The atmosphere of our Earth, of planets of our solar system and of exoplanets

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5. Air Pollution: Toxic gases, Particulates and Radioactive Fallout
5.1 General Aspects

Air Pollution: Definition and Examples

Air pollution is a partial aspect of environmental pollution. Air pollution is present if a deviation from the natural composition of air is present (s. p. 16), especially by smoke, particulates, soot, aerosoles, vapours or odourants. These substances are also referred to as pollutants. In most industrial countries, the local pollution has been strongly reduced in the last decades. In contrast, the emission of greenhouse gases such as carbon dioxide (CO₂) has, however, strongly increased all over the world.

In the Third World countries and in other emerging countries as well as in Russia and China, the local air pollution is still a very severe problem (see picture below: air pollution in Beijing - contamination by particulates !).

The Air Quality Index (AQI) is an index for reporting daily air quality. The Environmental Protection Agency (EPA) calculates the AQI for 5 major pollutants: Partical Pollution (also known as Particulate Matter (PM)), Carbon monoxide (CO), ground level Ozone (O₃), Sulfur dioxide (SO₂), and Nitrogen dioxide (NO₂).

In Beijing, pollution by PM’s are particularly severe. On Saturday 12. 1. 2013 at 8 p.m., the concentration of fine particles in the air was extremely large, reaching an AQI-value of as large as 755, exceeding the upper limit of the «Hazardous» category by some 255 points ! (see p. 5-A-1-2)
Forms and Sources of Air Pollution

Forms of Air Pollutants
Pollutants can be divided into two groups:

a) Primary pollutants: emitted directly from a natural source or from human action.

b) Secondary pollutants: form when primary pollutants react chemically in the atmosphere.

Sources of Air Pollutants

a) Pollutants from traffic: Gases and particles released from vehicles.

b) Stationary sources: Combustion of fossil fuels such as coal, oil, in power plants and households.

c) Other sources: Forest fires, biomass combustion (dead organisms, volcanic eruptions, etc).

Changes of Natural Composition of Air

Smoke

Dust

Vapors or Oderants

Gases

Aerosoles

Origin and Sources of Pollutants

<table>
<thead>
<tr>
<th>Primary Pollutants</th>
<th>Sources - Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbondioxide (CO₂)</td>
<td>Volcanic activity, Hot springs, Combustion processes, Cars, Power plants</td>
</tr>
<tr>
<td>Carbonmonoxide (CO)</td>
<td>Oxygen deficient combustion processes, wood, coal, fuel (also from cars)</td>
</tr>
<tr>
<td>Nitrogen oxides (NOₓ, NO₂)</td>
<td>Combustion of fuels in cars and industrial processes</td>
</tr>
<tr>
<td>Methane (CH₄)</td>
<td>Color- and odorless, combustible, reacts with O₂ to highly explosive mixtures</td>
</tr>
<tr>
<td>Sulfuric oxides (SO₃, SO₂)</td>
<td>By combustion of coal and oil</td>
</tr>
<tr>
<td>Ammonia (NH₃)</td>
<td>Pungent smelling and toxic gas; for fertilization of crop plants, etc.</td>
</tr>
<tr>
<td>Volatile org. Compounds (VOC’s)</td>
<td>From vehicle exhausts, detergents, furniture polish, fabric softener</td>
</tr>
<tr>
<td>Asbestos (mineral silicates)</td>
<td>Fibres penetrate into the lungs → cytotoxic effects</td>
</tr>
<tr>
<td>Radioactive noble gases</td>
<td>Unhealthy noble gases, e.g. Radon (Rn) from natural decay of Uranium</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>Occurring naturally, from lead smeltings, e.g. in pipings</td>
</tr>
<tr>
<td>Persistent org. pollutants (POP’s, e.g. PCB’s)</td>
<td>Produced by industrial processes and waste incineration Man-made synthetic chemicals; are irreversible</td>
</tr>
</tbody>
</table>

Secondary Pollutants

Particulate matter

Fine particles, originating from compounds such as sulfates and nitrates; Produced by man or by natural processes

Ozone (O₃)

Produced by chemical reactions in the presence of solar radiation
5.2 Primary Pollutants

Primary pollutants are emitted directly from a source. They can be released from natural ways or human action.

For Secondary Pollutants:

s. Section 5.5 (pp 238 – 244)

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Carbon Dioxide - CO₂: General Properties

Carbon Dioxide is a chemical compound containing carbon and oxygen and the molecular formula is CO₂. CO₂ is an incombustible, colorless and odourless acid gas, which is well soluble in water.

CO₂ is an important greenhouse gas (a heat-trapping gas) and it is a natural constituent of air where its mean concentration is 0.039% in volume (390 ppm). CO₂ is either formed by complete combustion of carbon-containing substances in the presence of sufficient oxygen concentrations as well as in living organisms as by-products of cell breathing.

The total mass of CO₂ in the atmosphere is 3’000 Gigatons, corresponding to about 800 Gigatons of carbon (the ratio of the molar masses of CO₂ and C is 11/3 (molar mass of CO₂ = 12+32 = 44, molar mass of C is 12). The concentration of CO₂ varies seasonally and locally, especially near the ground. In urbane regions, the CO₂ concentration is in general higher than in rural areas.

1 pm = 10⁻¹² m
= 0.01 Å = 0.001 nm

The CO₂ molecule is linear: all 3 atoms are on a straight line and the molecule has no dipole moment. The 2 C=O double bonds are covalent with 2 electron pairs from each O- atom. The 2 C=O bonds are polar but cancel each other and the C=O distance is 116.32 pm.
Carbon Dioxide - CO₂: Physiological effects and dangers

The adverse effects of CO₂ to animals and humans is not only due to the displacement of O₂ in the air. Depending on the CO₂ concentration of air, the room air is divided into 4 quality grades: For values below 800 ppm, the indoor quality is considered to be good. Values between 800 and 1'400 ppm (0.08 to 0.14 Vol.-%) are of average to medium quality. For higher concentrations, CO₂ can have toxic effects: for values larger than 1'400 ppm, the indoor quality of the air is considered to be bad. For a CO₂ concentration of 1.5%, the total lung ventilation per minute (minute ventilation) increases by more than 40%. The presence of elevated CO₂ levels in the blood is the stimulant that the respiratory center responds to in order to signal the respiratory muscles to breathe.

Inspired air containing about 5% CO₂ gives rise to headaches and vertigo. For still higher concentrations, the heart beat and the blood pressure increase. This can lead to breathlessness and unconsciousness. High CO₂ concentrations in fodder silos, cesspools and wells repeatedly give rise to serious accidents.

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Carbon monoxide - CO: Physical and Chemical Properties

Carbon monoxide is a chemical compound with the molecular formula CO. CO is a colourless, odourless, tasteless and non-perceptible toxic gas. Among others, it is produced during incomplete combustion.

CO is combustible and it burns with a blue flame to CO₂. As a component of a city gas, it has been used in Germany as a fuel gas and illuminating gas until mid-20th century. In chemical industry, H₂ and CO are used to synthesize Methanol (CH₃O or CH₃OH) as well as of other basic chemicals.

The formation of CO is favoured by high temperatures or by oxygen deficiency according to CO₂ + C ⇌ 2 CO. At temperatures of 1'000 °C, the equilibrium concentration of CO in this reaction is only about 1%. Pure CO can then be obtained by rapid cooling to room temperature and a stable chemical compound is obtained. CO is weakly polar with a dipolar moment of 0.122 D (1 D = 1 Debye ≈ 3.336 × 10⁻¹⁸ C m; 1 C = 1 Coulomb = 1 Ampere x s). World-wide, most CO is produced by photochemical reaction in the Troposphere (about 5 x 10¹² kg per year). Other natural sources are volcanos, forest fires, chimneys and other combustion processes.
Carbon monoxide - CO: Toxicity

CO is a dangerous respiratory poison. If it passes the lungs and enters the blood circulation, it disables the oxygen transport in the blood. This can cause death by suffocation. Light intoxication causes headache and dizziness while higher doses are very harmful for the central nervous system and the heart. This can also lead to serious complications of the development of foetuses. Since CO is colourless, odourless and tasteless, it is hardly discerned. On average, pollutants higher than 100 ppm are hazardous. The maximum allowable concentration at a workplace is 30 ppm.

Nitrogen oxides: NOx

«Nitrogen oxides» is a collective term for gaseous oxides of nitrogen. They are also abbreviated as NOx because there exist many oxidation states of nitrogen. Examples are NO (Nitrogen monoxide), NO2 (Nitrogen dioxide), N3O, N2O, N2O2, N2O3, N4O6, N2O4 and N2O5.

Without exceptions, nitrogen oxides are endothermic compounds, i.e. they are formed from their elements only at external constraints (energy input). With the exception of N2O (nitrous oxide or laughing gas) they react with water to form an acid. Because of this acidification (on the mucosae) they have an irritating and poisonous effect. In the one hand, laughing gas has medical and industrial applications. In the other hand, it is emitted unintentionally into the atmosphere during technical and agricultural processes. There, it acts as a greenhouse gas and as an ozone killer (see Chapter 2).

NO and NO2 are produced nearly exclusively by combustion reactions in technical facilities and by motors and is emitted mainly as NO. In the presence of air, NO is oxidized to NO2.
NO and NO₂ develop at high temperatures (> 600–800 °C) as a result of combustion processes, especially from road traffic heating systems. 90 to 95% are emitted as NO and in the atmosphere they are chemically transferred to the more poisonous NO₂. The major portion stems from traffic (passengers cars, utility cars, Off-road vehicles). The concentrations of NO and NO₂ have an early cycle: the highest values are measured in winter half years.

In the denitrification plant (DENOX), the nitrogen oxides are chemically decomposed into nitrogen and water and the Dioxins (p. 213) are decomposed. The purified flue gases leaving the chimney, consist mainly on water vapour. Primarily, nitrogen oxides are naturally generated by lightnings. Electrical discharges in air occur at temperatures as high as 30'000 °C thereby oxidizing N₂. In addition, nitrogen oxides are generated by forest fires (about 40 t/Jahr) as well as by fertile soils. Microorganisms in the soils are emitting about 6'600 t/year into the atmosphere.

- Nitrogen oxides are present in tobacco smoke!
- Experiments suggest the unique role of vegetation as a sink of NO₂.
- Inhalation of NO₂ is poisonous. Because of the penetrating smell, inhalation can normally be prevented.

Methane is a hydorcarbon and the simplest Alkane. It is a colourless and odorless gas. As a main component of natural gas, it is of greatest importance as a heating gas for chemical industry and as starting product for technical systems. CH₄ appears at diverse conditions and is permanently reformed, for example by biological and chemical processes. On the Earth, approximately 60 million tons of CH₄ are emitted each year.

The density ρ of Methane is smaller than that of air (at 0 °C, 1 bar: ρ(CH₄) = 0.708 kg/m³, ρ(air) = 1.292 kg/m³); therefore, CH₄ ascends to higher layers of the Earth’s atmosphere. It is more effective than CO₂ by a factor of 20 to 30, however, its concentration is much smaller than that of CO₂. There, it reacts with O₂ to form CO₂ and water (chemical half time ≈ 14 Jahre; [CH₄ + 2 O₂ → CO₂ + 2 H₂O]).

Methane is generated at high temperatures and pressures in the deeper underground below the surface of the Earth. In most cases, it is released by volcanic activities. It is the main component of natural gas (85 – 98 %), which appears primarily in conjunction with fossil oil. [Natural gas is a combustible gas which often appears together with fossil oil and consists mainly on highly-inflammable methane].

The Figure shows the methane molecule CH₄: The carbon atom C is located at the centre of the tetrahedron which is formed by 4 hydrogen atoms H. 1 pm = 10⁻¹² m.
Methane \( \text{CH}_4 \): Handling, Dangers and Safety

At a volume fraction between 4.4% and 16.5% in the air, methane forms explosive mixtures i.e. dangerous explosive atmospheres. The unnoticed escape of natural gas repeatedly leads to fatal gas explosions. In addition, the greatly feared mining explosions in coal mines (fire damps) are due to methane-air mixtures. Methane is highly flammable. The flash point is at \(-188^\circ\text{C}\) and the ignition temperature is at \(600^\circ\text{C}\).

Methane is nontoxic. The inhalation of methane can, however, cause increased breathing frequency (hyperventilation) and increased heart beat. In addition, it can cause low blood pressure, numbness in the extremities, sleepiness, mental confusion and loss of memory (amnesia). All these symptoms are due to the lack of oxygen. However, methane does not cause permanent damage.

- Due to the worldwide rice agriculture, 50 to 100 tons methane are produced per year. This kind of methane production is probably the highest man-made generation of methane.
- Rice is produced worldwide and the quantity of methane production depends strongly on the actual location. Among other things, it depends on the average temperature, the water depth and period of time during which the rice is exposed to water.
- As a consequence of the increase in global population and the associated increase of rice cultivation, the concentration of methane increases.

Rice production by «Wet Rice Agriculture»  

Sulfur oxides: General

Sulfur oxides (chemical formula: \( \text{S}_x\text{O}_y \)) are oxides of the chemical element sulfur (S). Since sulfur can exist in several different oxidation states, several sulfur oxides exist:

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Oxidation state</th>
<th>Structural formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{S}_2\text{O}_2 )</td>
<td>0, +II</td>
<td><img src="image" alt="Structural formula" /></td>
</tr>
<tr>
<td>( \text{S}_2\text{O} )</td>
<td>0, +II</td>
<td><img src="image" alt="Structural formula" /></td>
</tr>
<tr>
<td>( \text{SO} )</td>
<td>+II</td>
<td><img src="image" alt="Structural formula" /></td>
</tr>
<tr>
<td>( \text{S}_2\text{O}_2 )</td>
<td>+II</td>
<td><img src="image" alt="Structural formula" /></td>
</tr>
<tr>
<td>( \text{SO}_2 )</td>
<td>+IV</td>
<td><img src="image" alt="Structural formula" /></td>
</tr>
<tr>
<td>( \text{SO}_3 )</td>
<td>+VI</td>
<td><img src="image" alt="Structural formula" /></td>
</tr>
<tr>
<td>( \text{SO}_4 )</td>
<td>+VI</td>
<td><img src="image" alt="Structural formula" /></td>
</tr>
</tbody>
</table>

Sulfur oxides are formed by combustion of sulfur and sulfur-containing combustibles (coal, petrol, fuel oil, Diesel fuel), but also by natural processes such as by volcanic eruptions.

As a result of combustion processes, sulfur reacts mainly to the two following oxides:

- Sulfur dioxide: \( \text{SO}_2 \) and
- Sulfur trioxide: \( \text{SO}_3 \) (in small quantities)

In aqueous solutions, both sulfur oxides react to acids. \( \text{SO}_2 \) reacts to the unstable sulfuric acid \( \text{H}_2\text{SO}_3(aq) \) and \( \text{SO}_3 \) reacts to the very important sulfuric acid \( \text{H}_2\text{SO}_4 \). Both acids play an important role for the acidification of lakes due to acid rains. These acids are also poisonous in the gases state.
Sulfur dioxide - SO₂ and Sulfuric acid

Sulfur dioxide is the anhydrate of the sulfuric acid H₂SO₃. SO₂ is a colorless and poisonous gas with a pungent odor and an irritating taste. It is well water-soluble and in contact with water it partially reacts to sulfurous acid.

SO₂ is primarily formed by combustion of sulfurous fossil fuels such as coal or petroleum products which contain up to 4% sulfur. Thereby, it contributes to an essential degree to air pollution. It is at the origin of acid rain; here, SO₂ is first oxidized to SO₃ and by reacting with water it is converted to sulfuric acid (H₂SO₄). (The H₂SO₄-molecule has a tetrahedral structure, see above).

There are two sources of how SO₂ can raise into the atmosphere: The first one has a natural origin, namely by volcanic eruptions; these eruptions can eject 2 to 20 million tons per year. The second source is man-made, i.e. by fossil fuels such as coal and oil.

In high concentrations, SO₂ causes harm to man, animals and plants. The acid rain is harmful for the ecosystem such as woodland and lakes. The largest contribution of emission into the air is due to ship traffic.

Sulfur trioxide - SO₃

Sulfur trioxide, SO₃, is an anhydrate of sulfuric acid, H₂SO₄. At normal conditions, it is colourless and forms needle-shaped crystals which are extremely hygroscopic and which react violently (explosive) with water. Gaseous sulfur trioxide is a monomer (monomers are reactive and low molecular molecules, which among others can form molecular chains, nets or branched polymers). The SO₃ – molecule is planar (all 4 atoms are in the same plane) and have a trigonal symmetry (three 120°- angles) and it contains three double bonds of equal lengths (s. picture below).

Inhalation of vapour causes irritations and in the lungs, sulfuric acid is formed. This can provoke a life-endangering pulmonary oedema. Since SO₃ is strongly corrosive and hygroscopic, inhalation or incorporation causes serious injuries. Therefore, SO₃ should be treated with extreme caution. With water, it reacts violently and converts into highly corrosive sulfuric acid.
Ammonia - NH₃: General Properties

Ammonia is a chemical compound of nitrogen (N) and hydrogen (H) atoms with the chemical formula NH₃. Since ammonia reacts easily with acid compounds, gaseous ammonia appears only in small quantities on Earth. It is formed by decomposition of dead plants and animal faeces. Ammonia is also formed by humification, in which nitrogen-containing compounds of biomass are decomposed by microrganisms.

At room temperature, ammonia is a colourless diamagnetic and pungent-smelling gas. Below –33°C, it liquifies.

Ammonia is built up from separate NH₃-molecules. The molecule is not planar but rather forms a three-sided pyramid. The N-atom is at the top of the pyramid while the tree H-atoms form the base of the pyramid. The H-N-H angle is 107.3 °C, slightly smaller than the ideal tetrahedron angle of 109.5°.

Important sources for ammonia emission are volcanic eruptions, the cattle ranching, the cattle fattering as well as the traffic.

Ammonia - NH₃: Toxicology

The unpleasant odor of ammonia which is already perceivable at low concentrations, is a warning and therefore, cases of injuries and poisoning are very seldom.

Gaseous NH₃ reaches the lung primarily by respiration. By reaction with wet air, NH₃ is strongly pungent to the mucosae. In addition, the eyes are also strongly damaged by NH₃. In the case of inhalation of concentrations higher than about 1'700 ppm, mortal danger exists because of damages in the respiratory passages (laryngeal oedema, laryngospasm, pulmonary oedema, pneumonitis and respiratory arrest). By transfer of substantial quantities of NH₃ into the blood, the blood level of NH₄⁺ ions increases above 35 μmol. This leads to central nervous phenomena such as hand tremor, language disorder, vision disorder and mental disorder. In extreme cases of poisoning it can cause comas and death.

In addition to respiration, acute poisoning by NH₃ can also occur as a consequence of liver failure (hepatic failure).
5.3 Toxic Organic Gases

Volatile Organic Compounds - General

Volatile Organic Compounds (VOC's) is the general term for organic, i.e. carbon-containing compounds, which evaporate easily (are volatile). They exist already at low temperatures (i.e. at room temperature) in the gaseous form. In the case of NMVOC's (Non Methane Volatile Organic Compounds), Methane gas, CH₄ (pp 203, 204), is excluded from the group of VOC’s.

VOC’s are emitted into the environment by a plethora of biogenic and anthropogenic processes. Plants, animals, soils and Seas are natural, biogenic sources; the most important anthropogenic sources are industrial applications of solvents and traffic.

Biologically generated VOC’s

All living beings (humans, animals, plants and microorganisms) are emitting organic compounds into the environment. Many plants are emitting terpenes and other organic compounds. The simplest terpene is the isoprene shown at the right hand side.

Anthropogenic sources

The release of volatile organic compounds by humans is dominated by applications of solvents and by the traffic. If the emission of methane caused by rice cultivation is considered as an anthropogenic source, a significant contribution is added to the VOC’s.

In addition to atmospheric VOC’s in the atmosphere, volatile organic compounds are also present in the indoor air. For the latter VPC’s, there are different sources such as plastics, construction materials, furniture, carpets, detergents and tobacco smoke.

5 – 10
Volatile Organig Compounds (VOC's): Toxicity

Pollution with VOC's by indoor air: Persons can suffer long-term illnesses. Children and older persons are affected most often. Symptoms such as headaches, allergies, tiredness, degradation of performance, drowsiness and irritations of the respiratory tract are summarized under the term «Sick-Building Syndrom». This cluster of syndroms is internationally used and defined by WHO («World Health Organization»).

Properties and Toxicity of vapours of four VOC's

- **Formaldehyde**: CH$_2$O
  - Melting point: -117 °C
  - Present in blood of mammals, by photo-oxidation in the atmosphere, by incomplete combustion, etc.
  - Toxicity: Allergies, irritations of skin, respiratory passages and eyes. Acute danger of life for higher concentrations (pulmonary oedema, pneumonia; carcinogenic)

- **Dichlormethane**: CH$_2$Cl$_2$
  - -94.92 °C
  - Applications: Dichlormethane (DCM) is a good solvent for many compounds. Toxicity of DCM is due to the harmful effect of metabolically effective carbon monoxide (CO). Inhalation can be fatal. For animals: breast cancer, lung cancer and liver cancer.

- **Tetrachlorethane**: C$_2$Cl$_4$
  - -22 °C
  - Properties: C$_2$Cl$_4$ is a colourless and volatile liquid, the vapors of which are heavier than air. Toxicity: widely applied in trade and industry. → Contamination of ground waters! C$_2$Cl$_4$ is a carcinogenic dangerous substance!

- **Benzene**: C$_6$H$_6$
  - 5.5 °C
  - Properties: volatile organic compound having an aromatic smell. Toxicity: poisonous by inhalation. Both, the toxic effect as well as the carcinogenic effect is due to the development of a cancerous metabolite.

Hydrogen cyanide (HCN) in the Atmosphere

HCN is one of the strongest poisons known. In very small concentrations it is also present in the atmosphere. It has been shown, that HCN present in the troposphere and in the lower stratosphere is produced by combustion of biomass from the Earth. The lifetime of HCN observed in the atmosphere is only a few months. It is believed that this limited lifetime is due to the absorption of HCN by the oceans.

As an example we consider the concentration of HCN in combustion gases. Today, about 5’000 poisonous components are present in these gases. For the acute medication, the following noxes are relevant: Carbon monoxide (CO), Hydrogen cyanide (HCN), and different lung irritants.

Among others. HCN is produced by combustion of wools, silk, Nylon, upholstered furnitures, curtains, carpets, cars, airplanes and paper. In addition, HCN is also contained in tobacco smoke. The smoke of an average cigarette contains 400 to 500 μg HCN.

Properties of HCN:
- Molar Mass: 27.03 g/mol; Density: 0.68 g/cm$^3$;
- Melting point: -13 °C; Boiling point: 26 °C;
- Vapour pressur at 20 °C: 816 hPa = 0.816 bar = 0.805 atm

An other name for HCN is Zyklon B; Zyklon B is extremely poisonous: already 1 - 2 mg per kg body weight is deadly! In World War II. Zyklon B has been used for mass poisoning of humans (s. p. 5-A-3-2).

[ (*) noxes: see Ref. R.5.3.4 - f]
Persistent Organic Pollutants (POP’s)

Persistent Organic Pollutants (POP’s) are organic compounds which are decomposed only very slowly in the environment (persistent organic compounds). Typically, the notion is used for organochlorine insecticides of the «first class» (examples are chlordane, DDT, Dieldrin, Toxaphene), for some industrially manufactured chemicals (PCB) as well as for some byproducts of combustion processes (Dioxin).

**DDT – molecule**  
C₁₄H₉Cl₅

**PCB – molecule**  
C₆Cl₅ - OH

**Dioxin:**  
C₁₄H₅Cl₅O₂

POP’s are «semi-volatile»: they can exist in the gaseous phase as well as bound to dust particles. For this reason they are mobile in the environment, at least to a certain extent, and by mechanisms of long-distance transport, they can be distributed globally. Persistent organic compounds are relatively resistant with respect to chemical, biological, and photolytic processes of degradation. In many cases, they are composed on chlorine and carbon atoms: The Cl-C bond is very resistant against hydrolysis. POP’s are difficult to dissolve in water but they are easily soluble in fat. They can be accumulated in the fatty tissue of animals and humans.

Defoliation of Virgin Forests in Vietnam by «Agent Orange»

The Vietnam War (1965 – 1973) of the Americans against Northern-Vietnam has been conducted in an extremely inhuman and cruel manner and at the same time, it was also extremely detrimental to the environment. Among others, the Americans used the dioxinated defoliant «Agent Orange» (Dioxin: s. p. 213). Their goal was a defoliation of the trees and finally a complete destruction of the forests. The resistance fighters used the forests as military camouflage and as channels of supply. In order to eliminate the basic food resources, the farming land was also destroyed. In case of poisoning with «Agent Orange», no method of detoxification is known.

For identification, the barrels in which the active agent containing the Dioxin has been transported have been provided with a an orangend-colored strip; hence the name «Agent Orange».

Depending on the sources, 72 to 90 million liters of chemicals have been sprayed!
Cruelest mutilation of newborns from exposure to «Agent Orange» (Dioxin) in Vietnam

According to the Vietnamese Red Cross, more than 3 millions of Vietnamese have been impaired by «Agent Orange» and almost 500’000 children suffered from most cruel birth defects. About 4.8 millions Vietnamese have been exposed to the poison «Agent Orange»; they died or have been mutilated.

«Agent Orange», a Dioxin-containing chemical defoliant, has been introduced by John F. Kennedy in 1963 and has been further used as a weapon by Lyndon B Johnson!

In the areas which have been contaminated by «Agent Orange», children suffered from diverse health problems such as cleft palate, serious mental disabilities, hernia (protrusion of intestines through hernial orifices), as well as the formation of additional fingers and toes. In the years after 1970, high concentrations of Dioxin have been detected in mothers’ milk of women from South Vietnam.

Seveso - Disaster with Dioxin - 1

At July 10, 1976 an explosion occurred in the Chemical Laboratory ICMESA in Seveso, a small city in Northern Italy. A very large quantity of TCDD (Dioxin) has been released. As a consequence, a deadly cloud of the highly toxic chemical hovered over the city and its 8’000 inhabitants. Ten days past until the population has been informed by the management about the possible severe hazards originating from this toxic gas! For this reason, the protective measures for the population started much too late.

Although the responsible managers of ICMESA knew already at the day of the accident that Dioxin has been released, they announced it officially only 8 days after the catastrophe. The partner Company Roche in Switzerland has internally been informed already on July 12 about the accident and the released Dioxin but it neither went public.
The consequences of the Dioxin catastrophe in Seveso - 2

A deadly cloud howered for days over the area of Seveso and its environment.

More than 200 persons suffered from burns and acute symptoms of poisoning and had to be hospitalized. Most of these victims suffered from Chloracne, a severe skin disease, which is directly related to Dioxin.

In the case of unborn children, severe deformities had to be expected. For this reason, many pregnant women performed an abortion. It is estimated that more than 37'000 persons were affected by the accident.

An area of more than 320 hectares populated by about 5'000 persons, has been contaminated. Five days after the accident, widespread dying of animals started, mainly birds, rabbits and sheeps. In the following days, leaves of trees and bushes started to withering. 3’300 carcasses have been found.

The large number of carcasses is due to the fact that the animals ate from the pastures and from other contaminated feed found in nature.

The Bhopal – Catastrophe - 1

The catastrophe of Bhopal occurred at December 3, 1984 in the Indian city of Bhopal, the Capital of the Indian State Madhya Pradesh. It happened in an industrial plant of the US Chemical Company Union Carbide Corporation (UCC) [after 2001: the Chemical giant Dow Chemical Company (DCC)]. As a result of technical failures caused by an unvorgivable greed for profit and negligence, a very large quantity of highly toxic gases escaped into the Atmosphere. It is one of the worst chemical catastrophes and environmental disasters of history. Thousands of humans died at the direct impacts of this terrible accident.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{Methyl isocyanate:} \\
\text{N} & \equiv \text{C} \equiv \text{O} \\
\end{align*}
\]

is extremely poisonous!

In Bhopal, the pesticide Sevin was produced. As an intermediate, the highly toxic Methyl-Isocyanat (MIC), \(\text{H}_3\text{C(NCO)}\) (s. Figure) was used. At the time of the accident, no production was carried out because of overcapacities of Sevin. Only inspection work and cleaning work were carried out. By an unfortunate and unusual chain of events as well as due to severe omissions of the maintenance of the system, water penetrated into one of the tanks containing MIC. An exothermal reaction occurred which produced a huge amount of \(\text{CO}_2\) thereby increasing strongly the internal tank pressure. As a consequence, about 25 to 40 tons of MIC and other reactive gases escaped through the overpressure valve into the Atmosphere. The entire contents of the tank evaporated in less than two hours.
Bhopal: Consequences of the chemical catastrophe

Left-hand picture: This is the place at which the most terrible Industry-Catastrophe started: Ruins of the pesticide factory in Bhopal.

Right-hand photos: Warren Anderson (1921 - 2014), CEO of UCC is one of the primarily responsible persons of the catastrophe. Upper Photo: Anderson at the time of the accident; lower Photo: at the age of about 90. At 1986 he fled to the US! It took more than 25 years until 8 executing indian employees have been convicted.

It is not really known how many humans died by poisoning. It can, however, be assumed that within the first 72 hours after the accident, about 10’000 people died a horrible death! Up to today about 15’000 persons died by long-term effects. Human Right Organisations believe that altogether about 30’000 humans died. At least 100’000 people became chronically ill.

The Apocalypse of Bhopal

Apocalypse - Widespread death!

Life-long severely damaged people
5.4 Particulate Matter (PM’s) in the Atmosphere: Formation and Dynamics

A distinction is made between Primary Particles and Secondary Particles:

**Primary Particles** are emitted directly from a source, such as construction sites, unpaved roads, fields, smokestacks of fires. (see Analogy with Primary Pollutants, Section 5.2)

**Secondary Particles** make up most of the fine particles. They form in complicated reactions in the atmosphere of chemicals such as sulfur dioxides and nitrogen oxides that are emitted from power plants, industries and automobiles. (see Analogy with Secondary Pollutants, Section 5.5)

Particulates: General Remarks

«Particulates» are a part of suspended dust, also called «Particulate Matter» (PM’s).
Let $D_p$ be the diameter of the PM’s; depending on $D_p$ the following PM’s are distinguished:

**PM10**: Particle P with $2.5 \, \mu\text{m} < D_p < 10 \, \mu\text{m}$ – inhalable suspended dust; ($1 \, \mu\text{m} = 10^{-6} \text{ m}$)

**PM2.5**: Particle P with $0.1 \, \mu\text{m} < D_p < 2.5 \, \mu\text{m}$ – respirable suspended dust

**PMUP**: Ultrafine Particles P with $D_p < 0.1 \, \mu\text{m} = 100 \, \text{nm}$ ($1 \, \text{nm} = 10^{-9} \text{ m} = 0.001 \, \mu\text{m}$)

PM’s are very small solid or liquid particles in the atmosphere of the Earth. They are suspended as atmospheric aerosols. PM’s can have a natural origin or they can be anthropogenic (produced by humans). PM’s can be harmful for human health. In addition, they may have adverse impacts on the climate and on precipitations.

**Examples and origin of natural PM’s:**
- Plants (polls)
- Volcanic eruptions
- Sea salt from foam
- Forest fires
- Sahara dust
- by erosion of rocks
- Particle formation from precursors in the atmosphere

**Examples of anthropogenous PM’s:**
- Economy: Industry, industrial combustion, bulk handling
- Traffic: Road traffic, rail traffic, other traffic
- Private households and small-scale consumers
- Electricity and district heating plants
- Agriculture

PM2.5 and PM10 compared with Human Hair and Fine Beach Sand
## Fine Particulates: Categorization of Suspended Particulate Matter

### Suspended Particulates

- **Soot in the Air:** Carbon particles; from incomplete combustion processes
- **Smoke in the Air:**
  - Fine, solid particles; from mechanical processes or from resuspension
  - Fine distributed particles from chemical or thermal processes

### Subdivision according to Dust Species:

<table>
<thead>
<tr>
<th>PM: Suspended Particulate Matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM10 (Inhalable fine particulates): $D_p &lt; 10 \mu m$</td>
</tr>
<tr>
<td>PM2.5 (Respirable particulates): $D_p &lt; 2.5 \mu m$</td>
</tr>
<tr>
<td>PMUP (Ultrafine particulates): $D_p &lt; 0.1 \mu m$</td>
</tr>
</tbody>
</table>

### Subdivision according to Dust Species:

- **House dust**
  - Rock dust
  - Skin scales
  - Foodstuffs
  - Abrasive material
  - Fungals spores
  - Bacteria
- **Fine Fibres**
  - Inorganic fibres, e.g. (Asbestos, Glass wool)
  - Organic fibres (e.g. Cotton dust)
- **Mineral dust**
  - Silicates (sand)
  - Loess
- **Pollen**
  - Farina

### Particle size $D_p$ and Knudsen – Number $Kn$

The particle size (Diameter $D_p$ for a spherical particle) plays a decisive role. The same applies for the so-called Knudsen-Number $Kn$. If $\lambda_A$ is the mean free path of the air molecules, $Kn$ is defined as:

$$Kn = \frac{\lambda_A}{D_p} \quad (5.1)$$

In the following, let $\lambda_A = 68$ nm = 0.068 $\mu m$ be the mean free path of air molecules at Standard Conditions ($25^\circ C$ and 1 bar). Depending on the range of values for $D_p$, the following three regions are distinguished:

**A) Continuum region:** $D_p \gg \lambda_L$

\[ 0.2 \mu m < D_p < 100 \mu m \rightarrow 0.00068 < Kn < 0.34 \ (Kn < 1) \]

**B) Kinetic region:** $D_p \ll \lambda_L$

\[ 0.001 \mu m < D_p < 0.01 \mu m \rightarrow 6.8 < Kn < 68 \ (Kn > 1) \]

In this case, the particles behave as free molecules.

**C) Transition region:**

\[ 0.01 \mu m < D_p < 0.2 \mu m \rightarrow 0.34 < Kn < 6.8 \]
**Knudsen-Number Kn and Cunningham Correction-Factor C_C**

For Stoke's theorem (p. 227) and for the rate of descent of a falling particle as a function of time (p. 228) we need the so-called Cunningham correction factor C_C. This factor is important if the diameter D_p of the falling particle is comparable to or smaller than the mean free path λ_A of the molecules of the air. In this case, the particles are moving almost freely, i.e., without collisions with the molecules of air. The Cunningham factor C_C is written in the form

\[ C_C(\lambda_A/D_p) = 1 + 2 Kn[ A_1 + A_2 \exp(-A_3/Kn)] \]  

(5.2)

where Kn = λ_A/D_p is the Knudsen number as defined in eq. (5.1). The constants A_1, A_2, and A_3 are: A_1 = 1.257, A_2 = 0.400, A_3 = 0.55. The Figure shows the functions Kn(λ_A) and C_C(λ_A) for 20°C and 1 atm with λ_A = 6.6*10^-6 m = 0.06 μm.

---

**Viscosity and mean free path for some gases**

The viscosity η is a measure of the tenacity of a fluid (liquid or gas). The larger η, the smaller is the fluidity, and the smaller η, the larger is the fluidity. The unit of η is Pa s; for gases, the unit μPa s = 10^-6 Pa s is used.

For the dynamic viscosity of gases, η is given by:

\[ \eta = \frac{1}{3} n \bar{m} v \lambda \]

where n is the number density, \(\bar{m}\) the (average) mass of the gas particles, v the average velocity of the particles, and \(\lambda\) the mean free path of the particles.

For relatively small pressures P (0.1 < P < 10 bar), the viscosity is essentially independent on P. η depends, however, on temperature T. Since the average velocity v increases with T (v is proportional to \(T^{1.2}\)), η increases with increasing temperature T (see Figure).

The Figure shows η(T) for some gases in the temperature range between 200 K to 1000 K (-73 °C to +727 °C).

For dry air, \(\eta_A(0 °C) = 17.1 \mu\text{Pa s}, \text{ and } \eta_A(20 °C) = 18.6 \mu\text{Pa s}. \) Since air contains about 80% Nitrogen, η(N_2) is similar to η(air).

[Note: For liquids, η decreases with increasing T: η(T) = η_0 * exp(E_A / R T)].

[The viscosity of air will be used for the friction force of a particle falling in air (pp 227-231)].
Theorem of Stokes with Cunningham-Correction

We first consider the Theorem of Stokes, which describes the friction force \( F_{\text{Stokes}} \) of a spherical particle \( P \) falling with constant velocity \( v_{\text{PS}} \) in a fluid \( F \) (liquid or gas). Let \( \eta \) be the viscosity of the fluid and \( R_p \) the radius of the particle. For non-spherical particles, the radius is approximated by half of an appropriate equivalent diameter. The friction force of Stokes is then given by:

\[
F_{\text{Stokes}} = 6 \pi r_p \eta v_{\text{PS}} = 3 \pi D_p \eta v_{\text{PS}}, \quad (D_p = \text{Diameter of spherical particle}) \tag{5.3}
\]

If the sphere is small enough that its radius is comparable to the grid spacing of the molecules of the gas, the number of collisions and hence \( F_{\text{Stokes}} \) will be reduced. This reduction is described by the Cunningham-Correction factor \( C_C \) (p. 225) and for particles falling in Air (\( \eta_g = \eta \)), the following Stokes-Cunningham factor \( F_{\text{Stokes-Cunningham}} \) is obtained:

\[
F_{\text{Stokes-Cunningham}} = 3 \pi D_p \eta v_{\text{PSC}} / \eta \cdot C_C. \quad (C_C \geq 1) \tag{5.4}
\]

The Stokes-Cunningham relation is the basis for the evaluation of the sedimentation velocity \( v_{\text{PSC}} \) of the spherical particle in a fluid (liquid, oil, gas, etc). If \( F_g \) is the weight, \( F_{\text{Stokes}} \) the friction force, and \( F_A \) the buoyant force, we have: \( F_g = F_{\text{Stokes}} + F_A \). Using \( F_g = M_p g = (4/3) \pi R_p^3 \rho_p g \) and \( F_A = (4/3) \pi R_p^3 \rho_a g \) \( \rho_a, \rho_p \): densities of particle and air respectively, the stationary Stokes-Cunningham sedimentation velocity \( v_{\text{PSC}} \) of the particle \( P \) is given by:

\[
v_{\text{PSC}} = \left(2/9 \eta_p \right)^{1/5} R_p^2 g \rho_p C_C \tag{5.5 a}
\]

\[(\text{since } \rho_a << \rho_p, \text{we have neglected } \rho_a).\]

\[
v_p = \left(1/18 \eta_p \right)^{1/2} D_p^2 g \rho_p \quad \text{(Stokes-velocity)} \tag{5.5 b}
\]

It follows: \( v_{\text{PS}}(D_p) = (D_p / D_p^2)^{1/4} v_{\text{PS}}(D_p) \)

Example: Root particles

- \( D_p = 100 \text{ nm} \)
- \( \rho_p = 2 \text{ g/cm}^3 \)
- \( \eta_p = 1.8 \times 10^{-4} \text{ kg/(ms)} \)
- \( C_C = 2.9 \)
- \( g = 9.81 \text{ m/s}^2 \)

\[\rightarrow v_{\text{PSC}} = 6.1 \text{ mm/h} \]

\[= 6.1 \times 10^{-3} \text{ m/h} \]

Setting velocity of dust particles \( P \) with and without Cunningham-Correction \( C_C \); Density \( \rho_p = 1 \text{ g/cm}^3 \); \( \rho_L << \rho_p \)

- \( v_{\text{PSC}} = v_p \cdot C_p(D_p \lambda_r) \)
- \( v_{\text{PS}}: \text{Stokes-velocity-without Cunningham-Correction} \)
- \( v_{\text{PSC}}: \text{Stokes-velocity-with Cunningham-Correction} \geq v_{\text{PS}} \)

\[227 \quad 228 \]

5 – 19
Velocity of fall \( v(t) \) and Acceleration \( a(t) \) of particles falling in Air

For the velocity of fall \( v(t) \) of a particle \( P \) with mass \( m_P \) and characteristic diameter \( D_p \) in still air of viscosity \( \eta_A \) the following differential equation must be solved:

\[
m_P \frac{dv}{dt} = m_P g - \left( 3 \pi \eta_A D_p / C_P \right) v(t)
\]

(5.6)

Here, \( g = 9.81 \, \text{m/s}^2 \) is the gravitational acceleration and \( C_p \) is the Cunningham Correction factor. With the initial condition \( v(t=0) = 0 \) and the stationary velocity \( v_0 = g^* \tau \) one obtains the following solution:

\[
v(t) = v_{PSC} \left[ 1 - \exp(-t/\tau) \right].
\]

(5.7)

\( \tau \) is a characteristic relaxation time: \( \tau = m_P C_C / (3 \pi \eta_A D_p) \).

For a spherical particle with density \( \rho_p \), the mass is \( m_p = (\pi/6) \rho_p D_p^3 \); hence

\[
\tau = (1/18 \eta_A) \rho_p D_p^2 C_C \quad \text{and} \quad v_{PSC} = g \tau = (1/18 \eta_A) \rho_p g D_p^2 C_C.
\]

(5.8)

The acceleration is given by

\[
a(t) = \frac{dv(t)}{dt} = g \exp(-t/\tau).
\]

(5.9)

**Example:** \( D_p = 100 \, \mu m = 10^{-4} \, m; \, \rho_p = 1 \, g/cm^3 = 10^3 \, kg/m^3; \, \eta_A = 18.2 \times 10^6 \, kg/(m \, s); \)
\( \lambda_A = 68 \, nm = 6.8 \times 10^{-8} \, m \) and \( C_C = 1.0178 \) (value for 298 K and 1 atm). At sea level one obtains: \( v_{PSC} = 1078 \, m/h = 0.2994 \, m/s \); \( \tau = v_{PSC}/g = 0.0305 \, s \) and \( a(t=0) = g \). For an altitude \( h = 10 \, km \) and the corresponding parameters from Literature one obtains the following values: \( v_{PSC} = 1350 \, m/h = 0.375 \, m/s \) and \( \tau = 0.038 \, s \) (calculated by P. Brüesch).
Velocity of fall $v(t)$ for a particle with diameter $D_p = 1 \mu m = 10^{-6} m$

$$v(t) = v_{PSC} \left[ 1 - \exp\left( - \frac{t}{\tau} \right) \right]$$

$$\tau = \frac{\rho_r^* D_p^3 \eta_{\lambda}}{18 \eta_{\lambda}} = 3.6 \mu s$$

$v_{PSC}$ = $g \times t = 12.5 \text{ cm/h}$;  
$C_C = 1.1659$;  
$\rho_r = 1 \text{ g/cm}^3$;  
$\eta_{\lambda} = 1.82 \times 10^{-5} \text{ kg/(m s)}$.

Asbestos Minerals - Morphology

White Asbestos or Chrysotile, also known as fibrous serpentine, is a member of the mineral family of serpentines. The composition of the sheet silicate is

$$\text{Mg}_3 \text{Si}_2 \text{O}_5 \text{(OH)}_4$$

Ribeckite or Crocidolite has essentially a blue colour and is therefore also referred to as «Blue Asbestos» (Bläueisenstein). It has a fibrous crystal structure and its chemical composition is

$$\text{Na}_2[\text{Fe}^{3+}_2 \text{Fe}^{2+}_3] \text{Si}_3 \text{O}_{22} \text{(OH)}_2$$

White Asbestos or Chrysotile takes its name from its golden brown colour

Fibrous Ribeckite or Crocidolite
Asbestos is a collective term for various, naturally occurring fibrous silicate minerals. There are different minerals belonging to Asbestos. One important modification is Chrysotile, also called «White Asbestos». Chrysotile was used most extensively for technical applications, to a large part for concrete reinforcement fibres in Asbestos cement. Asbestos has been called the «miraculous fibre». The reason for this name is its great mechanical strength, its heat- and acid resistance, its excellent thermal insulation and the fact that it can be interwoven.

Due to these properties, Asbestos could also be used in the shipbuilding industry for navigation, for heat insulation in construction industry and for car-tyre industry. In the mean time, however, the severe health risks originating from working with Asbestos have been clearly recognized and since 1990, Asbestos is forbidden in many countries, for example in the EU and in Switzerland. Today, Asbestos is a severe disposal problem.

Fibre length: 5 μm
Fibre diameter: < 3 μm
Density: 2.53 – 2.65 g/cm³
Tensile strength: larger than steel wire
Chemical resistance: very good

Asbestos-related diseases: Asbestosis - Lung cancer

Asbestosis is a lung disease and belongs to the so-called Pneumoconiosis (Silicosis). It is caused by inhaled asbestos dust and for this reason, the utilization of Asbestos is forbidden in Austria and Switzerland since 1990, in Germany since 1993 and in the EU since 2005.

Pathophysiology

Fibrosis: Depending on the duration of exposition and concentration of the Asbestos fibres and on personal disposition, inhaled asbestos dust gives rise to fibrosis and lung parenchyma after a delay of 15 to 20 years.
Lung cancer: After a latency period of 25 – 40 years, Asbestosis can lead to lung cancer. Cancer of visceral pleura: Development of a Mesothelioma, a malignant tumour of the pleura (about 20 to 40 years after exposition).
Nanoparticles pollutants

Ultrafine Particles (UP) are smaller than 0.1 μm, i.e. smaller than 100 nm. The particle size is decisive of whether a dust particle can be inhaled and where the deposition takes place in the respiratory tract.

Particles with a size of 10 μm (PM10, pp 223, 224) are deposited to about 50 % in the bronchia. With decreasing size of the particles, the ratio of particles which reaches the pulmonary alveoli increases. There exist indications that particles of 1 μm and ultrafine particles smaller than 0.1 μm (100 nm) are penetrating through the Alveoli blisters and are reaching the blood.

<table>
<thead>
<tr>
<th>Sites of attack</th>
<th>Particle diameter D₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nasal area and pharyngeal space</td>
<td>5 – 10 μm</td>
</tr>
<tr>
<td>Trachea</td>
<td>3 - 5 μm</td>
</tr>
<tr>
<td>Bronchia</td>
<td>2 - 3 μm</td>
</tr>
<tr>
<td>Bronchioles</td>
<td>1 – 2 μm</td>
</tr>
<tr>
<td>Pulmonary alveoli</td>
<td>0.1 – 1 μm (100 - 1000 nm)</td>
</tr>
</tbody>
</table>

Deposition of particulate matter in the human respiratory tract

The Chernobyl Disaster of the Nuclear Reactor

The Chernobyl disaster was a catastrophic nuclear accident that occurred on 26 April 1986 at the Chernobyl Nuclear Power Plant in Ukraine. An explosion and fire released large quantities of radioactive particles into the atmosphere, which spread over much of the western USSR and Europe. The Chernobyl disaster was one of the worst nuclear power plant accidents in history in terms of casualties and cost, and it is one of only two classified as a level 7 event (the maximum classification). (The other being the Fukushima nuclear disaster in 2011).

The disaster began during a systems test on Saturday, 26 April 1986 at reactor number 4 of the Chernobyl plant, which is near the city of Pripyat. There was a sudden and unexpected power surge, and when an emergency shutdown was attempted, this led to rupture of the reactor vessel and to a series of steam explosions. The resulting fire sent a plume of highly radioactive fallout into the atmosphere and over an extensive geographical area including Pripyat. The plume drifted over larger parts of the western Soviet Union and Europe. From 1986 to 2000, 350'000 people were evacuated and resettled from the most severely contaminated areas of Belarus, Russia and Ukraine. According to official post-Soviet data, about 60% of the fallout landed in Belarus.

Nuclear reactor after the disaster-Reactor 4: Center
The estimated total death toll of the Chernobyl disaster varies extremely: Between 1984 and 2004 it ranges between about 4'000 and 985'000 (!!) depending on the source!

Invalids: in Belarus, Russia and Ukraine: ≈ 148'000 (!)
Land affected: ≈ 63'000 square miles or ≈ 163'000 km² (!)

(see also Appendix p. 5-A-4-5 for more information)
5.5 Secondary Pollutants

Secondary pollutants such as Ozone (O\textsubscript{3}) are those that are not directly emitted from a source but form when primary pollutants react chemically in the atmosphere (s. Ref. R.5.5.1).

Other Secondary Pollutants are:

- Peroxyacetyl nitrate: C\textsubscript{2}H\textsubscript{3}NO\textsubscript{5}
- Hydrogen peroxide: H\textsubscript{2}O\textsubscript{2}
- Aldehydes: R – CHO

In the following we consider only Ozone, O\textsubscript{3}. Ozone is ambivalent, i.e. it has both, positive and negative properties:

Positive: Screening of dangerous UV- radiation from the Sun

Negative: Ground-level Ozone irritates breathing and is an important Secondary Pollutant.

In Chapter 2, pp 22, 23, 37 - 42, we have already discussed some aspects of Ozone. Ozone is ambivalent: Without stratospheric Ozone, terrestrial life would not be possible; on the other hand, ground-level Ozone is a pollutant. For this reason, we include here some complementary information.
Ozone (O₃) is a molecule containing three oxygen atoms. At normal conditions, traces of ozone gas decay within a couple of days into the dimeric stable molecules O₂. On the one hand, O₃ is a strong oxidizing agent which can be harmful for living beings. On the other hand, the ozone layer present in the lower stratosphere protects human beings from damage caused by the harmful UV radiation of the Sun (see p. 241).

O₃ is a very strong oxidizing agent (much stronger than O₂) and is used for many industrial goods and consumer products. But on the other hand, its large oxidation potential is harmful for the mucosae and the tissues of the respiratory tract of humans and animals. In addition, also plant tissues are damaged if exposed to concentrations larger than 100 ppb (p. 244). For this reasons, ozone present near the ground is a severe danger and a pollutant for respiration.
Without Ozone no Life

The Ozone contained in the Ozone layer filters out the UV- radiation emitted by the Sun in the wavelength region between 200 nm and 315 nm; the intensity maximum is located at about 250 nm (1 nm = 10^{-9} m). This absorption of the UV- radiation by Ozone is of prime importance for life on Earth.

It should be mentioned that already the natural oxygen molecules \( \text{O}_2 \) and nitrogen molecules \( \text{N}_2 \) do absorb UV- radiation with wavelengths smaller than 200 nm. But the \( \text{O}_3 \) – molecules of the Ozone layer absorb in addition the UV-C radiation (200 nm – 280 nm) and the whole UV-B band (280 – 315 nm). The small remaining part of UV-B, which still reaches the surface of the Earth is responsible for sunburn as well as for the decomposition of the DNA in living tissues of humans, animals and plants.

The most important effect of Ozone in the medium UV-B range at 290 nm is drastically apparent if one realizes that the radiation intensity in the Stratosphere above the Ozone layer is about 350 million times larger than at the surface of the Earth. Despite of this enormous reduction of the UV-B radiation, a small intensity of UV-radiation still reaches the surface of the Earth. On the one hand, this UV- radiation is responsible for sunburn, but on the other hand it also enables the production of Vitamin B12 for humans.

The Ozone layer has a very small effect for the absorption of the long wavelength radiation of UV-A (315 – 400 nm), but this radiation neither produces sunburn nor does it destroy the DNA.

Temporal development of Ozone hole (see also Chapter 2, p. 41)

There is evidence for the fact that the size of the Ozone hole in the Antarctic reduces slowly and that it could be recovered by the year 2050.
Ground-level Ozone

Ozone is ambivalent, i.e. it has positive and negative effects (pp 240 – 243). While the stratospheric Ozone is protecting us against harmful UV-radiation, ground-level Ozone is usually harmful for humans, animals and plants.

At sunny and windless periods in summer, the Ozone pollution increases. This pollution is harmful for both, human health (Asthma, other respiratory problems, irritation of nucous, etc.) as well as for vegetation, buildings, materials and the climate.

Ground-level Ozone is formed by the two following precursor pollutants: nitrogen oxides (NO$_x$: pp 200, 201) and volatile organic compounds (VOC: pp 210, 211); under the influence of sunlight, Ozone and other secondary pollutants are formed.

Main contributors for these precursor stages are:

- Motorised traffic (most important)
- Industry and commerce

EU-benchmarks for O$_3$- concentrations c:
- No danger for c < 110 µg/m$^3$.
- For one-hour mean values of c ≥ 180 µg/m$^3$: information of the population.
- For c ≥ 200 µg/m$^3$: Respiratory tract irritation.
- For one-hour mean values of c ≥ 360 µg/m$^3$: warning the population, since for larger concentrations there is danger for human health.
The air pollution in China takes on a dramatic scale!

People wear masks on a day with Air Quality Index (AQI) of 320 and larger!

For AQI-values and ranges see pp. 192 and 5-A-1-2.

The AQI converts concentrations of fine particles (Particulate Matter (PM)) to a number on a scale ranging from 0 to 500. Air quality conditions range from «Good» (0 < AQI < 50) over «Unhealthy» (151 < 200) to «Hazardous» (301 < 500).

[At December 12, 2013, an AQI-value of 755 has been measured! (s. p. 192)].
Global warming is unambiguous today. This conclusion follows from observations of the global increase of the average temperature of air and oceans, the melting of ice and snow over large areas, as well as from the global increase of Sea levels.

The most important part of the increase of the mean temperature observed since the middle of the 20th century is due (with a high degree of probability) to the observed increase of the concentration of anthropogenic greenhouse gases, in particular CO$_2$, which accounts for about 60\%.

Gas warfare of World War I (1914 – 1918)

The Gas warfare of World War I was the beginning of the utilisation of chemical weapons with chlorine gas (Cl$_2$) by German forces at April 22, 1915. The famous chemist and later Nobel Price winner Fritz Haber suggested already by the end of 1914 to employ this lethal gas. The equally famous Nobel-Price winner Walther Nernst was also substantially involved in the study of the scientific aspects of this weapon. In addition to chlorine gas, the much more toxic phosgene gas, (CCl$_2$O), was also used.

The German Chief of General Staff, Erich von Falkenhayn, and the chemist and industrialist Carl Duisberg were strongly involved and responsible for the application of toxic gases.

As a response of the toxic gas attacks of the Central Powers (Germany, ...) the opposing military allians (the «Triple Entente»: England, France, Russia, ...) also used toxic gases.

It can be assumed, that out of the 10 millions deads of World Ware I, about 90'000 victims were killed by gas warfare! 

Victims of gas warfare

Fritz Haber
Walter Nernst
Erich Falkenhayn
Carl Duisberg
Zyklon-B: Poison for Mass Destruction of Nazi-Germany

The deadly effect of hydrogen cyanide, HCN, has been used in the National Socialist death camps as for example Auschwitz-Birkenau for murdering millions of people (Holocaust). The HCN-concentrations (Zyklon B) in the Gas Chambers were different depending on the special conditions, but they were always larger than 300 ppm ≈ 0.332 g/m³ = 332 mg/m³ HCN at 25 °C. (s. Appendix 5-A-3-3).

Since the liquid evaporates already at room temperature, the vapours are easily inhaled or are diffusing through the skin. Zyklon B blocks the cellular respiration. In case of an intoxication, the cells are unable to convert the vital oxygen.

Large concentrations are causing rapid breathing, paralysis, fainting, convulsions and respiratory arrest. A concentration of 300 ppm for several minutes is deadly.

Concentrations of foreign gas in Air: Conversion from ppmv to mg/m³

Definition: 1 ppmv = 1 parts per million by volume:

1 ppmv = 1 μL_FG / 1 L_A ; (FG = Foreign Gas; A = Air) 1)  

Ideal gas law: \( P_A V_{FG} = n_{FG} (R \cdot T_A) = (m_{FG} / M_{FG}) (R \cdot T_A) \) 2)  

\( P_A \) = Air pressure; \( V_A \) = Air volume; \( V_{FG} \) = volume of foreign gas; \( R \) = universal gas constant  

\( m_{FG} \) = mass of foreign gas; \( M_{FG} \) = Molar mass of foreign gas; \( n_{FG} \) = \( m_{FG} / M_{FG} \);  

From 1) and 2):  

\[
\text{ppmv} = V_{FG} / V_A = (R \cdot T_A) \cdot (P_A V_A) / (m_{FG} / M_{FG}) 
\]

or:  

\[
(m_{FG} / V_A) = (M_{FG} P_A) / (R \cdot T_A)^* \text{ppmv} 
\]

Example: Hydrogen cyanide (HCN) (s. p. 5-A-3-2)

\[ M(\text{HCN}) = 27.0253 \text{ g}; \quad T = 298 \text{ K (25 °C)}; \quad P_A = 1 \text{ atm}; \]

\[ R = 8.314'463 \text{ J/(mol K)} = 8.207*10^{-5} \text{ (atm*m}^3)/(\text{mol*K}) \];

Let: \( c(\text{ppmv}) = 300*10^6 \) (s. p. 5-A-3-2) for HCN;

\[ \Rightarrow c(\text{mg(m}^3) = [27.0253 / (8.207*10^{-5} \times 298)] \times 300 \times 10^6 ; \]

It follows: \( c(\text{HCN}) = 0.332 \text{ g / m}^3 = 332 \text{ mg / m}^3 \)

In the mass destruction chambers of the Nazi (p. 5-A-3-2), such a concentration was already deadly!
Sinkgeschwindigkeit $v(t)$ für Partikel mit Durchmesser $D_p = 0.01 \, \mu m = 10^{-8} \, m$

\[
v(t) = v_{PSC} \left[ 1 - \exp\left(-\frac{t}{\tau}\right)\right] \]

\[
\tau = \frac{\rho_p D_p^2 C_c}{(18 \eta_l)} \quad \tau = 6.9 \, ns; \quad v_{PSC} = g \tau = 245 \, \mu m/h; \quad C_c = 22.45; \quad \rho_p = 1 \, g/cm^3; \quad \eta_l = 1.82 \times 10^{-5} \, kg/(m \, s).
\]

**Sahara – Staub: Herkunft und Partikelgrössen**


Mit ca. 1,8 Milliarden Tonnen pro Jahr ist Winderosion von Mineralstaub die stärkste Aerosolquelle der nördliche Hemisphäre; fast zwei Drittel davon ist Sand aus der Sahara. Wenn die feinsten Partikel mit der Grösse des Schluffs (Korngrösse von 0.002 bis 0.063 mm oder 2 μm bis 63 μm) in dichten Wolken hoch in die Luft gehoben werden, nennt man das Phänomen einen Staubsturm. Dieser ist nicht zu verwechseln mit einem Sandsturm, bei dem die grösseren Sandpartikel (Korngrössen 0.002 mm bis 2 mm) verfrachtet werden. Bei diesen wird eine niedrige Wolke aus bewegtem Sand gebildet, der lediglich wenige Zentimeter bis maximal 2 m vom Boden in die Höhe reicht.

**Saharastaub in Nordafrika vom 4. 4. 2014**

**Sahara-Dielle**

<table>
<thead>
<tr>
<th>Component</th>
<th>% Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>49.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.1</td>
</tr>
<tr>
<td>CaO</td>
<td>11.5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>10</td>
</tr>
<tr>
<td>C₂O</td>
<td>9</td>
</tr>
<tr>
<td>MnO₂</td>
<td>2</td>
</tr>
<tr>
<td>MgO</td>
<td>0.4</td>
</tr>
<tr>
<td>Organics</td>
<td>5.5</td>
</tr>
<tr>
<td>Traces</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Sahara – Dust in Austria and Germany

Sahara-Dust in Tyrol

Seefeld in the Federal Province Tyrol (Austria) at the afternoon of February 21, 2004. The Sahara dust darkened the sky. (Picture from Friedrich Föst)

Visit from North Africa

«A glaring red Sky, loaded with finest sand particles»: This was the appearance of the Sunrise on April 3, 2014 over Remscheid (Governorate Düsseldorf in North-Rhine Westphalia). The darkening was due to a low-pressure area which extended from England to Marocco where it lifted the desert sand.

Chernobyl: Radioactive contamination Areas from Fallout

Here, we confine ourselves to the nuclear Fallout caused by the catastrophe. It was the Graphite-fire in the Reactor that released most of the radioactive particles into large altitudes of the atmosphere (1500-10'000 m).

The clouds containing the radioactive Fallout have initially been distributed over large parts of Europe and finally over the whole Northern Hemisphere. Changing air streams drove the clouds to Scandinavia, then over Poland, Chechia, Austria, Southern Germany and Northern Italy. A third cloud reached the Balkans, Greece and Turkey. Depending on the regional rainfalls, the ground was contaminated to different degrees. The quoted data indicate the start of the radioactive Fallouts.

The Sievert (unit symbol Sv), according to the Swedish physician and physicist Rolf Sievert, is a measure for the radiation dose. It is used for the determination of the radiation load of biological organisms and for the evaluation of radiation risks; 1 mSv = 0.001 Sv.

- 0.01 – 0.03 mSv: Dose obtained by an X-ray of the thorax.
- 10 – 20 mSv: Dose obtained from a Computer Tomography of an adult.
- 1’000 mSv: About 10% of the exposed people are developing cancer and Leukemia.
- 3’000–4’000 mSv: without medication; 50% of exposed persons are dying.
- > 8’000 mSv: Death within very short times after short-time radiation exposure.

some examples

5-A-4-3

5-A-4-4

5 - 33
References: Chapter 5

5.1 Air Contamination - General

R.5.1.1 p. 192: Air pollution – General
a) Air quality index: http://en.wikipedia.org/wiki/Air_quality_index
b) Beijing Air Pollution Exposes China’s Health & Environmental Risks
http://www.globalsherpa.org/shona-air-pollution-health-environment

c) Luftverschmutzung: http://de.wikipedia.org/wiki/Luftverschmutzung
d) Bild: «Luftverschmutzung in Peking: Atmen kann tödlich sein» – Bernhard Zand (Spiegel Online)
http://www.spiegel.de/wissenschaft/natur/feinstaub-pekings-luftverschmutzung-erreicht-drastische-werte...

R.5.1.2 p. 193: Form and Sources of Air Pollution
a) Outdooe Air Pollution - European Lung Foundation - ELF
b) Indoor Air Pollution - European Lung Foundation - ELF
c) left: Arten und Quellen der Luftverschmutzung – European Lung Foundation (ELF)
d) right: Arten der Luftverschmutzung - Changes of Natural Composition of Air:
(Arranged and adapted to English by P. Brüesch)

R.5.1.3 p. 194 : Origin and Sources of Pollutants
Table from Reference R.5.1.2 c) - (Translated from German to English by P. Brüesch)

R.5.1.4 Luftverschmutzung: Ein Leitprogramm für den Geographieunterricht
ETH – Institut für Verhaltenswissenschaften
Geographisches Institut - [PDF] www.edu.org/Umweltverschmutzung
[Herausgegeben von S. Reinfried und J. Roth]
5.2 Primary Air Pollution

R.5.2.0  p. 195: Definition of Primary Air Pollutants
Primary Pollutants: (pp 195 – 220) ; Secondary Pollutants: pp 221 - 233)

a) Air Pollution - [link]
b) What is the difference between primary and secondary pollutants? [link]
c) Primary Pollutants - [link]
d) Primary & Secondary Pollutants [link]
e) Unit 11: Atmospheric Pollution / Section 3: Primary Air Pollutants [link]
f) What are the Primary and Secondary Air Pollutants? [link]

R.5.2.1  pp. 196 - 197: Carbon dioxide – CO₂

a) Carbon dioxide - [link]
b) Respiratory center - [link]
c) Kohlenstoffdioxid - [link]
p. 196: Pictures of «Levis structure of CO₂» from: [link]
p. 196: Picture of «Space-filling model» of CO₂, from: [link]
p. 197: Picture of «Carbon dioxide toxicity» from Reference R.5.2.1 a)

R.5.2.2  p. 198: Carbon monoxide – CO

a) Carbon monoxide - [link]
b) Kohlenstoffmonoxid - [link]
c) CO: Farblos, geruchlos und tödlich: Gefährliches Kohlenmonoxid, [link]

R.5.2.3  p. 199: Carbon monoxide - Poisoning

a) Carbon monoxide Poisoning - [link]
b) Carbon Monoxide – Health Effects - [link]
c) Kohlenmonoxid (CO) - [link]
p. 196: Figure text translated from German to English by P. Brüesch

d) Fabrios, geruchlos und tödlich: Gefährliches Kohlenmonoxid [link]

R.5.2.4  p. 200: Nitrogen oxides NOₓ and Nitrous oxide N₂O

a) NOₓ - [link]
b) Nitrogen dioxide: NO₂ - [link]
c) Nitric oxide: NO - [link]
d) Nitrous oxide: N₂O - [link]
e) Stickoxide - [link]

R.5.2.5  p. 201: NOₓ Toxicity and Emissions

a) Nitrogen Dioxide Toxicity - [link]

5 - 35
h) Untersuchungen zur Rolle der Vegetation beim Austausch von Stickstoffdioxid mit der Atmosphäre
(Urban, A. J., & Kesselmeier, Jürgen. (Max-Planck-Institut für Chemie, Mainz))


l) Natural gas (with molecular structure) - http://en.wikipedia.org/wiki/Methane

m) Methan - http://de.wikipedia.org/wiki/Methan


R.5.2.6 p. 202: Methane - CH₄

http://en.wikipedia.org/wiki/Methane - (with molecular structure)


c) Methane Sources - Rice Paddies d) - Nassrastelder sind ein Entstehungsort für Methan
http://www.gwhorganic.org/methaneice.htm

d) Flammability diagram (of Methane) - http://en.wikipedia.org/wiki/Flammability_diagram

R.5.2.7 p. 203: Methane - Dangers

a) Reference R.5.2.6 a) under Safety

b) Methane Safety - http://www/lagri.gov.ab.ca/EDepartment/dep/docs.nsf/all/ayde903

c) Methane Sources - Rice Paddies d) - Nassrastelder sind ein Entstehungsort für Methan

R.5.2.8 p. 204: Sulfur oxides - General


b) Sulfur oxides (SO₂) - Swedish Pollutant Release and Transfer Register
http://www.agsluppliftror.naturvardsverket.se/EN/Substances/Other-gases/Sulphur-oxides/

c) SULPHUR OXIDES (SO₂) - http://dwb.unl.edu/teacher/nfs/cf9/conflinks/www casinghome.org/sulphur.htm

R.5.2.9 p. 205: Sulfur dioxide and Sulfuric acid

a) See References d), h), and i) of p. R.5.2.8

b) Air Pollution from Sulfur Dioxide - https://www.tceq.texas.gov/airquality/sip/criteria-pollutants/sip-so2

c) Sulfur Dioxide - http://www.cleanairtrust.org/sulfurdioxide.html

d) About Sulfur Dioxide - http://nae. defra.gov.uk/overview/pollutants/pollutant_id=8

R.5.2.10 p. 206: Sulfur trioxide


b) Sulfur Trioxide & Sulfuric Acid (H₂SO₃) - http://www.atdrr.cdc.gov/substances/oxsubstance.asp?topic=47

R.5.2.11 pp 207 - 208: Ammonia (NH₃)


5 - 36
5.3 Volatile Organic Compounds

R.5.3.1 p. 209: Toxic Organic Gases - Title
R.5.3.2 p. 210: Volatile Organic Compounds - VOC's - General
b) Flüchtige organische Verbindungen (http://de.wikipedia.org/wiki/F1%C3%BCchtige_organische_Verbindungen)
Figure of the Isoprene-molecule: s. Isopren – Images
Figure: zeitlicher Verlauf von VOC in der Schweiz: s. Flüchtige organische Verbindungen

R.5.3.3 p. 211: Volatile Organic Compounds - Toxicity
b) Flüchtige organische Verbindungen (VOC)
f) Dichlormethan (DCM) - CH₂Cl₂ - (CAS-Nummer: 75-09-2) - Begründung zu Dichlormetan in TRGS 900
  www.baua.de/can/service/_900-dichlormethane.pdf
g) Tetrachloreylen - C₂Cl₄ - http://en.wikipedia.org/wiki/Tetrachloreylen
h) Tetrachlorehren - C₂Cl₄ - http://de.wikipedia.org/wiki/Tetrachlorehren

R.5.3.4 p. 212: Hydrogen Cyanide (HCN) in the Atmosphere

R.5.3.4 (cont.)

R.5.3.5 p. 213: Persistent Organic Compounds - POCS
a) Persistent organic pollutant
http://en.wikipedia.org/wiki/Persistent_organic_pollutant
http://www.epa.gov/international-cooperation/persistent-organic-pollutants-global-issue-global-response
c) [PDP] Persistente Organische Verbindungen (POP's)
www.ids.unibi.de/.../POP_de.pdf

R.5.3.6 p. 214: Agent Orange - Dioxin - Vietnam War -1

R.5.3.6 (cont.)

R-5-6

R-5-7
### 5.4 Particulate Matter (PM's) in the Atmosphere - Formation and Dynamics

| R.5.3.7 | p. 215: «Agent Orange» – Dioxin - Vietnam War – 2  
|---------|--------------------------------------------------|
| d) Agent Orange - [http://www.agentorange-vietnam.org/background/](http://www.agentorange-vietnam.org/background/)  

| R.5.3.8 | p. 216 – 217: The Seveso Disaster with Dioxin  
|---------|--------------------------------------------------|
| d) Seveso - Unglück - [http://de.wikipedia.org/wiki/Sevesoung%C3%BCck](http://de.wikipedia.org/wiki/Sevesoung%C3%BCck)  
| f) Dioxin-Scandale - Seveso - p. 217; Picture: Chloracne – victim - [http://einstages.spiegel.de/static/entry/das_ieberal_fit/78322/chorakne.html](http://einstages.spiegel.de/static/entry/das_ieberal_fit/78322/chorakne.html)  
| g) Als die Giftwolke kam - [http://www.wissen.de/als_die_giftwolke_kam](http://www.wissen.de/als_die_giftwolke_kam)  
| h) Seveso - Opfer des Chemikalienwahnsinns - [http://www.greenpeace.de/themen/chemie/nachrichten/artikel/seveso_opfer_des_chemikalienwahnsinns](http://www.greenpeace.de/themen/chemie/nachrichten/artikel/seveso_opfer_des_chemikalienwahnsinns)  

| R.5.3.9 | pp 218 – 220: The Catastrophe of Bhopal  
|---------|--------------------------------------------------|
| e) Methyl isocyanate - [http://en.wikipedia.org/wiki/Methyl_isocyanate](http://en.wikipedia.org/wiki/Methyl_isocyanate)  

### 5.4.0 p. 221: Primary and Secondary Air Pollutants

| R.5.4.0 |  
|---------|--------------------------------------------------|

| R.5.4.1 | p. 222: Secondary Air Pollutants and Particulates  
|---------|--------------------------------------------------|
| d) Particulate Matter (PM) - Basic Information - contains Figure of p. 222 - [http://www.epa.gov/pm/basic.htm](http://www.epa.gov/pm/basic.htm)  

R.5-8

R.5-9

5 - 38
R.5.4.2 pp 223: Fine Particulates: Categorization
Feinstaub – Kategorisierung von Schwefelteilchen
(Taken from Reference R.5.4.1 e); translated from German to English by P. Brüesch

R.5.4.3 p. 224: Particle size Dp and Knudsen-Number Kn - Partikelgrösse Dp ung Knudsen-Zahl Kn
a) Part of the Information is contained in the Article from Otto Klenner: [PPT] – Partikel - Unweltmeteorologie – 11. Aerosolpartikel
http://www.uni-muenster.de/.../vern_metep_u11aerosolphysik...
(Representation and Text adapted and translated from German to English by P. Brüesch)

R.5.4.4 p. 225: Knudsen number Kn and Cunningham Correction Factor Cc
Contains also information about the relation between the Knudsen-Number Kn and the Cunningham Correction factor Cc in addition, it contains a Figure illustrating the functions Kn(Dp) and Cc(Dp) versus the particle diameter Dp.
b) Particulate Matter - http://www.ce.udel.edu/~dentel/434/Lecture%203a.pdf - (with Figure of Slip Correction)

R.5.4.5 p. 226: Viscosity of air

R.5.4.6 p. 227: Stokes Law: Friction force acting on a falling spherical particle

e) s. Reference R.5.4.4 a) for Cunningham Correction Factor

R.5.4.7 p. 225, p. 227: (cont.): Remarks to Knudsen-number Kn(Dp) and Cunningham correction factor Cc(Dp)
f) see Reference R.5.4.4 for Figure (complemented by P. Brüesch )
g) Slip Correction Factor
http://aerosol.ees.ufl.edu/aerosol_trans/section06.html

This Reference contains a physically appealing comment explaining the Cunningham «Slip Correction factor Cc»:
«For very small particles (with a diameter of less than 1 μm), it is found that the settling velocity (Sinkgeschwindigkeit) is faster than that predicted by Stokes law, Why is that?
Answer: A critical assumption of Stokes law is that the relative velocity of the gas (air molecules) right at the particle surface is 0. This is true if the medium (air) is «continuous». As the particle gets smaller, the medium is no longer «continuous» to the particle and each gas molecule is no longer invisible to the particle. Gas molecules moving around the particle may miss the particles which we call «slip» (ein Teilchen schlüpft durch die umgebenden Luftmoleküle). So, the velocity of the gas right at the surface is no longer 0 due to the missing collision. Since the collision is the source of drag (Reibung), the particle's settling velocity becomes faster than previously theorized due to smaller-than-expected resistance. (The article cited also contains an illuminating motion picture of both, a «continuous» air-medium with larger particles as well as for small slipping particles in a non-continuous «medium».

R.5.4.8 p. 228: Particle's settling velocity – Figure
a) Stationary setting velocity with and without Cunningham correction factor. The Figure has been constructed by P. Brüesch from Literature data (viscosity and mean free path of air, etc.) and a MATLAB-Program.
The calculation has been performed for normal conditions.
b) Physical quantities::;
Value for air: ηa = 1.82*10^-5 kg/(m s) at 20 °C and 1 atm from:
Tabelle 2, «Stoffgrössen für trockene Luft» bei 0.013 bar und 20 °C
- www.versorgung.entsorgung.w.h.s.de/.../Tabelle_2-Stoffgr...
2) Mean free path λa of air . Molecules - Mean free path - http://en.wikipedia.org/wiki/Mean_free_path
λa = 68 nm = 6.8*10^-10 m at 1 bar and at room temperature

R-5-11

5 – 39
R.5.4.9  p. 229: The velocity of fall and the acceleration of particles falling in air.

The equation (5.6) for a particle falling in air is an inhomogeneous differential equation of first order of the form: $dv/dt = a(t)v + b(t)$ with initial conditions $v(0) = 0$. In the present case, $a$ and $b$ are independent on time $t$ which simplifies considerably the solution. One obtains immediately the solution for the time-dependent velocity $v(t)$ as quoted in equation (5.7) at p. 229:

<table>
<thead>
<tr>
<th>a)</th>
<th>Differential equation of a particle falling in air:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Part of the information is contained in the Article of Otto Klemm: Partikel-Umweltmeterologie-11…Aerosolpartikel <a href="http://www.uni-muenster.de/%E2%80%A6/emn_meteo_u11aerosolphysic%E2%80%A6">www.uni-muenster.de/…/emn_meteo_u11aerosolphysic…</a> (Differential equation solved by P. Brüesch)</td>
<td></td>
</tr>
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</table>

R.5.4.10  p. 230: Velocity of fall $v(t)$ of a spherical particle $P$ with diameter $D_p = 100 \mu$m (Calculation and Figure from P. Brüesch)

R.5.4.11  p. 231: Velocity of fall $v(t)$ of a spherical particle with diameter $D_p = 1 \mu$m (Calculation and Figure from P. Brüesch)

R.5.4.12  p. 232: Asbestos Minerals–General


R.5.4.13  p. 233: Properties - Problems

| a) | Classification of hydrous layered silicates - http://www.ovy.uga.edu/Schroeder/geo6550CM07.html |

R.5.4.14  p. 234: Asbestosis

| b) | http://de.wikipedia.org/wiki/Asbestose |

R.5.4.15  p. 235: Nanoparticles - Pollutants

| b) | Landesanstalt für Umwelt, Messungen und Naturschutz - Baden - Württemberg Wirkungen (von Feinstaub) auf den Menschen http://www.lubw.baden-wuerttemberg.de/servlet/is/18796/ (Bild (retouchiert)): Ablagerung von Feinpartikeln im menschlichen Atemtrakt) |

R.5.4.16  pp. 236, 237: Effect of the Chernobyl disaster

| a) | Chernobyl disaster http://en.wikipedia.org/wiki/Chernobyl_disaster |
| d) | Chernobyl Q&A http://www.friendsforchernobyl.org/quests.html |

5 – 40


5.5 Secondary Pollutants

R.5.5.1 p. 238: Secondary Pollutants - General
b) Beispiele für Sekundärschadstoffe - FACHWISSEN WEBSEITE (/)
   http://www.yibacon.com/beispiele-fuersekundarschadstoffe/

R.5.5.2 pp 239 - 243: Ozone
c) Ozone Science: The Facts Behind the Phaseout
   http://www.epa.gov/ozone/science/sc_facts.html
e) p. 241: Picture of Ozone layer in the Stratosphere
s. Images: Ozone layers in the Stratosphere // s. Bilder: Ozonschicht in der Stratosphäre
   Figure Text translated from German to English by P. Brüesch
f) Ozonschicht soll sich bis 2050 regeneriert haben
   www.welt.de/wiznzenschacht/imweb/article109659663/Ozonschicht-soll-sich-bis-2050-regeneriert-haben.html
   (Pictures of p. 243 Ozone layers 1998 and 2012; Figure Text rewritten by P. Brüesch)

R.5.5.3 p. 244: Health problems caused by ground-level Ozone
a) Ground-Level Ozone - https://www.epa.gov/air/default.asp?lang=En&n=590611CA-1
b) Ground-Level Ozone - EPA: Environmental Protection Agency
   http://www.epa.gov/groundlevelozone/
c) Ozone (O₃) Standards - http://www.epa.gov/tn/naaqs/standards/ozone/s_o3_index.html
d) Ground-level Ozone - Health Effects
   http://www.epa.gov/groundlevelozone/health.html
e) How Ozone Pollution Works - Avoiding and Reducing Ozone
   http://science.howstuffworks.com/environmental/green-science/ozone-pollution1.htm
   (Picture: Ozone-damaged plant and healthy plant)
(g) Ozon - Grenzwerte - Richtwerte / Allum – Allergie, Umwelt und Gesundheit
   http://www.allum.de/stoffe-und-ausloeser/ozon/grenzwerterichterte

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Appendix – Chapter 5

R.A.1.1 p. 5.A-1-1: Air pollution in Beijing
a) Six years of Beijing air in one scary chart
   http://go.viz197798/six-years-of-beijing-air-pollution.summed-up-in-one-scary-chart/
b) Die Luftverschmutzung in China nimmt dramatische Formen an (Keystone);
   www.blick.ch/-/ausland/chinas-behoerden-geben- - upper Picture – Air contamination
   lower Picture found under «Air pollution in Beijing» - Pictures

R.A.1.2 p. 5.A-1-2: Air Quality Index (AQI) – A Guide to Air Quality and Your Health
   http://airnow.gov/index.cfm?action=aqibasics.ag

R.A.2.1 p. 5.A-2.1: Global Warming
a) s. In «WATER»: (P. Brüesch) - Reference R-0-4 - Chapter 5: pp 246 - 249
c) Globale Erwärmung - http://de.wikipedia.org/wiki/Globale_Erwa%C3%9Fung

R.A-3-1 Use of toxic gas in World War I (1914 – 1918)
d) Gaskrieg während des Ersten Weltkrieges
   http://de.wikipedia.org/wiki/Gaskrieg_w%C3%A4hrend_des_Erstes_Weltkrieges
e) Fritz Haber - http://de.wikipedia.org/wiki/Fritz_Haber
l) Phosgen - http://de.wikipedia.org/Phosgen

R-5-14

R-5-15

5 – 41
a) Hydrogen cyanide: [link]
b) Cyanic acid - [link]
(Vergiftung der Juden durch den Nationalsozialismus in Auschwitz-Birkenau – Holocaust)
c) Zyklon B: [link]
d) Allgemein – Zyklon – B: [link]
e) The Holocaust - [link]
f) Auschwitz - Birkenau: [link]
g) Gaskammer (Massenmord): [link]
h) Die sieben Gaskammern von Auschwitz
[link]
i) Gaskammer Auschwitz – Bild & Foto von Bernd 1959 aus Krieg und seine Folgen (14103841) /
[jewishvirtuallibrary.org]
j) akdh.net - Auschwitz and Leugnung des Holocaust: Der Leuchterreport
[link]
R-A-3-3 p. 5-A-3-3: Conversion of ppm to mg/m^3
a) EPA, On-line Tools for Site Assessment Calculations - Indoor Air Unit Conversion
[link]
b) Air Dispersion Modelling Conversions and Formulas
[link]
c) Konzentrationsrechner (Umrechnung von Konzentrationsgrössen, Gehaltsgrössen)
[link]
d) For a general conversion relation based on the ideal gas law of ppmv to mg/m^3 and vice versa
see p. 5-A-3-3; Application to HCN: ppmv → mg/m^3
R-A-4-1 p. 5-A-4-1: Sinkgeschwindigkeit v(t) für Partikel mit Durchmesser D_p = 0.01 mm
(Berechnung und Figur erstellt von P. Brüesch)

R-5-16

R-A-4-2 p. 5-A-4-2: Origin and Particle Size
a) Mineral dust. Sahara dust - [link]
b) Intercontinental Transport of Dust: Historical and Recent Observational Evidence
Rudolf B. Husar; Chapter 11 of the Book: Intercontinental Transport of Pollutants., A. Stohl, Ed.
Springer Verlag 2004 - (right-hand picture)
c) SaharaStaub über Bayern: [link]
d) SaharaStaub
[link]
Wetter und Klima – Deutscher Wetterdienst – GIZON, GAW, Luftchemie - Umwelthemen: SaharaStaub
[e) Sandsturm: [link]
f) Schluff - [link]
R-A-4-3 p. 5-A-4-3 Sahara Dust in Europe
a) Sahara Dust In European Skies
[link]
b) Wetter – Sahara-Staub in den Alpen - upper picture
[link]
c) Besuch aus Nordafrika – lower picture - [link]
R-A-4-4 p. 5-A-4-4 Chernobyl – Spread of radio-active contaminates
a) Global Radiation Patterns
(Spread of radio-active contaminates into the atmosphere from the Chernobyl accident …)
[link]
b) Fragen und Antworten zu Strahlenschutz – Aspekte in Japan
[link]
enthält: «Einige wichtige Dosis- und Grenzwerte» contains: «Some important Doses and limiting values»
c) Picture of contaminated area of radio-active Fallout found under:
«Ausbreitung des Fallout von Tschernobyl - Bilder»

R-5-17