VORLESUNG
GEOMEDIZIN

im Wintersemester 2007 / 2008

Dr. Christian Gruber und Dr. Peter Schatzl
Montag von 18.30 bis 20.00 Uhr

Blauer Hörsaal (HS 402),
Naturwissenschaftlichen Fakultät,
Universität Salzburg

Fächerübergreifende Lehre / Wahlfach

www.medint.at

10-08-13
Today’s Menu:

• **Megacities**: Urban hotspots across the globe; facts and figures

• **Aerosols**: Definition, Properties and Characteristics;

• **Exposure**: Anatomy, Respiration, Modeling, Clearance;

• **Conclusion**: take home message

About myself:

• electronics engineer

• MSc in ecology

• PhD student

• part time service technician

Dep. of Material Science, Faculty of Natural Sciences
Urban Hotspots
A Megacity is usually defined as a recognized metropolitan area with a total population in excess of 10 million people. Some definitions also set a minimum level for population density (at least 2,000 persons/square km). A megacity can be a single metropolitan area or two or more metropolitan areas that converge upon one another. The term megacity is also sometimes used to describe cities with more than 20 million people.


Chemical composition & optical properties of Megacity Aerosols in Paris/Beijing/Cairo: A comparative study

Megacities (2/8)

Paris (FRA)

Location: Europe
Level of Development: High
Climatic Domain: Oceanic (temperate)
Altitude (above SL): 40 m
Population (UN, 2000): 11.9 E6

Analysis of Air-Samples: Particle fraction with a Diameter of 2.5 μm: PM2.5 approx. 15 μg/m³

Sources:
- Traffic
- Condensation of semivolatile material
- Photochemical processes

Chemical composition & optical properties of Megacity Aerosols in Paris/Beijing/Cairo: A comparative study
Megacities (3/8)

Beijing (CHN)

Location: Asia
Level of Development: Medium
Climatic Domain: Continental
(cold winters; hot & humid summers)
Altitude (above SL): 54 m
Population (UN, 2000): 10.8 · E6

Analysis of Air-Samples: Particle fraction with a Diameter of 2.5μm: PM$_{2.5}$ approx. 80μg/m$^3$

Sources:
- Traffic
- Industries / domestic (coal)
- Condensation of semivolatile material
- Photochemical processes
- Dust storms

Source: O. Favez et al., EAC 2007


Chemical composition & optical properties of Megacity Aerosols in Paris/Beijing/Cairo: A comparative study
Megacities (4/8)

Beijing (CHN)

Analysis of Air-Samples: Particle fraction with a Diameter of 2.5 micrometer

Summer Dust Storms:

- 06\textsuperscript{th} Aug 2007: SWerly winds are loaded with desert sand.
- 07\textsuperscript{th} Aug 2007
- 08\textsuperscript{th} Aug 2007: Hygroscopic particle growth impairs visibility
- 09\textsuperscript{th} Aug 2007
- 10\textsuperscript{th} Aug 2007

Source: Courtesy of M.H. Pertuisot

Source: Favez et al., EAC 2007

Source: O. FAVEZ\textsuperscript{1}, J. SCIARE\textsuperscript{3}, H. CACHIER\textsuperscript{1},M. ABDELWAHAB\textsuperscript{2}, T. YU\textsuperscript{3}, L. MARTINON\textsuperscript{4}, O. D’ARGOUGES \textsuperscript{1}, K. OIKONOMOU\textsuperscript{1}, R. SARDA-ESTEVE\textsuperscript{3}

Chemical composition & optical properties of Megacity Aerosols in Paris/Beijing/Cairo: A comparative study
Megacities (5/8)

Cairo (EGY)

Location: Africa
Level of Development: Low
Climatic Domain: Semi-arid (hot & dry)
Altitude (above SL): 23 m
Population (UN, 2000): 10.6 · E^6

Analysis of Air-Samples: Particle fraction with a Diameter of 2.5μm: PM$_{2.5}$ approx. 80μg/m$^3$

Sources:
• Traffic
• Vegetative & trash burning
• Photochemical processes
• Industries
• Dust storms

Chemical composition & optical properties of Megacity Aerosols in Paris/Beijing/Cairo: A comparative study
Megacities (6/8)

Cairo (EGY)

Dust storms are of frequent occurrence in winter and summer:

- 2004/01/22 – 16:28
- 2004/01/23 – 16:36

Source: O. Favez et al., EAC 2007

CairoCity image: http://www.wunderground.com/data/wximagemew/n/Nefertiti/0.jpg
**Megacities (7/8)**

**Mexico City (MEX)**

Location: N-America  
Level of Development: Medium  
Climatic Domain: Oceanic (mild)  
Altitude (above SL): 2241 m  
Population (UN, 2000): 18.1 · E⁶

Analysis of Air-Samples: Particle fraction with a Diameter of 2.5μm: PM₂.₅ approx. 59μg/m³

Sources:
- Traffic
- Condensation of semivolatile material
- Industries
- Photochemical processes

Source: Chow et al., EAC 2001

Particles and the Human Respiratory System: The ideal gate for the penetration of air contaminants is the lung. Because of its small size, Fine Particle Matter (<PM$_{2.5}$) can be deposited deep into the lungs, where it can cause health problems and is known to alter lung functions [1]. NO$_X$ and SO$_2$ are also major sources of fine PM. Recent studies have shown an association between PM and premature mortality from respiratory and cardiovascular disease, and increased incidence of respiratory illness, particularly in children and the elderly. For adults with heart or lung conditions, exposure to fine PM can cause more illness and in some cases premature death. More than 90% of the particulates found in diesel exhaust are fine particles.


O. FAVEZ, J. SCIARE, H. CACHIER, M. ABDELWAHAB, T. YU, L. MARTINON, O. D'ARGOUGES, K. OKONOMOU, R. SARDA-ESTEVE

CairoCity image: http://www.wunderground.com/data/wximagew/new/Nefertiti/6.jpg
Aerosols – Patterns & Properties
Aerosol (1/2)

Aerosols
(from Gk: aer, air & sol, fluid)

Are colloids in which liquid or solid particles are suspended;

Size: Comparison b/w
• sand vs. boulder correlates with
• exhaust particle vs. dust

Using the boulder–sand relationship one can estimate the orders of magnitude aerosols can cover;

http://www.ica1.uni-stuttgart.de/~hans/sand.html
http://www1.istockphoto.com/file_thumbview_approve/240969/2/istockphoto_240969_sand_grain.jpg
Aerosol (2/2)

An aerosol is an assembly of liquid or solid particles suspended in a gaseous medium long enough to enable observation or measurement. Generally, the sizes of aerosols are in the range from 0.001 to 100 μm.

There is no such thing as a strict category; there is a continuum of one size class to the next.

Aerosol: an assembly of liquid or solid particles suspended in a gaseous medium long enough to enable observation or measurement. Generally, the sizes of aerosols are in the range from 0.001 to 100 μm. **Definition:** Der Begriff wurde von Gibbs (1924) geprägt; er definierte es als zeitlich relativ konstante Suspension von festen oder flüssigen Teilchen in einem gas(förmigen) Medium. **Particle:** small discrete objects - **Particulate:** a particle.

**Dust:** solid particles formed by crushing or other mechanical breakage of a parent material. These particles generally have irregular shapes and are typically around 0.5 μm.

**Fog & mist:** liquid aerosol particle of 10 μm – 100 μm ion diameter.

**Fume:** particles that are usually the result of vapour condensation with subsequent agglomeration usually <0.05 μm.

**Smog:** an aerosol consisting of solid and liquid particles, created at least in part, by the action of sunlight or vapour, thus <2 mm.

**Smoke:** a solid or liquid aerosol, the result of incomplete combustion or condensation of supersaturated vapour; typically <1 mm.

**Nature of Aerosols:**

**Natural sources:** soil and rock debris, forest fires, sea salt, volcanic debris, biogenic (pollen, viruses, bacteria, etc.). Meteorologically speaking, invisible particles (<400 nm) act as surfaces onto which water vapor can condense, which is an important function in the formation of clouds and fog. Interestingly only 0-4% of the lower troposphere is water (compared to 78% N₂ and 21% O₂), however, this amount coupled with the even lower percentage of aerosol accounts for the rain we get! **Blue Mountains:** The sky is blue because the air in the atmosphere scatters blue light. If the sky was not blue we would be looking out into space and we would see the deep black of space (just as on the moon). When we look at a distant object such as a mountain range we can also see the blue light scattered in the air. This is what gives distant mountains their blue colour. When you can see rows of ranges you will notice the further away the more blue the mountains appear. This is due to the furtherest mountains being viewed through a “thicker” atmospheric stratum, resulting in more scattered blue light.

**Anthropogenic sources:** fuel combustion and industrial processes, industrial processes fugitive emissions, non-industrial fugitive emissions, transportation, etc.

Source: Lutgens & Tarbuck, 1998; p.7
Cunningham & Cunningham, 2003; p.371
http://www.zwei-m.ch/images/brandung.jpg
http://optics.kulgun.net/Blue-Mountains/
Although visible dust sometimes clouds the sky, dust is relatively large and too heavy to stay in air for very long. Still many particles are microscopic and remain suspended for considerable periods of time.

Grössenvergleich von Beispielobjekten, vom Niesaerosol, zum menschlichen Haar, über Pollen, Pilzsporen, Bakterien, Dieselruss bis hinunter zu den Viren.

Die horizontale Achse des zentral abgebildeten Diagramms stellt die Größenskala eines Aerosols dar (1nm bis 10mm). Auf der vertikalen Achse ist die Absetzgeschwindigkeit des jeweiligen Aerosols aufgetragen (100nm/s bis 10m/s). Im obrigen Teil befindet sich auch eine Grobklassifizierung des dargestellten Spektrums in dem auch das kleine Band des „sichtbaren Lichts“ abgebildet ist.

**RAIN:** Formation of rain starts about the size of 200nm (condensation nuclei), while typical cloud droplets are 20 μm in size,

Whereas the typical raindrop is 2mm in size,
Aerosol Inventory cont’d (2/8)

Comparison of Size Classes

Source: Madl, 2003
Aerosol Inventory cont’d (3/8)

Comparison of Size Classes

Source: Madl, 2003
Aerosol Inventory cont’d (4/8)

Comparison of Size Classes

Source: Madl, 2003
Aerosol Inventory cont’d (5/8)

Comparison of Size Classes

Source: Madl, 2003
Aerosol Inventory cont’d (6/8)

Comparison of Size Classes

Source: Madl, 2003

10-08-13 Madl
Comparison of Size Classes

Source: Madl, 2003
Aerosol Inventory cont’d (8/8)

Comparison of Size Classes

Source: Madl, 2003
EPAs use mass (PM) rather than number (PN). Why Number instead of Mass?

… obviously ….
• a large object (like a basketball)
• compared with a light object (stack of pin-pong-balls)

… is dominated by the mass of the larger object;

Ergo: the reference (here mass) is totally inappropriate for tiny particles!

Why do we use this system?
• Gravimetric determination fails under a certain threshold value – EPA’s usually measure PM10, PM2.5 and eventually PM1; (PM = Particle Mass); PM totally ignores the numeric abundance of the lighter counterparts;
• Mass is a misleading parameter as number concentration act much more thoroughly than mass;

Example: comparing the mass of 100 table-tennis balls to that of 1 baseball, it becomes obvious that the baseball dominates by mass units, while the table-tennis balls dominate by their number;

Hence the particle in its nucleation mode exerts a far deeper action onto the respiratory organ than a particle cluster in accumulation mode or even in coarse mode;

Why particle Number instead of Mass?

\[ m_p = \rho_p \frac{\pi}{6} d_p^3 \]

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Source: Morawska, 2003;
Exhaust fumes (samples taken with a Tedlar bag):

- Diesel w/o cat

Source: Madl 2005
Exhaust fumes (samples taken with a Tedlar bag):

- Diesel w/o cat
- Petrol w/o cat

Source: Madl 2005
Exhaust fumes (samples taken with a Tedlar bag):

- Diesel w/o cat
- Petrol w/o cat
- Diesel w/ cat

Source: Madl 2005
Exhaust fumes (samples taken with a Tedlar bag):

- Diesel w/o cat
- Petrol w/o cat
- Diesel w/o cat
- ETS

Source: Madl 2005
Petrol-Diesel-ETS cont’d (5/7)

Exhaust fumes
(samples taken w/ Tedlar bag, normalized to 100 \cdot E/cm^3):

• Diesel w/o cat
• Petrol w/o cat
• Diesel w/o cat
• ETS-filter & w/o

Source: Madl 2007
Exhaust fumes of “dirty” combustions processes generate a broad polydisperse particle size spectrum, favouring the agglomeration of smaller particle fractions of the nucleation regime onto the forming cluster;

So-called cleaned exhaust fumes (using catalytic converters and/or filters) lack
- the necessary concentration of larger particle fraction onto which the smaller can condense onto;
- lack the time required to form larger aggregates before leaving the exhaust system;

Source: Morawska, 2003;
The sulfur content in fuel acts as a “binder” to glue the smaller fraction onto the agglomerating particle cluster;

Source: Grimm, 2004;
Here, the high particle load in the nucleation mode becomes strikingly evident – this sample of air is the characteristic cocktail of highway related air-exhaust mixture – especially when trapped in-between sound-absorbing protective-walls or tunnels;

Source: & Heinzlmann, 2006
Petrol-Diesel exhaust (2/2)

Automotive combustion exhaust

• Micrograph of petrol (left)

• Agglomerate of soot (right)

Source: Morawska 2003

Size - determines, in part, the lung deposition
Solubility:
soluble particles - generally have low or no lung toxicity
  can have systemic toxicity
insoluble particles – more likely to be toxic
  exhibit a wide range of toxicities
  dependent on other particle characteristics

Source: Morawska, 2003
Comparative diameters of particles involved in condensation and precipitation processes.

The collision-coalescence process: most cloud droplets are so small that the motion of the air keeps them suspended. Because large cloud droplets fall more rapidly than smaller droplets, they are able to sweep up the smaller ones in their path and grow.

Source: Lutgens & Tarbuk, 1998, p.115 & 118
Nuclei and accumulation modes contain two types of particles: (a) “less volatile”, probably elemental carbon core with a small organic component; and (b) “more volatile”. The organic component of all particles is comprised predominantly of unburned lubricating oil.

**Diesel-Soot**: The hydrophobic matrix of aromates stuck together to form a loose mesh. Agglomeration is a continuous process, thus the growing cluster adds layer upon layer until a “diesel” sphere with about 0.35 nm is obtained. This “crystalline” structure of soot corresponds is a graphite-like structure[1]. As this process already takes place in the combustion chamber, the primary particles keep growing to a diameter of 20-30 nm (with a considerable part still between 10-80 nm[2]). The density of these primary particles is about 1.5 g/cm³, the density of the agglomerates is about 0.02 - 0.06 g/cm³, in the deposited soot cake it can add up to 0.4 g/cm³.

Particle growth cont’d (3/7)

Particle Kinetics - Diesel Fuel exhaust

• Physico-chemical reactivity due to incomplete combustion

The physical characteristics of soot are inert, odourless, and insoluble in water and in organic solutions. It is, however, a high adsorbent for hydrocarbons, aldehydes, oxygen-containing odour compounds and sulfur containing molecules. The SO$_4^{2-}$ fraction of diesel exhaust particles is composed primarily of the sulfuric acid (H$_2$SO$_4$) formed from the sulfur contained in the fuel and or the lubricating oil. It is generated when SO$_2$ is oxidized to sulfur trioxide (SO$_3$). Upon exposure with water vapor (likewise a by-product of the combustion process) it converts to H$_2$SO$_3$ and eventually to H$_2$SO$_4$ [1].

These H$_2$SO$_4$ particles adhere to the carbonaceous structure. Formation of H$_2$SO$_4$ is widely load-dependent; only a small amount is produced in low load conditions, while more of it occurs at high load operation conditions. As sulfur content in diesel has a detrimental effect on diesel fume purification, it is a major player in the negative health effects on humans of diesel exhaust.

Unfortunately, the sulfur content in the exhaust stream makes catalysts useless, as it interferes with the precious metals or oxides the catalyst is coated with[2].

To really deal with the particle problem, the sulfur in the fuel has to be gotten rid off at the refinery. Reducing sulfur content to 5 ppm or lower brings dramatic improvements, by eliminating the sulfur nanoparticles. Only then can the exhaust particle stream react with the metal-coated substrate of the catalysts to further oxide them while the solid fraction could be trapped in particle filters[3].

Change in the Count Median Mean (logarithmic average) as time passes in a smoke-loaded closed environment of an Australian pub;

Source: Morawska, 2003;
Particle growth cont’d (5/7)

NaCl-Chamber Experiment

Animation revealing the dynamics of an atomized NaCl-sample in a closed setting (hermetically sealed stainless steel tank) as time passes:

- Animation covers a time window of 140min;
- Duration of injection: 60secs
- Holding capacity of tank: 800L

Source: Madl & Kwasny, 2006;
Animation revealing the dynamics of an atomized NaCl-sample in a closed setting (hermetically sealed stainless steel tank) as time passes;

- Animation covers a time window of 140min;
- Duration of injection: 60secs
- Holding capacity of tank: 800L

Source: Madl & Kwasny, 2006;
Aerosol Kinetics – there are three main Modi:

- Nucleation mode
- Accumulation mode
- Coarse mode

Aerosols can be classified as primary and secondary. **Primary aerosols** are mainly of natural origin and have only slightly changed during the past century. **Secondary aerosols** on the other hand, are predominantly of anthropogenic origin. Aerosols released into the atmosphere are subject to physical and chemical interactions, change their size, number, and chemical composition. Particles tend to fall into three size classifications referred to as modes. There are three principle modes:

- Nucleation mode: recently emitted particles undergo condensation as long as these are warmer than ambient air or are freshly formed within the atmosphere by gas particle conversion.
- Accumulation mode: coagulation and condensation of smaller nuclei generate a pool of larger aerosols. A characteristic of an aging aerosol.
- Coarse mode: mechanically generated aerosols like soil dust, sea spray, volcanic ash, or even pollen, and many industrially generated fumes.

Source: Madl, 2003
Particles and the Human Respiratory System

The ideal gate for the penetration of air contaminants is the lung. Because of its small size, Fine Particle Matter (<PM$_{2.5}$) can be deposited deep into the lungs, where it can cause health problems and is known to alter lung functions [1]. NO$_X$ and SO$_2$ are also major sources of fine PM. Recent studies have shown an association between PM and premature mortality from respiratory and cardiovascular disease, and increased incidence of respiratory illness, particularly in children and the elderly. For adults with heart or lung conditions, exposure to fine PM can cause more illness and in some cases premature death. More than 90% of the particulates found in diesel exhaust are fine particles.

Thus AEROSOLS have access to tiny spaces, such as:

• Stomata of Leaves; e.g.
  *Arabidopsis thaliana* (thale cress or mouse-ear cress)
  *Acer pseudoplatanus* (maple leaf)
  passive ventilation
  by diffusion

Structures of a leaf. The epidermis is often covered with a waxy protective cuticle that helps prevent water loss from inside the leaf. Oxygen, carbon dioxide, and water enter and exit the leaf through pores (stomata) scattered mostly along the lower epidermis. The stomata are opened and closed by the contraction and expansion of surrounding guard cells. The vascular, or conducting, tissues are known as xylem and phloem; water and minerals travel up to the leaves from the roots through the xylem, and sugars made by photosynthesis are transported to other parts of the plant through the phloem. Photosynthesis occurs within the chloroplast-containing mesophyll layer.

**Stoma / stomata**: the minute opening bordered by guard cells in the epidermis of leaves and stems through which gases pass; shown here is the surface view of the lower epidermis of a *Eucalyptus globulus* leaf taken with a SEM, flanked by two guard cells.

Stomata sense environmental cues, like light, to open. These cues start a series of reactions that cause their guard cells to fill with water. Let’s follow a scenario where the sun is rising and a cotton plant is signaled to open its stomata:

1. Signal received: The blue light at dawn is the signal that is recognized by a receptor on the guard cell.
2. The receptor signals the H⁺-ATPases on the guard cell’s plasma membrane to start pumping protons (H⁺) out of the guard cell. This loss of positive charge creates a negative charge in the cell.
3. Potassium ions (K⁺) enter the guard cell through channels in the membrane, moving toward its more negative interior.
4. As the potassium ions accumulate in the guard cell, the osmotic pressure is lowered.
5. A lower osmotic pressure attracts water to enter the cell.
6. As water enters the guard cell, its hydrostatic pressure increases.
7. The pressure causes the shape of the guard cells to change and a pore is formed, allowing gas exchange.

When the stoma is open, the stomata allow gas exchange, mainly CO₂ for photosynthesis and H₂O, between the leaf and the atmosphere. During a drought stress the plant has to close their stomata to limit water loss. ABA is the main actor of this response. Therefore, as a result of the reduction of the transpiration stream, stomatal closure leads to an increase of leaf temperature that can be measured very sensitively and non invasively by Infrared
The Human Lung: 5 lobes
   2 left lobes - superior and inferior
   3 right lobes - superior, middle, and inferior

Lung compartments:
   Nasopharyngeal - anterior nares to larynx
   Tracheobronchial - begins at larynx, trachea, bronchi, bronchioles, terminal bronchioles
   Pulmonary - respiratory bronchioles, alveolar ducts, alveoli

Source: Menache, 2004
         Postlethwait & Hopkins, 1995;
Anatomy cont’d (3/3)

Lung Casts

3-dimensional reconstruction of a human lung out of CT-images;


As the heart requires some space, the left lung lobe is usually smaller than the right lobe. This results in an asymmetrical bifurcation angle between right and left main bronchus – the angle to the right lobe poses less restriction to the flow of air than the left angle, thereby favouring ventilation of the right lobe. Hence inhaled particles are predominantly deposited in the right pulmonary lobe.

Source: http://de.wikipedia.org/wiki/Lunge
Respiration & Circulatory System

- Lung ventilation is passive, via rib-cage muscle & diaphragm;

Respiratory volume

V_{Tidal} @ rest: 0.5L
RateBreathing: 15/min
Total V_{inhaled}: 7.5L/min

Source: Guyton & Hall, 1996

Ventilation Pattern can Affect Deposition:

Respiratory Rate (breaths/minute)
- increase respiratory rate
- increase air velocity in the conducting airways
- enhance impaction
- decrease sedimentation and diffusion

Tidal Volume (V_T) volume of air entering or leaving the lung in a single breath

Increased V_T results in deeper lung penetration by particles

Person with increase V_T will likely have a decreased respiratory rate. Thus, particles stay in lung longer making deposition more likely.

Source: Guyton & Hall, 1996
Respiration &
Circulatory System

The respiratory system branches out in approximately 25 generations, and ends into about 500 million alveoli. The air speed becomes shorter, and the retention times longer, which means, the deeper the gas molecules penetrates the lungs, the longer the air (incl. aerosols stay for deposition). [1]

Shown here is the normalized amount of air ex/inhaled per breath at two different levels of activity (resting and light exercise). The deeper the gas molecules penetrate the lung the slower they become as the overall surface area / volume increases non-linearly;

Source: Hecht, 1994;
Respiration & Circulatory System

- Volumetric
- Surface Area

Generation number on the abscissa (equivalent to depth level within the lung) versus overall volume:
Person is ~1.5 m tall and ~0.08 m³.
Skin is ~2 m², so person as a box is ~1 m² × 0.1 m thick.
Lung is ~100 m² and ~0.01 m³, so lung as a sheet is (~7 m)² × ~10⁻⁴ m thick.
Intestine is ~300 m² and ~0.01 m³, so intestine as a sheet is (~12 m)² x ~10⁻⁴ m thick

Source: http://www.vendian.org/envelope/dir2/lungsout.html
Mercer, Russel Crapo 1994; Alveolar septal structure in different species;
Plopper C.G., Harding R., Pinkerton K.E., 2004; The Lung: Development, Aging and The Environment;
The alveolar surface area available for gas exchange is enormous, approximately 100m² in an adult human, and represents the contribution of approximately; Page 55
Thus AEROSOLS have access to tiny spaces, such as:

- Alveoli of the human Lung 
  **active** ventilation 
  by **respiration**

Both stomata and alveoli are excellent AEROSOL filters;

Source: Encyclopedie Britannica, 1985

**Alveolus / alveoli:** the thin-walled saclike structure in the vertebrate lung where gas exchange takes place.

Scanning electron micrograph of the adult human lung showing alveolar duct with alveoli. Capillary relief of interalveolar septa is clearly visible because alveolar surfactant has not been preserved by fixation procedures.

http://www.mfn.unipmn.it/~pons/index_file/Page1171.htm
Physiology cont’d (5/5)

Respiration & Circulatory System

Gradients of respiratory gases as they pass from the gas-exchanging domain into the liquid-transport domain all the way to the target area and back;

Source: Tortora & Grabowski, 1996;
Inhalation of airborne particles and its effects:

- deposition pattern;
- Elimination pattern

The physical characteristics of soot are inert, odourless, and insoluble in water and in organic solutions. It is, however, a high adsorbent for hydrocarbons, aldehydes, oxygen-containing odour compounds and sulfur containing molecules. The \( \text{SO}_4^{2-} \) fraction of diesel exhaust particles is composed primarily of the sulfuric acid (\( \text{H}_2\text{SO}_4 \)) formed from the sulfur contained in the fuel and the lubricating oil. It is generated when \( \text{SO}_2 \) is oxidized to sulfur trioxide (\( \text{SO}_3 \)). Upon exposure with water vapor (likewise a by-product of the combustion process) it converts to \( \text{H}_2\text{SO}_3 \) and eventually to \( \text{H}_2\text{SO}_4 \) [1].

These \( \text{H}_2\text{SO}_4 \) particles adhere to the carbonaceous structure. Formation of \( \text{H}_2\text{SO}_4 \) is widely load-dependent; only a small amount is produced in low load conditions, while more of it occurs at high load operation conditions. As sulfur content in diesel has a detrimental effect on diesel fume purification, it is a major player in the negative health effects on humans of diesel exhaust.

Unfortunately, the sulfur content in the exhaust stream makes catalysts useless, as it interferes with the precious metals or oxides of the catalyst is coated with [2].

To really deal with the particle problem, the sulfur in the fuel has to be gotten rid of at the refinery. Reducing sulfur content to 5 ppm or lower brings dramatic improvements, by eliminating the sulfur nanoparticles. Only then can the exhaust particle stream react with the metal-coated substrate of the catalysts to further oxide them while the solid fraction could be trapped in particle filters [3].

Ultrafine particles (UFP, < 100 nm) are ubiquitous in ambient urban and indoor air from multiple sources and may contribute to adverse respiratory and cardiovascular effects of particulate matter (PM). Inhaled UFP are efficiently deposited in nasal, tracheobronchial, and alveolar regions due to diffusion. **There were also indications that the olfactory bulb of the brain was targeted.** Our objective in this follow-up study, therefore, was to determine whether translocation of inhaled ultrafine solid particles to regions of the brain takes place, hypothesizing that UFP depositing on the olfactory mucosa of the nasal region will translocate along the olfactory nerve into the olfactory bulb. This should result in significant increases in that region on the days following the exposure as opposed to other areas of the central nervous system (CNS). We conclude from our study that the CNS can be targeted by airborne solid ultrafine particles and that the most likely mechanism is from deposits on the olfactory mucosa of the nasopharyngeal region of the respiratory tract and subsequent translocation via the olfactory nerve. Depending on particle size, >50% of inhaled UFP can be depositing in the nasopharyngeal region during nasal breathing. **Preliminary estimates from the present results show that 20% of the UFP deposited on the olfactory mucosa of the rat can be translocated to the olfactory bulb.**

Epidemiological studies have consistently shown an association between particulate air pollution and not only exacerbations of illness in people with respiratory disease but also rises in the numbers of deaths from cardiovascular and respiratory disease among older people. Meta-analyses of these studies indicate that the associations are unlikely to be explained by any confounder, and suggest that they represent cause and effect. We propose that the explanation lies in the nature of the urban particulate cloud, which may contain up to 100·E^3 nm-sized particles/mL, in what may be a gravimetric concentration of only 100-200µg/m^3 of pollutant. We suggest that such ultra-fine particles are able to provoke alveolar inflammation, with release of mediators capable, in susceptible individuals, of causing exacerbations of lung disease and of increasing blood coagulability, thus also explaining the observed increases in cardiovascular deaths associated with urban pollution episodes. This hypothesis is testable both experimentally and epidemiologically.


- Multiple sclerosis - Bizzozero Neurochem Res. 2005
- Parkinson's disease - Zhan et al Am J Pathol. 1999
Toxicology cont’d (3/7)

Nasal Deposition and absorption via the olfactory epithelium contributes to:

- Multiple Sclerosis
- Alzheimer’s D.
- Parkinson’s D.
- Amyotrophic lateral sclerosis

Image: Tortora & Grabowski, 1996;

Multiple Sclerosis (MS): also known as disseminated sclerosis or encephalomyelitis disseminata) is a chronic, inflammatory, demyelinating disease that affects the central nervous system (CNS). MS can cause a variety of symptoms, including changes in sensation, visual problems, muscle weakness, depression, difficulties with coordination and speech, severe fatigue, cognitive impairment, problems with balance, overheating, and pain. MS will cause impaired mobility and disability in more severe cases. Surrounding many of these neurons is a fatty layer known as the myelin sheath, which helps neurons carry electrical signals. MS causes gradual destruction of myelin (demyelination) and transection of neuron axons in patches throughout the brain and spinal cord. When the myelin is destroyed, the neurons can no longer effectively conduct their electrical signals. The name multiple sclerosis refers to the multiple scars (or sclerosis) on the myelin sheaths. This scarring causes symptoms which vary widely depending upon which signals are interrupted.

Alzheimer’s Disease: also known simply as Alzheimer's, is a neurodegenerative disease that, in its most common form, is found in people over age 65. Approximately 24 million people worldwide have dementia of which the majority (~60%) is due to Alzheimer's. It is characterized by progressive cognitive deterioration, together with declining activities of daily living and by neuropsychiatric symptoms or behavioral changes. It is the most common type of dementia.

Parkinson’s Disease: also known as Parkinson disease or PD is a degenerative disorder of the central nervous system that often impairs the sufferer's motor skills and speech. PD is characterized by muscle rigidity, tremor, a slowing of physical movement (bradykinesia) and, in extreme cases, a loss of physical movement (akinesia). The primary symptoms are the results of decreased stimulation of the motor cortex by the basal ganglia, normally caused by the insufficient formation and action of dopamine, which is produced in the dopaminergic neurons of the brain. Secondary symptoms may include high level cognitive dysfunction and subtle language problems. PD is both chronic and progressive.

Amyotrophic lateral sclerosis (ALS): also known as Lou Gehrig’s disease in the US, Maladie de Charcot in France and Motor Neuron Disease (MND) in the UK is a progressive neuromuscular disease characterised by the progressive degeneration of motor nerve cell in the brain (upper motor neurons) and spinal cord (lower motor). To date there is no cure for ALS. Present day medical management of the disease through the combinatorial use of medications and advancements in state-of-art technological devices for nutrition and breathing, have markedly increased the survival rate of ALS sufferers.

Source:
Bronchial and Alveolar Deposition affect all cell types:

- Epithelial cells
- Goblet cells (mucus secreting cells)
- Clara cells (surfactant, lysozyme)
- Pneumocytes (alveolar cells type I-III)

Epithelial cell, Granulocyte, Macrophage

Epithelial cells: Respiratory epithelium is a type of epithelium found lining the upper and lower respiratory tracts, where it serves to moisten and protect the airways. It also functions as a barrier to potential pathogens and foreign objects, preventing infection by action of the ciliary escalator. The cilia of the respiratory epithelium beat in a concerted effort to move secreted mucus containing trapped foreign particles towards the oropharynx for either expectoration or swallowing to the stomach where the acidic pH helps to neutralize foreign material and micro-organisms. This system is collectively known as the ciliary escalator and serves two functions: to keep the lower respiratory tract sterile, and to prevent mucus accumulation in the lungs from drowning the organism.

Goblet cells: Mucus-secreting cells in which the nucleus is also closer to the base of the cell. The majority of the cell's cytoplasm is occupied by mucinogen granules, except at the bottom. Rough endoplasmic reticulum, mitochondria, the nucleus, and other organelles are concentrated in the basal portion. The apical plasma membrane projects microvilli to increase surface area for secretion.

Clara cells: are non-mucous and non-ciliated secretory cells found in the primary bronchioles of the lungs. Clara cells are dome-shaped and have short microvilli. One of the main functions of Clara cells is to protect the bronchiolar epithelium. They do this by secreting a small variety of products, including Clara cell secretory protein (CCSP) and a component of the lung surfactant. They are also responsible for detoxifying harmful substances inhaled into the lungs. Clara cells also multiply and differentiate into ciliated cells to regenerate the bronchiolar epithelium. Clara cells play an important defensive role, and they also contribute to the degradation of the mucus produced by the upper Airways. The heterogeneous nature of the dense granules within the Clara cell's cytoplasm suggests that they may not all have a secretory function. Some of them may contain lysosomal enzymes, which carry out a digestive role, either in defense. Clara cells engulf airborne toxins and break them down via their cytochrome P-450 enzymes present in their smooth endoplasmic reticulum; or in the recycling of secretory products. Clara cells are mitotically active cells. They divide and differentiate to form both ciliated and non-ciliated epithelial cells.

Pneumocytes: The lungs contain about 300 million alveoli, representing a total surface area of 70-90 (?) m², each wrapped in a fine mesh of capillaries. The alveoli have radii of about 0.1 mm and wall thickness of about 0.2 µm. The alveoli consist of an epithelial layer and extracellular matrix surrounded by capillaries. In some alveolar walls there are pores between alveoli. There are three major alveolar cell types in the alveolar wall (pneumocytes):

- Type I cells that form the structure of an alveolar wall. They are very large, thin cell
Major Classes of Respirable Particles

- Coarse particles > 2.5 \(\mu\)m (measured gravimetrically, e.g. TEOM or aerodynamically, e.g. Impactor)
- Fine particles 0.1-2.5 \(\mu\)m (measured gravimetrically, e.g. TEOM or optically, e.g. OPC)
- Nano particles 0.001-0.1 \(\mu\)m (measured electro-optically, e.g. SMPS or electrostatically, e.g. FCE)

**Particle Deposition Mechanisms:** The lung can be seen as a selective filter, into which the particle are stripped off the gas stream in different ways[1]. In the upper air ways (nose, throat) the air-speed is high enough to cause particles to deposit by impaction. Airway branching pattern favors non-uniform (focal) areas of deposition, especially when impaction is an important deposition mechanism.

- Naso-pharyngeal: impaction, sedimentation, electrostatic (particles > 1 \(\mu\)m)
- Tracheo-bronchial: impaction, sedimentation, diffusion (particles < 1 \(\mu\)m)
- Pulmonary: sedimentation, diffusion (particles < 0.1 \(\mu\)m)


Ultrasound particles (UFP, particles < 100 nm) are ubiquitous in ambient urban and indoor air from multiple sources and may contribute to adverse respiratory and cardiovascular effects of particulate matter (PM). Depending on their particle size, inhaled UFP are efficiently deposited in nasal, tracheobronchial, and alveolar regions due to diffusion. Our previous rat studies have shown that UFP can translocate to interstitial sites in the respiratory tract as well as to extrapulmonary organs such as liver within 4 to 24 h postexposure. There were also indications that the olfactory bulb of the brain was targeted. Our objective in this follow-up study, therefore, was to determine whether translocation of inhaled ultrafine solid particles to regions of the brain takes place, hypothesizing that UFP depositing on the olfactory mucosa of the nasal region will translocate along the olfactory nerve into the olfactory bulb. This should result in significant increases in that region on the days following the exposure as opposed to other areas of the central nervous system (CNS). We generated ultrafine elemental \(^{13}\)C particles (CMD = 36 nm; GSD = 1.66) from \(^{13}\)C graphite rods by electric spark discharge in an argon atmosphere at a concentration of 160 \(\mu\)g/m\(^3\). Rats were exposed for 6 h, and lungs, cerebrum, cerebellum and olfactory bulbs were removed 1, 3, 5, and 7 days after exposure. \(^{13}\)C concentrations were determined by isotope ratio mass spectrometry and compared to background \(^{13}\)C levels of sham-exposed controls (day 0). The background corrected pulmonary \(^{13}\)C added as ultrafine \(^{13}\)C particles on day 1 postexposure was 1.34 \(\mu\)g/lung. Lung \(^{13}\)C concentration decreased from 1.39 \(\mu\)g (day 1) to 0.59 \(\mu\)g by 7 days postexposure. There was a significant and persistent increase in added \(^{13}\)C in the olfactory bulb of 0.35 \(\mu\)g on day 1, which increased to 0.43 \(\mu\)g by day 7. Day 1 \(^{13}\)C concentrations
Deposition within the Respiratory tract

The lung has, like any filter, a certain range in which neither impaction nor diffusion predominates and typically occurs at around 300 nm.

**Impaction:** The particle’s momentum in air stream prevents it from making turn at a bifurcation (occurs in the following compartments **naso-pharyngeal** and **tracheo-bronchial**).

**Sedimentation:** When gravitational forces on a particle are greater than air resistance and buoyancy, the particle will fall out of the air stream. As air moves deeper into the lung, air flow rate decreases. Sedimentation is proportional to:
- particle time in airway
- particle size and density
- respiratory rate, i.e. breaths/minute

(occurs in **naso-pharyngeal, tracheo-bronchial**, and **pulmonary** compartment).

**Diffusion:** Particles have random motion, resulting in random impacts. The diffusion coefficient is:
- inversely related to particle size
- independent of particle density

(diffusion occurs in the **tracheo-bronchial** and **pulmonary** compartment).

**Electrostatic Precipitation:** A minor mechanism, but may be more important for freshly generated particles because these particles tend to have greater surface charge. Particle surface charge induces an “image” charge on lung surface.

**Particle characteristic that affect deposition:**
Size: will effect location of deposition; sequential removal of particles as go through the lung.
Particle hygroscopicity: If a particle is hygroscopic, it can pick up water in the humidified air of the lung. This will increase particle density and alter deposition.
Particle surface charge: This will affect electrostatic deposition.

Pulmonary deposition of:

- Oil Aerosol
- NaCl Aerosol & Hygroscopicity

It is of great importance whether the inhaled particles are hygroscopic or not. Hygroscopic particles increase rapidly in size within the damp-close- and narrow range setting of the respiratory system. Thus, hydrophilic particles are sooner separated, while non-hygroscopic (hydrophobic) particles can penetrate all the way down into the alveolar region.

Freshly generated Diesel soot (not yet subject to agglomeration), is hydrophobic and still within the nucleation regime, they have a small diffusion pressure on the mucous area, and they can easily penetrate the alveoli\(^1\).

Oil: modelled distribution of the olive-oil aerosol deposition within the respiratory tract over 27 generations. Extrathoracic deposition 8.93% - total lung deposition: 25.8%.

NaCl: modelled distribution of NaCl-aerosol deposition within the respiratory tract. HGFx1: extrathoracic deposition: 10.0% - total lung deposition: 29.9%.

Source: \(^1\) AKPF (2000), p.11.
Clearance (1/6)

Bronchial Muco-Ciliar Clearance

Mucus secretion and clearance are extremely important for airway integrity and pulmonary defense.

It has been estimated that mucus secretion volume is between 10 and 100mL per day in healthy individuals.

Nostril hair filters out larger particles. Those over 5.0 μm diameter are stopped and deposited mainly in the nose and the throat. Smaller particles are stopped by mucous membranes that line the respiratory system and provide a surface to which the particles adhere. Dust is separated to damp surfaces, the mucous layer is moved by fine cilia constantly in the direction of the throat and a warning system with sensitive chemical sensors ensures that various mechanisms, ranging from coughs to sneezing that the lung remains at all cost free of particulates.

The sizes and shapes of air passages effectively block some of the other particle fraction between 0.5-5.0 μm in diameter[1] by depositing them in bronchioles. They usually do not reach beyond the air ducts or bronchi, and are soon removed by ciliary’s action[2].

Most particles deposited in the bronchioles are removed by the cilia within two hours. Indeed, the bronchi’s and bronchioles cilia wave back and forth and move mucous along in a current that carries trapped the smaller particle fraction out of the respiratory system to the throat, where they are swallowed or ejected as sputum.

Respiratory tract secretions consist of mucus, surfactant, and periciliary fluid. The airway surface fluid is present as a bilayer, with a superficial gel or mucous layer and a layer of periciliary fluid interposed between the mucous layer and the epithelium. A thin layer of surfactant separates the mucous and periciliary fluid layers.

The mucous layer extends from the intermediate airway to the upper airway and is approximately 2-10 μm thick in the trachea. Airway mucus is the secretory product of the goblet cells and the submucosal glands.

Sputum consists of lower respiratory tract secretions, nasopharyngeal and oropharyngeal material (including saliva), microorganisms, deposited aerosols and cells. Mucus clearance such as cough is critically important for airway hygiene.

Scanning electron microscope image of lung trachea epithelium. There are both ciliated and non-ciliated cells in this epithelium. Note the difference in size between the cilia and the microvilli (on non-ciliated cell surface)


10-08-13 Madl

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Clearance cont’d (2/6)

Clearance: Getting rid of deposited particles w/n the lung;

The muco-ciliary escalator operates in the tracheo-bronchial region:

• up to generation 12
• fading out at generation 16

Source: CDC, 2006

Particle Clearance mechanisms:

The Naso-pharyngeal Compartment:
• mucociliary clearance (transport back to nasopharynx)
• mechanical clearance (sneezing, coughing, swallowing)
• absorption into circulation (soluble particles).

The Tracheo-bronchial Compartment:
• mucociliary clearance (transport to oropharynx)
• endocytosis into peribronchial region (insoluble particles)
• absorption into circulation (soluble particles)

The Pulmonary Compartment:
• alveolar macrophage mediated clearance
• endocytosis by lung epithelial cells into interstitum
• absorption into circulation (soluble particles)

Source: CDC, 2006
Alveolar macrophage-mediated particle clearance:

- endocytosis by epithelial cells;
- cells absorption into blood & lymph

Source: AKPF, 2000

Clearance in the deeper lungs:

Nano-particles (less than 0.5 μm in diameter) enter the human body almost exclusively by the way of the respiratory system – they do in fact reach the alveolar regime and settle there. The removal of such particles from these areas is less rapid and less complete than in the upper respiratory region. Some of the particles retained in the alveoli are absorbed into the bloodstream. Nano-particles can exert a toxic effect in three different ways:

1. Hydrophobic aerosols easily penetrate the alveolar regime. As there are no nerve receptors within the alveoli, they do not signal the brain of inflammatory reactions; i.e. pain. One can easily inhale large quantities of aerosols without feeling really any effects. Once there, these aerosols are transferred to the blood system where they can easily spread and affect tissues and target organs away from the lung system.

2. Diesel engine exhaust for example, exhibit sizes that are 100s of times smaller than the natural types of dust. Such nano-aerosols discourage the fine defense mechanisms of the lung: these tiny particles penetrate past the protected regimes of the bronchioles to reach the alveolar section and stay there for months or even years.

3. The human body is not without defensive mechanism for this cilia-less area. Mobile devouring cells (macrophages) digest these particles are (phagocytes) and remove them in a timely manner so that these ultrafine particles do penetrate the gas exchange barrier. The only factor regulating this final barrier is the concentration of nano-particle load. The risks that this particle fraction crosses over into the blood vessel system or the lymphatic systems and thus spreading throughout the entire organism is quite high. After spreading though the entire organism, acute irritating effects can be released, for example, an increase of the blood viscosity or influence of the heart rhythm. On the other hand if these particles do not cross over or are digested by macrophages, they settle themselves into the lung fabrics, where they constantly irritate the lung epithelium. It is known that Diesel soot – among other ailments - induces coronary heart disease, heart attacks.

Source:

Phagocytosis of nanoparticles produces intracellular ROS (reactive oxygen species);

ROS interferes with:
• metabolic equilibrium
• protein synthesis
• DNA activity
• lipid peroxidation
• cell-cycle

Source: Limbach et al, 2005

Fibroblast: Fusiform cell with cytoplasm that is usually indistinguishable from the surrounding matrix; tapering processes are present but are difficult to visualize in most sections; some very active cells have basophilic cytoplasm; has elliptical nucleus, sometimes slightly folded, with sparse chromatin that presents a "speckled" appearance (may be mistaken for plasma cell); has one to two nucleoli; makes fibers and ground substance;


www.medinfo.ufl.edu/year1/histo/glossary.html#mesothelial_cell

xxx
Clearance cont’d (5/6)

Phagocytosis of nanoparticles has:

• Longterm effects ....

mutagenicity (mutations of DNA-sequences)
teratogenicity (deformations of cells)

• Acute effects ....

apoptosis (accelerating programmed cell death)
necrosis (traumatic cell death)

Source: Limbach et al, 2005

Exposure of human lung fibroblast cells to ceria nanoparticles of 20-50 nm in diameter results in the uptake of agglomerates.

(A) Vesicles inside a fibroblast cell with ceria agglomerates. The high atomic mass of ceria and resulting contrast make the particles visible as dark spots.

(B) A series of nanoparticle agglomerates close to the cell membrane.

(C) Nanoparticles both inside the cell (vesicle) and outside are exclusively found in the form of agglomerates, confirming the dominant role of agglomeration. All bar sizes are 1.5 microm.

Cell death can occur by either of two distinct mechanisms – necrosis or apoptosis. In addition, certain chemical compounds are said to be cytotoxic to the cell – i.e., to cause its death:

- **Necrosis** ("accidental" cell death) – pathological process which occurs when cells are exposed to severe physical or chemical attack
- **Apoptosis** ("programmed" cell death) – physiological process by which unwanted or unused cells are eliminated during development and other normal biological processes

In either event, macrophages and other intact cells try to dispose of the remains by phagocytosis

**Necrosis**:
- i) tissue damage
- i) due to trauma or other environmental factor impairing the structural integrity
- i) intracellular contents released
- i) thus may elicit local damage or inflammatory response

**Apoptosis**: programmed cell death (akin to suicide)
- i) fragmentation of cell compartments
- i) does not cause peripheral damage
- i) regulated
- i) failure to apoptose may result in tumor formation

Source: Wilde et al., 1999
KANDUC, MITTELMAN, SERPICO, SINIGAGLIA, SINHA, NATALE, SANTACROCE, DI CORCIA, LUCHESE, DINI, PANI, SANTACROCE, SIMONE, BUCCI and FARBE; 2002; Cell death: Apoptosis versus necrosis (Review)
Conclusion
Conclusion

Nano-Aerosols in a Nut-Shell:

- crucial for our CLIMATE (rain, snow); micro-organisms and plants could not easily spread – are essential for LIFE as we know it;
- Quantity (number) and Quality (chemo-physical property) are important (not mass);
- are INVISIBLE (particle diameter below the wavelength of light, <400nm);
- readily penetrate micrometer structures (diffusion, gravimetric settlement);
- are not STATIC, depending on their hydro-phobic/-philic property are subject to ongoing dynamic interactions with their environment;
- are CARRIERS of adsorbing agents (from therapeutic to toxic substances);
- with quantitative and qualitative effects on biological tissue (Trojan Horse);
- remain suspended in the troposphere for extended periods of time

there is no such thing as a GOOD or BAD aerosol:
Hence,

only the DOSE makes the poison (Paracelsus, 1493-1541)

Danke für Eure Aufmerksamkeit - Thanks for your attention

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Madli