dust, but not the adjacent Qaidam or Gonghe basins in this case. Lanzhou city (L), near the outlet of the Hexi Corridor, has a thick dust pall over it as well as its own locally generated pollution cloud. The dense dust plume is split by the NNW-SSE aligned Liupan Shan (L-P-S). East of this mountain range, the plume completely covers the twin basins of the Jing and Luo rivers (draining the central and southern part of the Loess Plateau). This part of the plume just covers the city of Xi'an (Xn); its pollution pall is more modest than that of Lanzhou. The southeastern margin of the plume is very sharp as it comes up against the ~3700 m high Qinling Shan (on which several snow-covered areas can be seen). The plume extends eastward, crossing the sharp bend of the Yellow River at Fenglingdu (75 km west of the Sanmenxia Reservoir on the lower Yellow River). The dust plume over the green farmlands of Henan and Hebei provinces in the southeastern part of the image is much more diffuse, which suggests that it may be the product of a pre-frontal trough.

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Dust storms

2. Mongolian-Chinese corridor

Results: (i) proximal – “dark storm”, visibility gone, temperature drops to -6.6°C, frost, crop loss, snowfall, 380 people and 120,000 animals die

(ii) at distance (distal) “loess rain”

www.chinadaily.com.cn/

Dust storms

earthobservatory.nasa.gov/

3. Other dust sources (natural and man made)
    a) Volcanoes (previous lecture)
    b) fossil fuel – forest burning (black carbon)
    c) mining and other man-made activity
    d) In general we have through forestry, agriculture and mining, enhanced dust impacts.

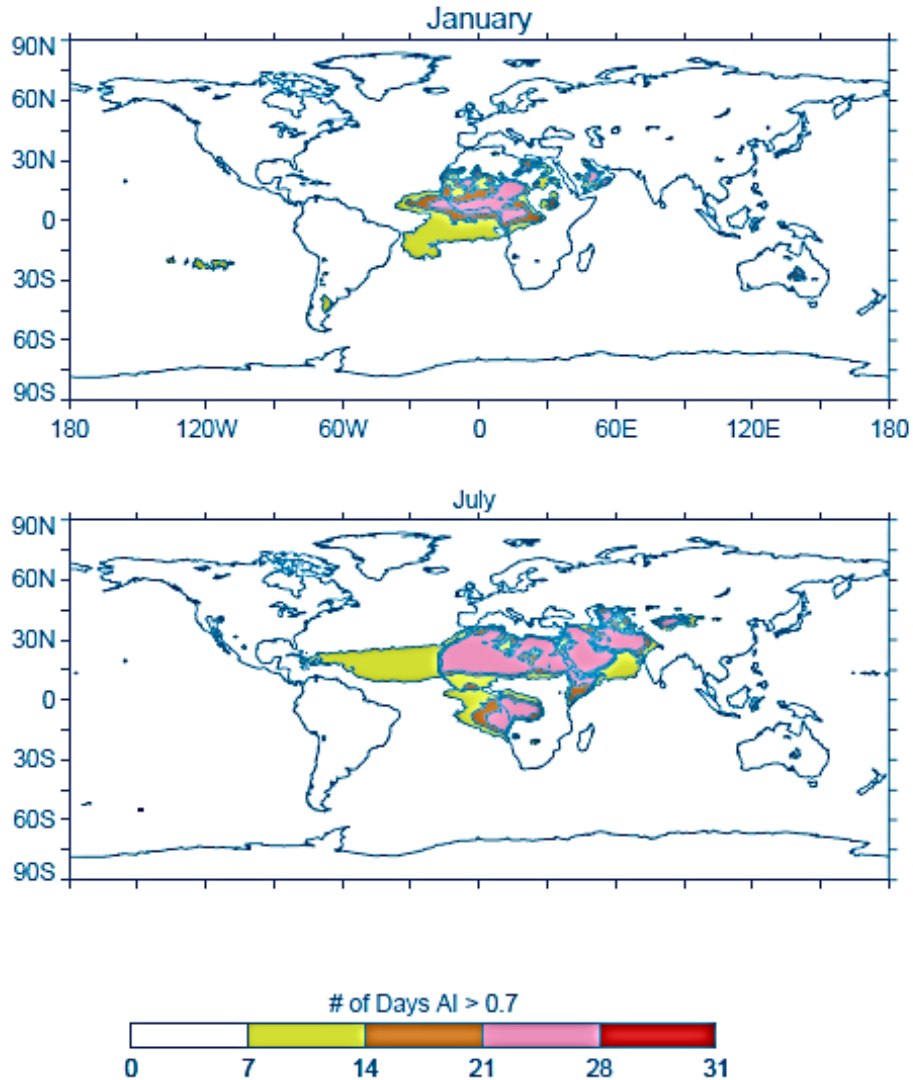

FIGURE 11 Global distribution of dust and smoke. Monthly frequency of TOMS absorbing aerosol product for January (top) and July from 1980 to 1992. Scale: number of days per month when the AAI equaled or exceeded 0.7. The large, dark area in southern Africa in July is a product of biomass burning, and there is also evidence of biomass burning in January just north of the Equator in Africa. Part of the plume over the Equatorial Atlantic is smoke. All other distributions shown are due to the presence of dust. After Prospero et al. (2002), with kind permission of the first author.

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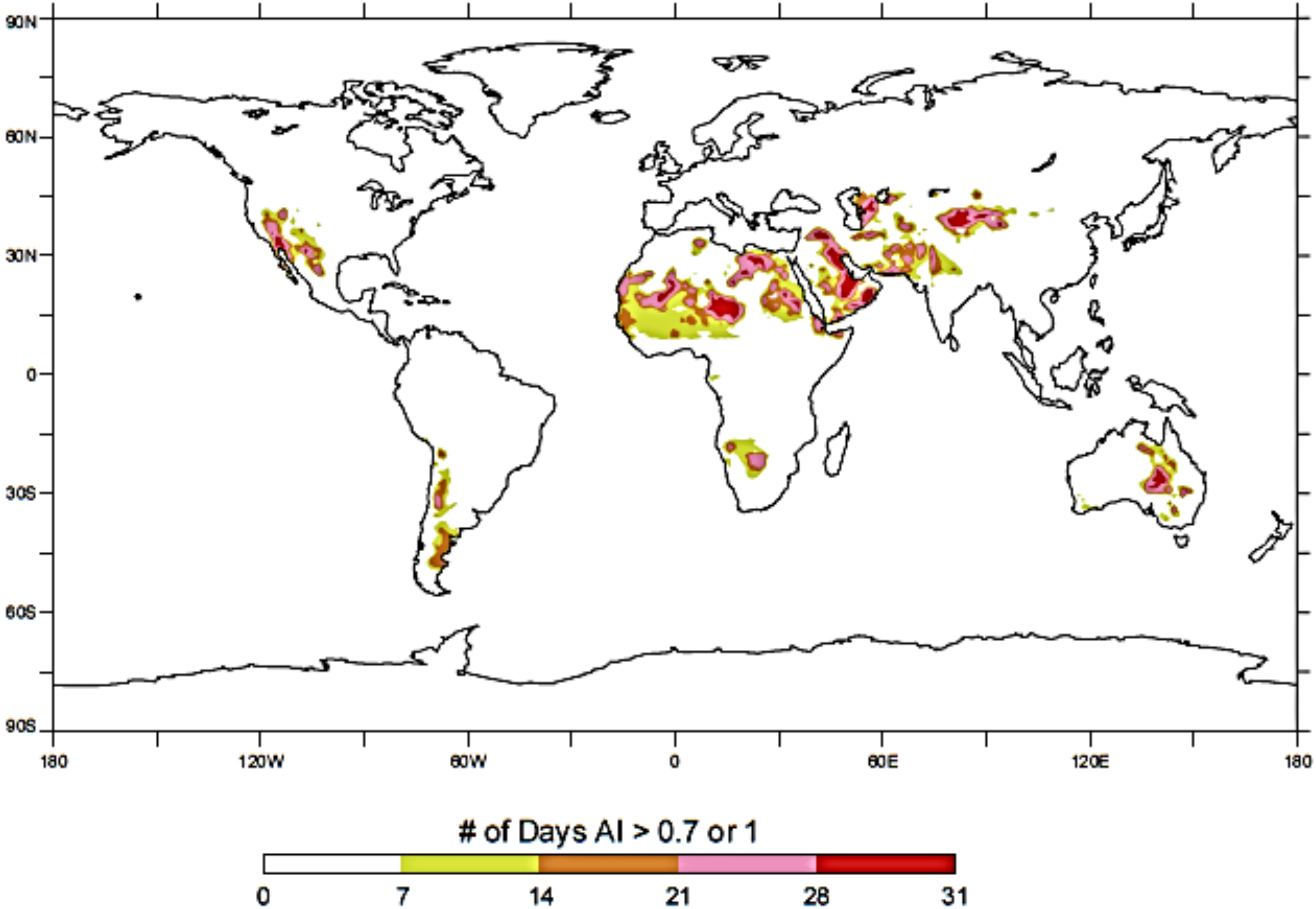

FIGURE 12 Global distribution of TOMS dust sources. This is a composite of selected monthly mean TOMS AAI frequency of occurrence distributions for specific regions using those months that best illustrate the configuration of specific dust sources. The distributions were computed using a threshold of 1.0 in the "global dust belt" (west African Saharan coast, through the Middle East, and central Asia to the Yellow Sea), and 0.7 elsewhere. After Prospero et al. (2002), with kind permission of the first author.

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FIGURE 14 Orbital image of the Aral Sea area taken on June 30, 2001, from Space Station Alpha (Earth Sciences and Image Analysis Laboratory, Johnson Space Center). A major dust storm can be seen, driven by strong westerly winds. The sharp northern margin of the dust pall coincides with the Syr Darya River. This is beyond the area of exposed sea floor sediments, where soil moisture and vegetation cover impede deflation.

Dust storms – frequency

a) number of days that visibility is < 1 km

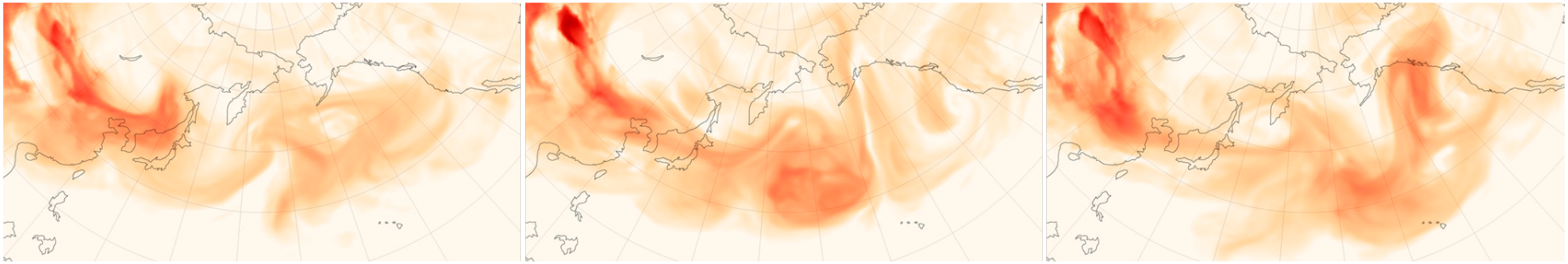
b) For example:

   i) Southwest Asia 80/year;

   ii) Hexi corridor

   iii) North Africa ~30/year

   iv) Australia > 15/year



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Watch aerosol distribution here: http://earthobservatory.nasa.gov/Features/Aerosols/images/aerosol_ortho_200907_h264.mov

Dust and Pathology

Inhalation – deposition in the lungs – irritation to exposed parts of the body

a) particle size (Figure 3)
b) composition

- Large particles - cough them out (usually)
- < 10 μm - may become trapped
- < 5 μm - can penetrate deeply and cause silicosis, asbestosis, etc. depending on composition

(Many Chinese post-mortem cases dust < 3μm. Also denser dust higher chronic respiratory disease.)(e.g. The Olympics & Smog)

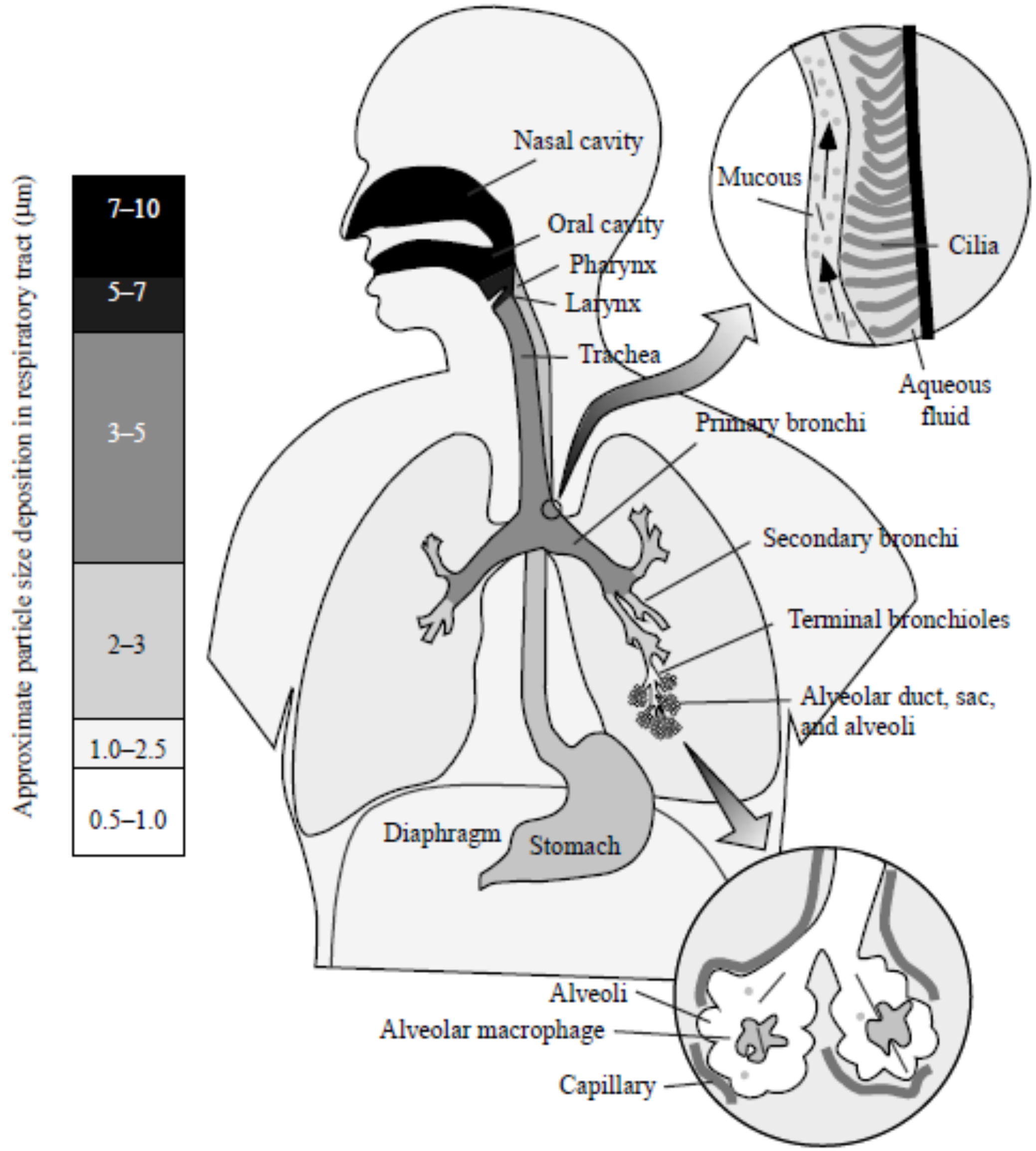

Figure 3 A schematic diagram of the respiratory system shows the fractionation of particle sizes that occurs with progressive depth in the system (after Newman, 2001).

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blogs.dickinson.edu/

images.china.cn/

nytimes.com/

Pneumoconiosis

a) Chronic and prolonged exposure
- occupational dust – asbestos miners
- non-occupational – dust clouds, asbestos at Libby, Montana

Image credit Harry Rowed. National Film Board of Canada. Photothèque. Library and Archives Canada

www.mnn.com/

Pneumoconiosis

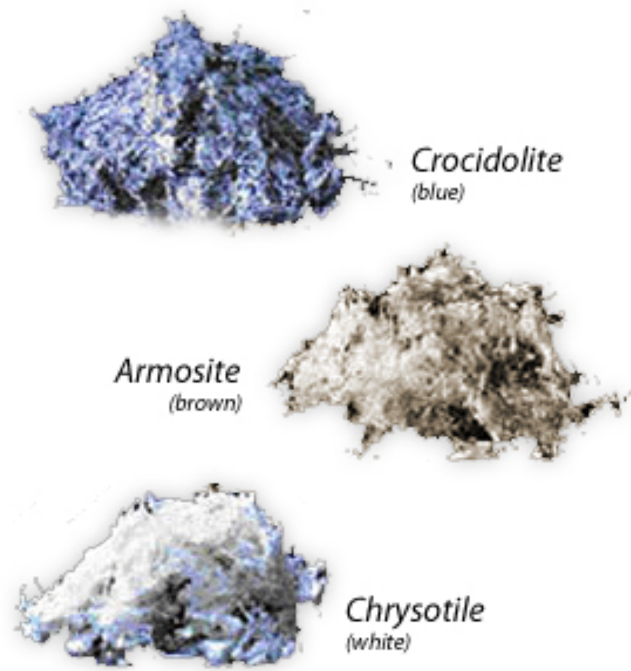
b) Results

- silicotic nodules – not easy to spot on Xray
- fibrosis – shadows in lungs
- some particles can degrade – dissolve, be incorporated beyond the lungs (earlier figures)
- increases risk of tuberculosis, pneumonia
- Desert Lung syndrome
  - even found in Egyptian mummies – many Bedouins have fibrosis – progressing with age (higher incidence in women)
  - High Himalayas – Ladakh – no mines or industry, but lots of dust ~40% of the people are over 50 years of age had silicosis (higher incidence in women)
  - mineral dust extracts from lungs, quartz and other minerals 54% silica, 19% Al

"You are what you breathe"

Asbestos

- amphiboles are usually the bad minerals (tremolite)
- in some cases, e.g. northern Corsica, cases of asbestosis (mesothelioma) found in ~4% of the people. The area is rich in serpentine, crysotile asbestos. The mountains to the south are a barrier to transport
- Libby, Montana: mined vermiculate used as an insulator was contaminated with tremolite-actinolite, People were 4 times more likely to have lung problems



www.adfa.org.au/

www.picsauditing.com/

Exposure Pathways

a) Respiratory
b) Gastrointestinal
c) Skin

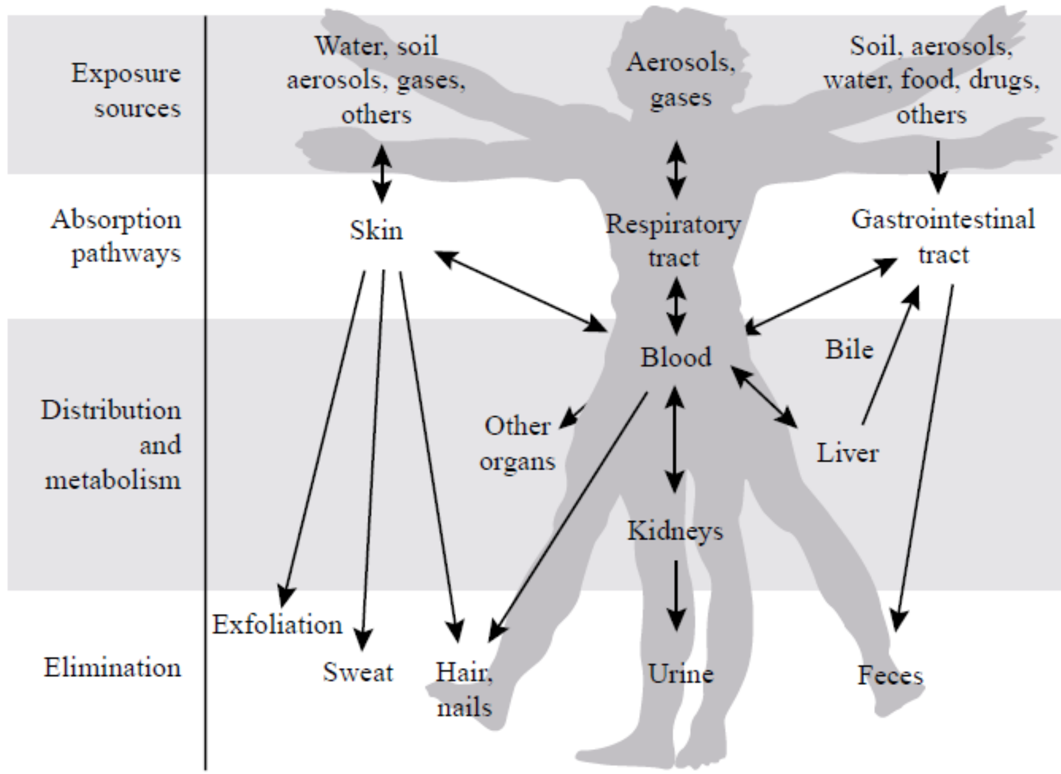


Figure 2 This schematic diagram shows the absorption pathways and systems of distribution, metabolism, and elimination for potential toxins. "Aerosols" include dusts, other solid particulates (such as smoke), and liquid droplets (such as fog, mists, etc.). Distribution may involve deposition of a toxin within a target organ and/or metabolism with or without excretion of the toxin by the target organ (after Goyer and Clarkson, 2001).

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How does dust hurt you?

Chronic Obstructive Pulmonary Disease

COPD, also called Chronic Obstructive Airways Disease (COAD), a blanket term for 'obstructive' lung conditions like bronchitis and emphysema. Reduces airflow out of the lungs. HSE estimates 15-20 per cent could be work-related.

Asthma

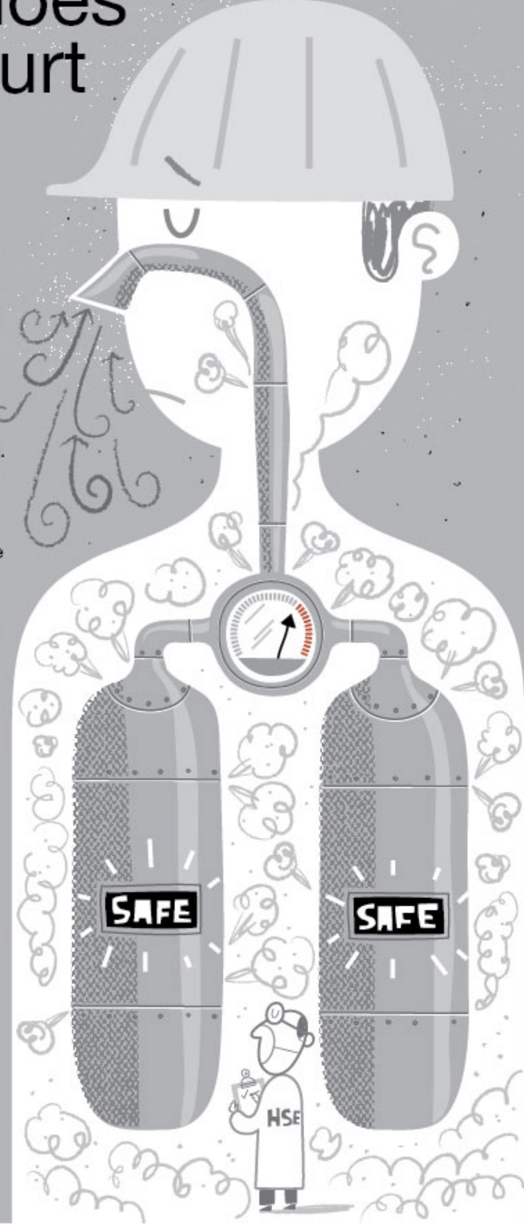
Another obstructive lung disease, linked to exposure to irritants or allergens ('sensitisers') at work. A reversible shortness of breath, between 15 and 20 per cent of all cases are work-related.

Extrinsic allergic alveolitis (EAA)

An allergic condition which affects workers exposed to biological dusts, causing conditions including farmers' lung and pigeon fanciers' lung.

Fibrosing alveolitis

Also known as pulmonary fibrosis, can be caused by some occupational dust exposures, for example work with cobalt or 'hard metals' in cutting tools. Related conditions, for example 'flock workers' lung' and 'popcorn lung' (Hazards 104), have been discovered recently.



Pneumoconiosis

A group of 'restrictive' lung diseases like silicosis, talcosis and asbestosis, where dust exposure causes debilitating lung scarring.

Cancers

Tumours, particularly of the lung and nose, are related to substances commonly encountered at work including asbestos, silica, chrome VI, nickel, cadmium and wood dust. These account for thousands of work-related deaths each year.

Heart disease

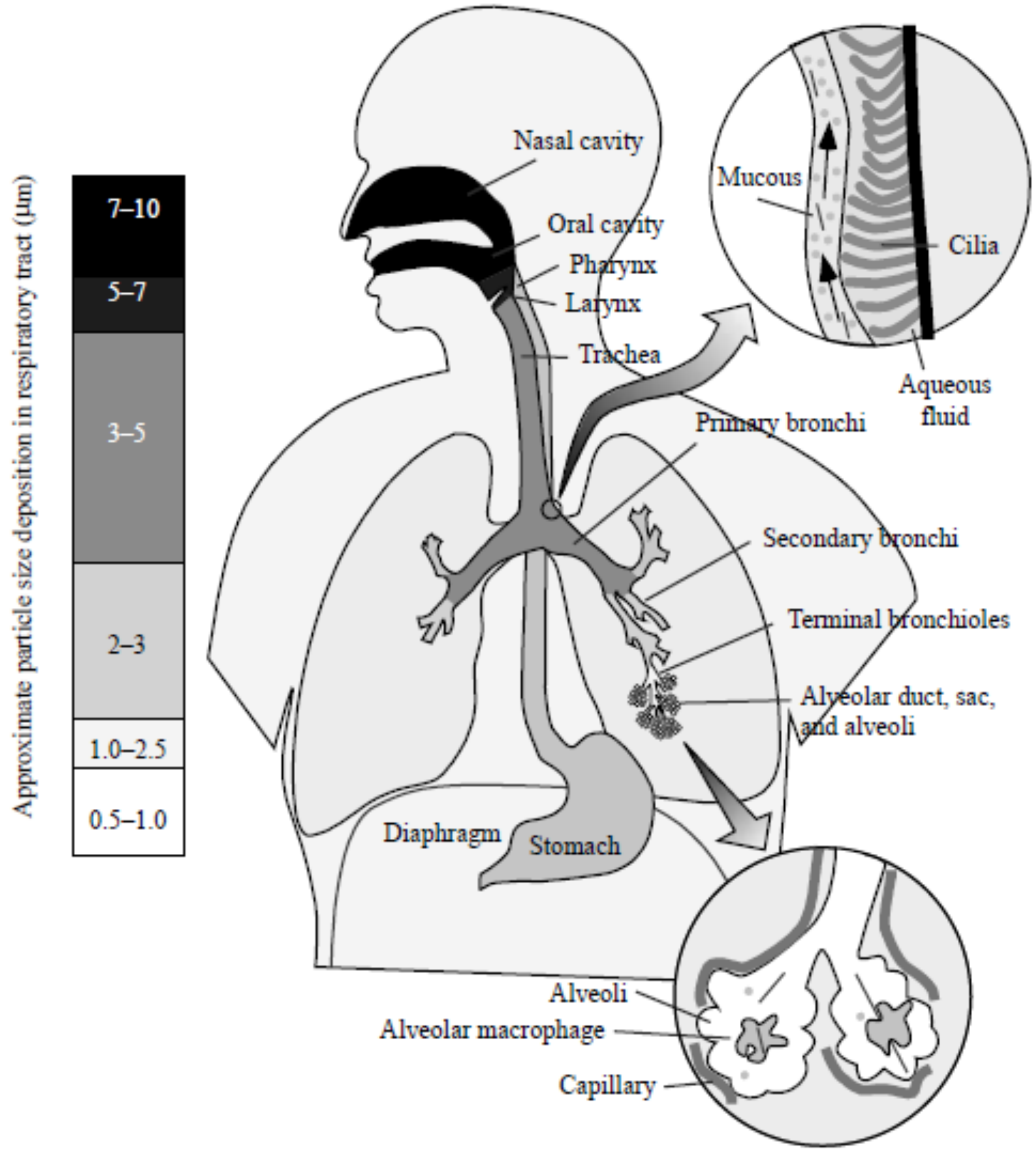
Dust-affected lungs put extra strain on the heart, which can lead to right-sided heart failure. Some occupational exposures, like hard metal dust, can cause potentially fatal conditions like cardiomyopathy.
Very fine dust particles cause inflammation of the heart and a higher risk of heart attacks.

Other problems

Exposure levels half the level allowable for most workplace dusts overwhelm the body's first line of defence, the 'mucociliary clearance' that filters out dust in the upper respiratory tract. This can leave the worker more vulnerable to infections and more susceptible to occupational lung disease. Lots of other dust-related conditions occur, some specific to particular exposures; beryllium is linked to sarcoidosis, chrome dust to chrome ulcers.

www.hazards.org/

- **Bioavailability:** defined as the fraction of an administered dose of a substance that is absorbed via an exposure route and reaches the blood stream.
- **Bioaccessibility:** of a substance is the fraction that can be dissolved by body fluids and therefore is available.
- **Biopersistance:** resistance to all clearance mechanisms
- **Biosolubility:** Extent to which elements/compounds are soluble in body fluids.
- **Bioreactivity:** extent to which an element/compound can modify key body fluid parameters such as pH, concentration of electrolytes and redox



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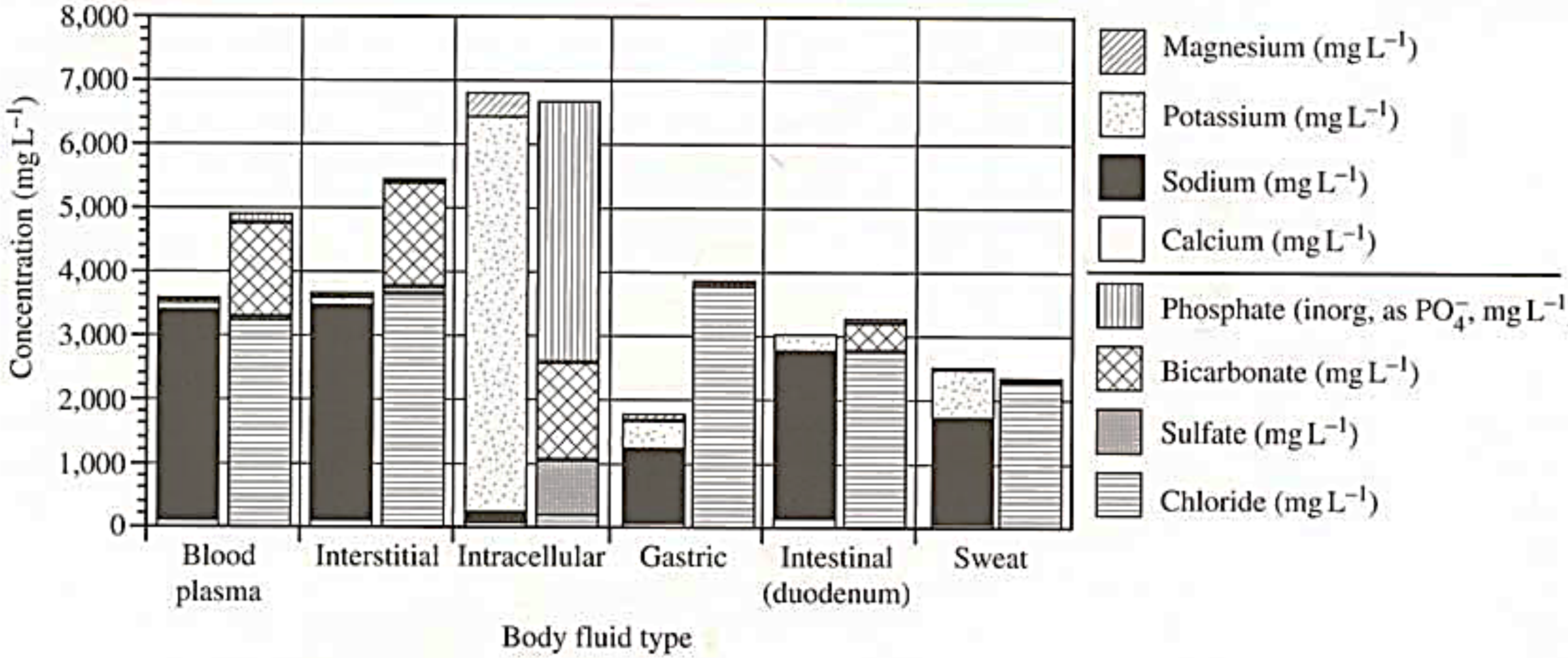

Figure 4 Concentrations of the major inorganic electrolyte species can vary substantially between the different body fluid types. These variations likely play an important role in the relative stability of a variety of minerals and earth material components in the body's different body fluid types. For a given fluid, cations are shown on the left, anions on the right.

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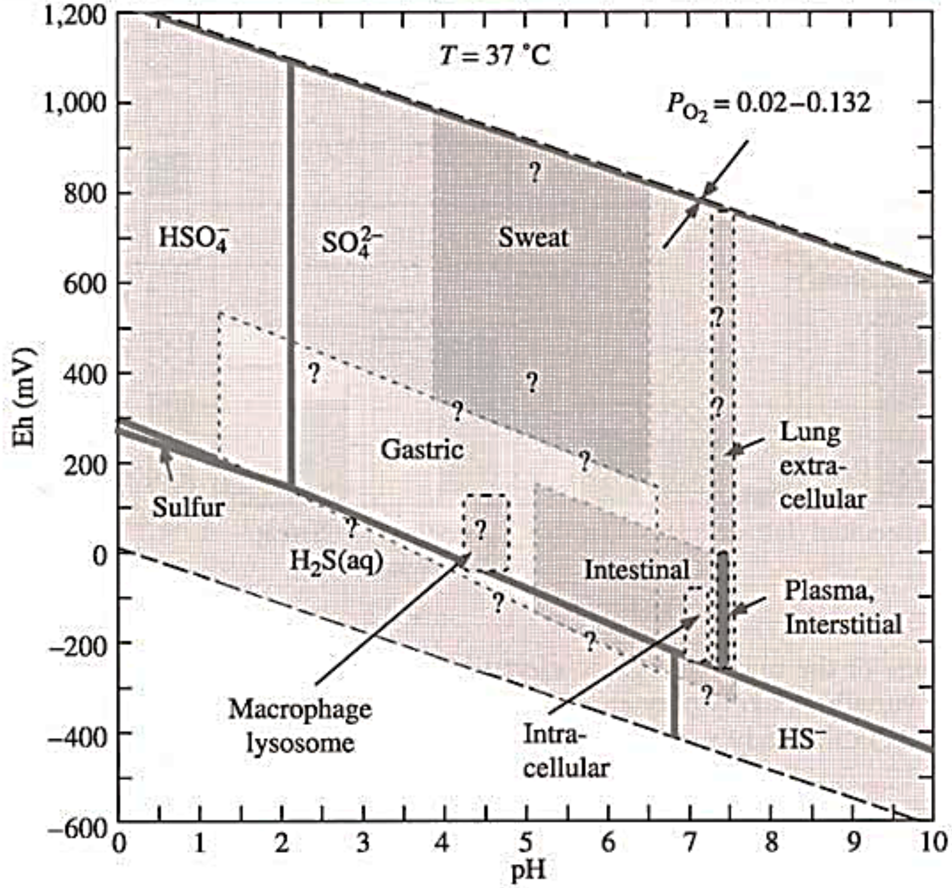

Figure 5 A plot showing variations in pH and speculated variations in Eh further illustrates the variability between different body fluid types. For comparison, the light gray area shows the Eh–pH stability field for water, the medium gray lines mark the stability fields of major inorganic sulfur species, and the darker gray line along the upper stability limit for water shows the range of Eh values in equilibrium with dissolved oxygen at arterial (upper edge of area) and venous (lower edge of area) oxygen pressures. The Eh ranges for the various body fluid types are highly speculative, and are postulated based on comparison to inferred Eh values for the plasma (black area) (see discussion in text). While there are indications that most body fluids have an overall Eh that is quite reduced and well out of equilibrium with dissolved oxygen in the plasma, there are substantial uncertainties in the extent to which the different potential redox couples in the body fluids reach equilibrium with each other and, especially in the case of sweat and lung fluids, dissolved oxygen.

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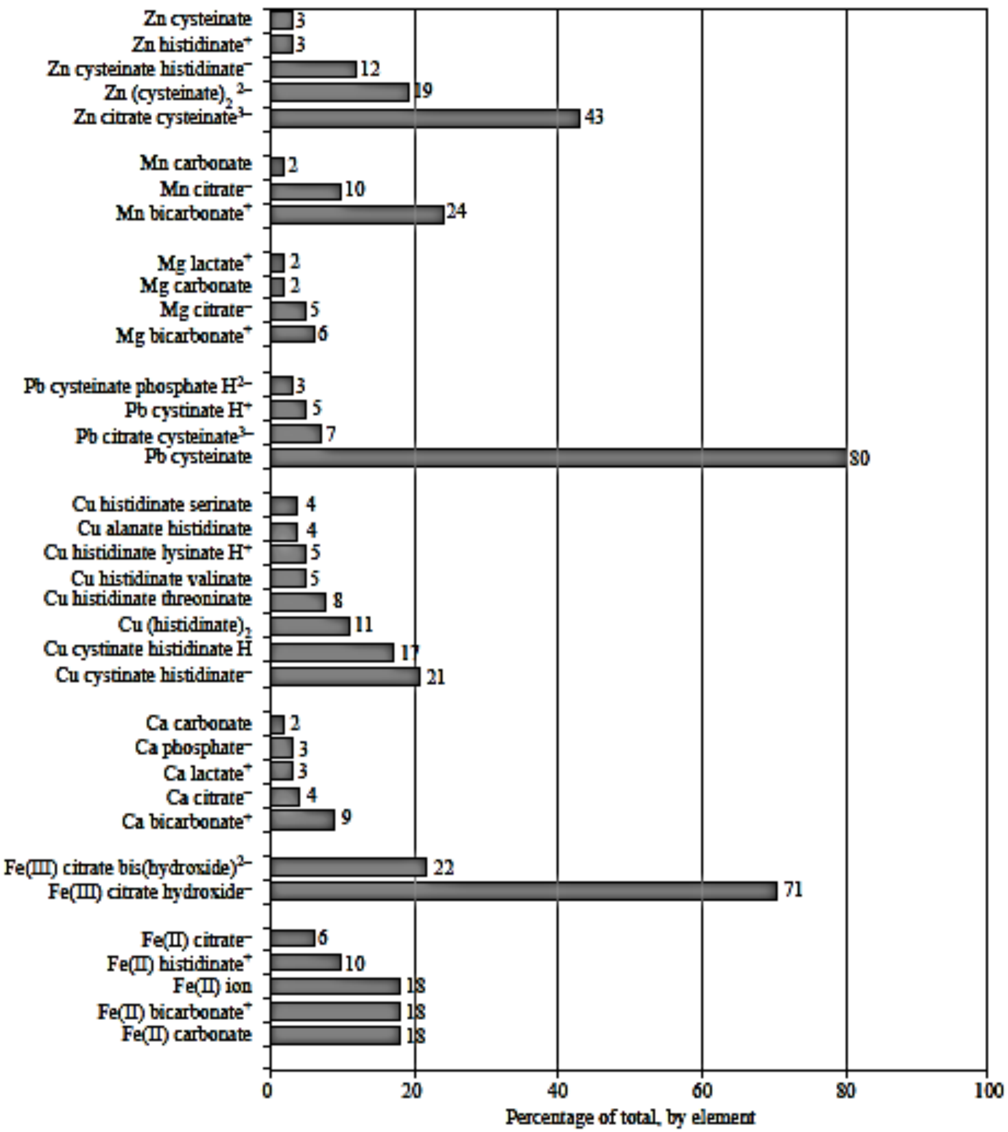

Figure 6 Chemical speciation calculations have been used (May *et al.*, 1977; May and Williams, 1980) to estimate the dominant low-molecular-weight organic and inorganic complexes for various metals in the plasma. The results show that each metal can be complexed by a unique set of ligands. Results of such speciation calculations can be used to infer the important chemical complexes and complexing ligands in other body fluids such as extracellular fluids.

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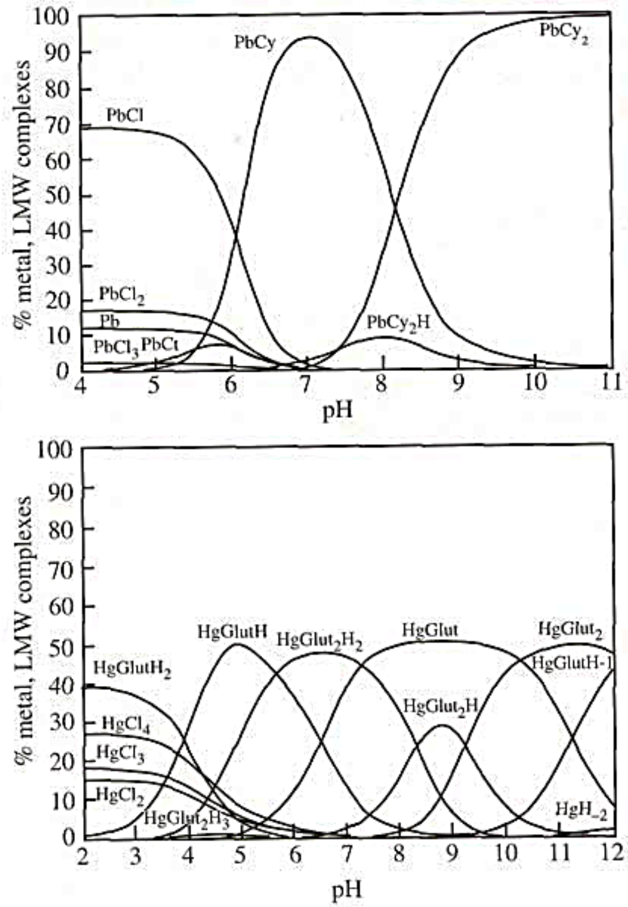

Figure 7 Letkeman (1996) used chemical speciation calculations to estimate the major complexes for lead and mercury as a function of pH in a fluid having overall plasma composition. The results show that most metal complexes with low-molecular-weight organic ligands such as amino acids diminish in importance with decreasing pH (such as in the gastric fluids) due to the increased protonation of the organic ligands. Cl—chloride; Cy—cysteinate; Ct—citrate; Glut—glutathione (reproduced by permission of the Division of Chemical Education Inc. from *J. Chem. Educat.* **1996**, *73(2)*, 165–170).

From Plumlee and Ziegler (2005) *in* Vol. 9 *Treatise on Geochemistry*

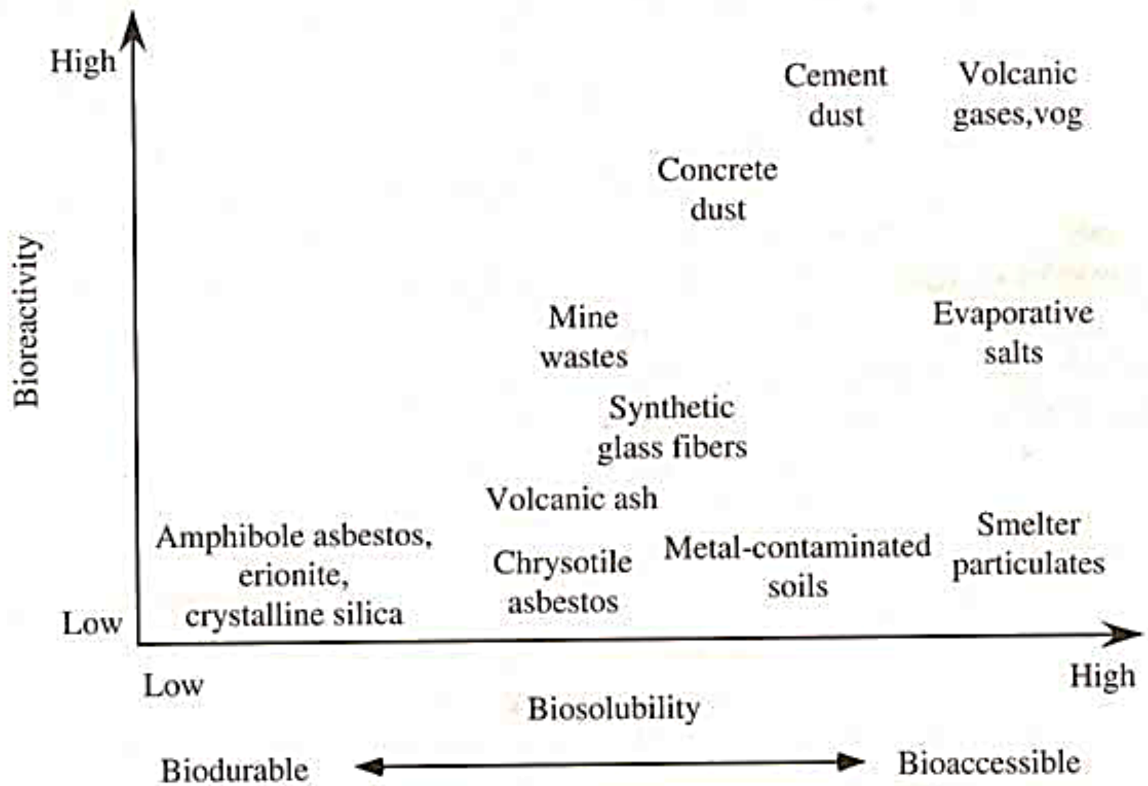

Figure 8 This schematic plot shows the inferred biosolubility and bioreactivity of general classes of earth materials. Many types of earth materials (i.e., mine wastes, volcanic ash, soils) can contain a complex variety of minerals having quite different biosolubilities and bioreactivities, so the particular location of a given earth material on the plot should be considered as an averaged approximation.

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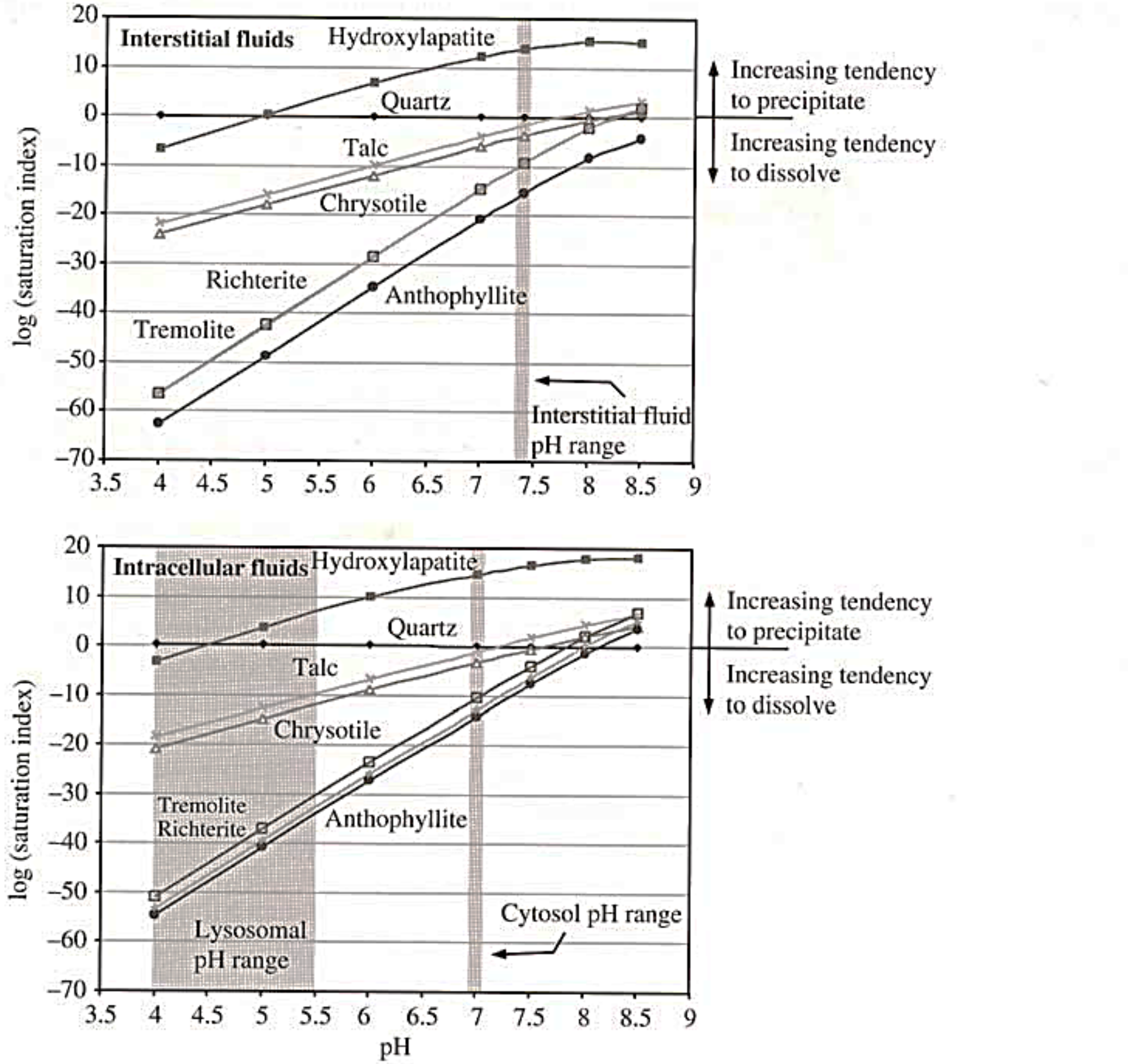

Figure 9 Plots showing the calculated mineral saturation indices as a function of pH for hydroxylapatite, quartz, and various asbestos-forming minerals in electrolyte solutions approximating the electrolyte compositions of lung fluids (approximated by interstitial fluids, upper plot) and intracellular fluids (lower plot). Electrolyte concentrations used as input were taken from Table 4. The CO_2 partial pressure was fixed at the value for venous plasma for each speciation at a different pH. Organic species such as amino acids and other organic acids were not included in the calculations, but likely would have the effect of decreasing the calculated saturation indices somewhat due to their complexation with cations.

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Increasing bioaccessibility →

Encapsulation	Encapsulation by insoluble minerals (i.e., quartz)		Encapsulation by somewhat soluble minerals (i.e., Fe-oxides)		Encapsulation by soluble minerals (i.e., Fe-sulfates)
Trace elements	Low concentrations in mineral		Moderate concentrations in mineral		High concentrations in mineral
Crystal morphology	Equant, blocky, prismatic (large crystal faces)		Massive (no crystal faces)	Botryoidal	Colloform, framboidal
Grain size	Coarse grained (cm)		Medium grained (10's mm–cm)		Fine grained (µm–mm)
Mineralogy Silicates	Quartz K-feldspar Muscovite	Na-feldspar, Amphiboles, Pyroxenes, Calc-silicates	Ca-feldspar, Serpentine, Chrysotile, Olivine Volcanic glass, Slag		
Sulfides		HgS, MoS_2	Cu_3AsS_4, $CuFeS_2$ Cu_5FeS_4, FeAsS, FeS_2 (Pyrite, Marcasite)	ZnS, PbS, As-sulfides FeS, Cu2S	
Phosphates			Pb-, Ca- ,Ca-As-phosphates		
Oxides. hydroxides			Fe-, Mn-, Al-oxides, hydroxides	Pb-As-, Mn-As-, Fe-As-, oxides	PbO As2O3 Ca-, Mg-oxides, hydroxides
Carbonates			$MgCO_3$	Mn-, Fe-Carbonates	Pb-, Ca-, Zn-, Cu-, Cd-, Ni-, Ba-Carbonates; Na-bicarbonates
Sulfates			Jarosite, Fe-, Al- hydroxy-sulfates	$PbSO_4$ some Cu sulfates	Na-, Ca-, Mg-, Fe(II, III)-, Zn-, Ni-, some Cu- sulfates
Others			Au°, Pt°	Pb° Ag° Fe°	Na-,K-Chlorides; Nitrates

Increasing bioaccessibility →

Figure 10 Influence of mineral type, crystal morphology, grain size, degree of encapsulation, and trace element content on bioaccessibility. Differences in bioaccessibility between different mineral types should be considered as qualitative, and may vary depending upon the chemistry of the surrounding fluids. For example, sulfides are all substantially much more bioaccessible under oxidizing conditions than reducing conditions. Similarly, carbonates are much more bioaccessible under acidic than alkaline conditions (sources Ruby *et al.*, 1999; Plumlee, 1999; Nordstrom and Alpers, 1999).

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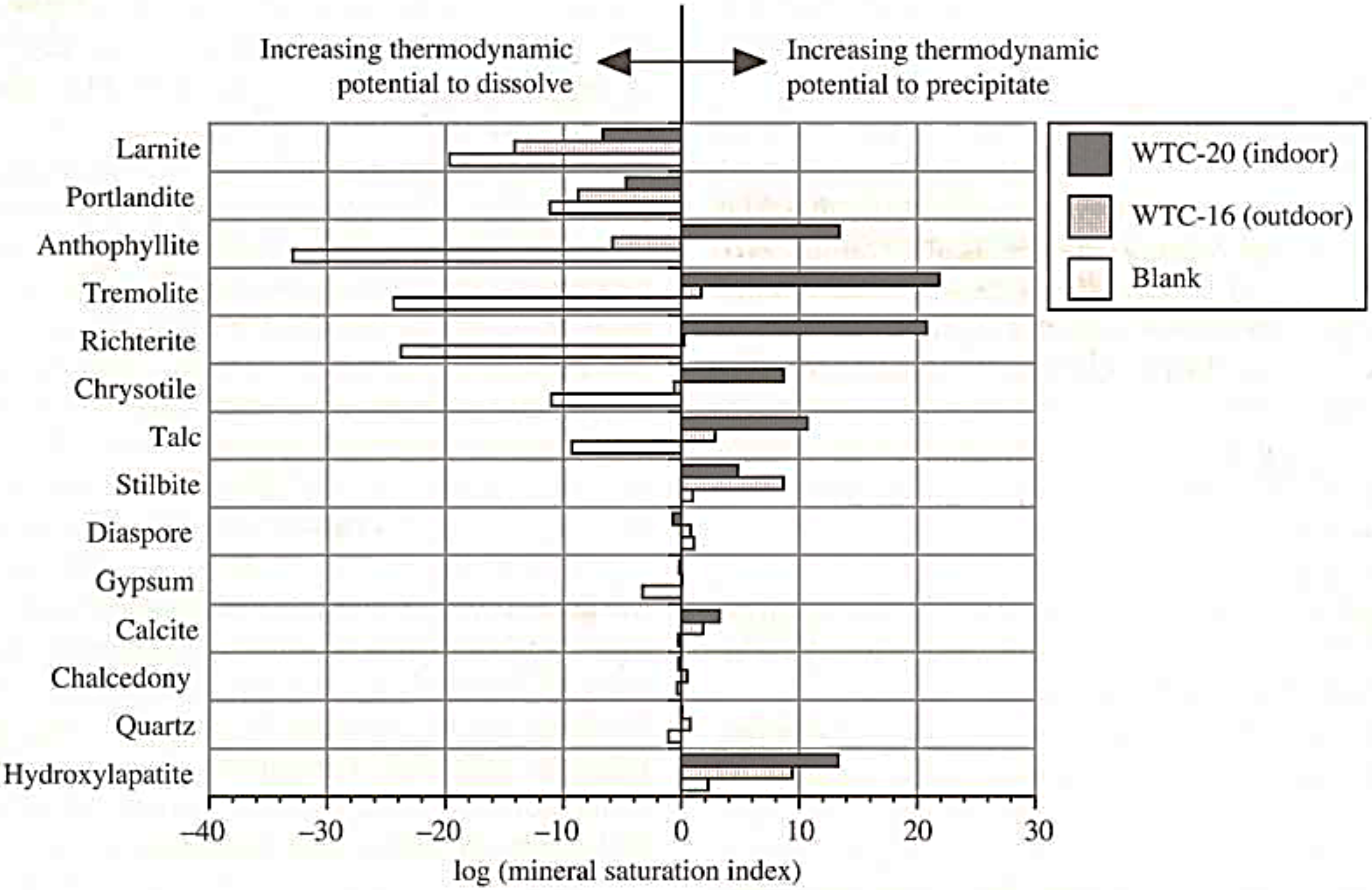

Figure 12 Plot comparing calculated saturation indices of various minerals of interest in SLF blank, and filtered (<0.45 μm) SLF leachates of an indoor WTC dust sample (WTC-20) and outdoor WTC dust sample (WTC-16). The extreme supersaturations in the WTC dust leachate samples may result in part (but not entirely) from inclusion of some colloidal material less than 0.45 μm in size in the analyzed filtrate.

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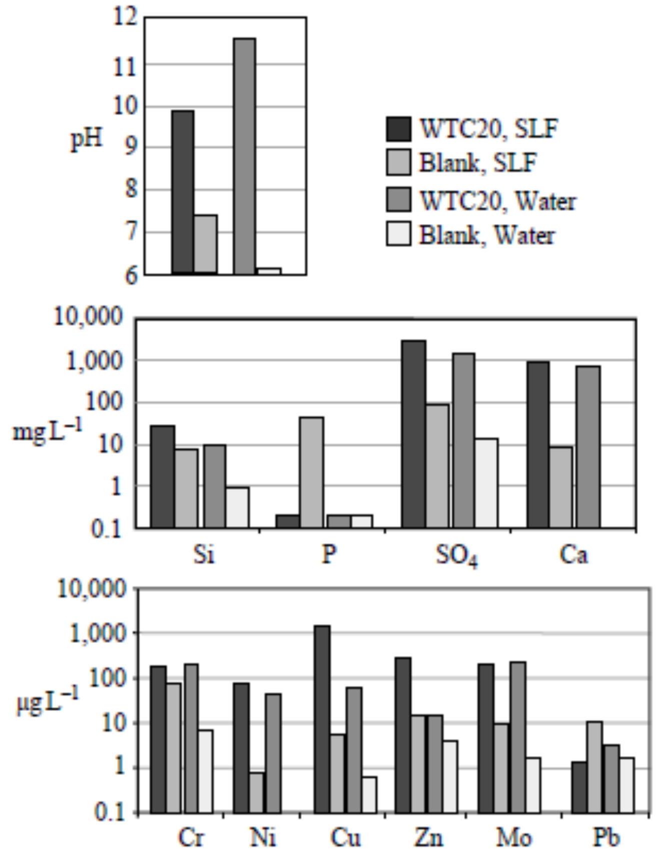

Figure 11 Plots comparing results of water and SLF leach tests performed on settled dusts generated by the WTC collapse. One part dust is added to 20 parts water or SLF at 37 °C and mixed for 24 h, with the leachate filtered (<0.45 μm) and analyzed. The composition of the SLF used in the extraction is a variation on the recipe provided by Bauer *et al.* (1997): pH 7.4; Na—150.7 mM; Ca—0.197 mM; NH_4—10 mM; Cl—126.4 mM; SO_4—0.5 mM; HCO_3—27 mM; HPO_4—1.2 mM; Glycine—5.99 mM; Citrate—0.2 mM. Other metals shown in the SLF blank were contributed as trace constituents of the various chemical reagents used to make up the fluids.

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