

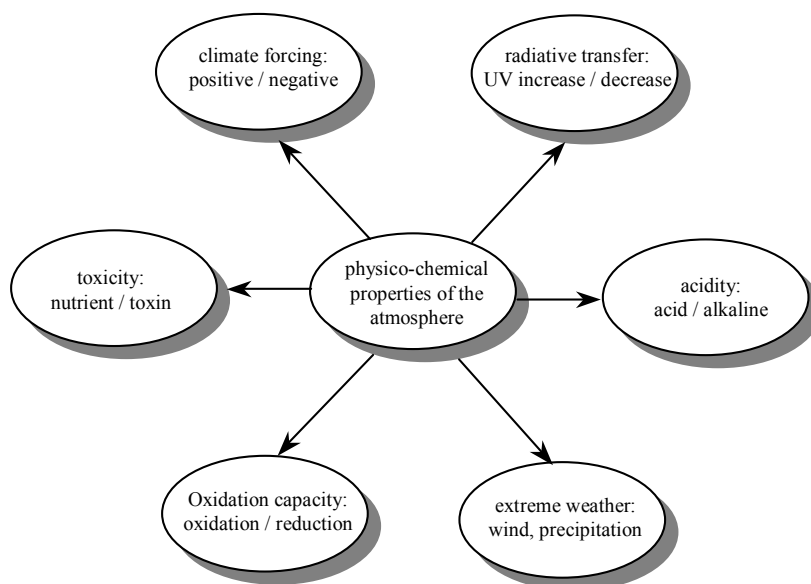
## 4 Impact of air pollutants

As mentioned in the Introduction (chapter 1), the problem is not the increasing concentration of trace species (or changing chemical composition of the atmosphere) but the *effects* as a result from *impacts* of trace species. Trace species (gaseous, particulate matter and dissolved in hydrometeors<sup>1</sup>) which show an increased concentration compared to natural levels are called *pollutants*.

### 4.1 Atmospheric impact potentials

Trace species (pollutants) in air lead, individually and/or together with other trace species, to different impacts (and subsequent effects) on the properties of the atmosphere and the reservoirs (biosphere, geosphere, technosphere) and its compartments (plants, animals, humans, soils, materials etc.). The following impact potentials result from the atmosphere (Fig. 1)

- oxidation potential (oxidative stress),
- acidifying potential (“acid rain”),
- toxicity (toxicological impact of individual pollutants),
- climate forcing (warming or cooling the atmosphere),
- UV(B) increase (stratospheric ozone depletion),
- extreme weather (storm, flooding etc.).



**Fig. 1**

Impact potentials

The pollutants may have individual properties (e.g. toxicity, radiation absorption) but also contribute to summarizing properties (acidity, greenhouse effect etc). Some properties (impacts) might be synergistic (i.e. the resulting impact of two or more pollutants is different from the sum of individual impacts of

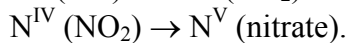
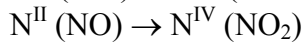
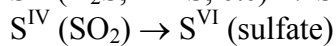
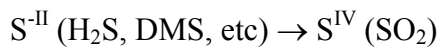
single pollutants). The only atmospheric impact not directly resulting from changing chemical composition of the atmosphere are so-called *extreme weather* situations, e.g. heavy rain and hurricane, which may have strong effects on nature and mankind (harms on forest and buildings, fatalities). However, the discussion is going on, whether warming of the atmosphere (see chapter “greenhouse effect”) will lead to increased extreme weather events.

<sup>1</sup> Hydrometeors are all *aqueous* particulates in the atmosphere: droplets from clouds, fog and rain, and different frozen particles (snow crystals, hails, ice grains etc.) in clouds and precipitation. Due to formation of hydrometeors from cloud condensation nuclei (CCN) or ice nuclei (IN), which represent a chemical substrate of particulate matter as well as sorption processes from gas phase into hydrometeors they contain dissolved (and undissolved) chemicals.

Thus, this impact may be a result of climate change. This example should also emphasize that the impact potentials are partially linked to each other. Production of atmospheric acidity is based on availability of oxidation capacity. Moreover, trace species can contribute to different impact potentials, e.g. CH<sub>4</sub> to warming the atmosphere (greenhouse effect) and increased oxidation capacity (tropospheric O<sub>3</sub> formation). The *effects* of the impact potentials, which also can be identified as the *problem*, are

- vegetation injuries,
- health effects (humans, animals),
- damages on materials (corrosion),
- erosion (soils, sediments, rocks),
- climate change effects.

The *oxidation potential* (or capacity) is the ability of the atmosphere to oxidize (reduced) trace species, e.g.



In this way primary emitted pollutants will be oxidized to “stable” products (e.g. nitrate, sulfate). This process is also called *self-cleansing* of the atmosphere. Intermediary, however, often more reactive (and more toxic) substances will be produced. Connected with the production of sulphate and nitrate is the formation of acidity (in terms of dissolved H<sup>+</sup>). Production of sulphates in form of particulate matter and other aerosol particles<sup>2</sup> (e.g. organics from VOC – volatile organic compounds) is also associated with climate forcing, i.e. solar scattering by particulate matter. Thus, between the impact potentials exist many feedbacks – or with other words – the system is complex due to multipollutant effects.

On the other hand, the oxidation capacity is also expressed as the sum of (photo)oxidants: ozone (O<sub>3</sub>), radicals (OH, HO<sub>2</sub>, NO<sub>3</sub> etc.) and peroxides (H<sub>2</sub>O<sub>2</sub>, ROOH). All these species contribute in different reaction to oxidation of reduced components as mentioned above, but also have a direct impact on life which is called *oxidative stress*.

The *acidifying potential* describes the ability of the atmosphere to make the environment more acidic. This happens via *deposition*<sup>3</sup> of acidifying components (acid deposition). The

<sup>2</sup> Atmospheric aerosol is defined being a dispersion of *non-aqueous* particles (not molecules) within air. Due to totally different chemical and physical properties of aqueous droplets (hydrometeors) we will not call them belong atmospheric aerosol (in technics, however, also droplets dispersed in gas are defined as aerosol). Aerosol particles may also contain significant amounts of water (e.g. activated CCN) but they are predominantly solid. Aerosol particles may also be *liquid*, e.g. hydrates of sulfuric and nitric acid in stratosphere at low temperatures, but water content is minor.

<sup>3</sup> Deposition in contrast to emission is the output flux of trace species from the atmosphere. Several physical processes will remove substances from the atmosphere. *Sedimentation* is the process for removal of particles larger than about 5 μm due to gravitational settlement (*Stokes-law*). Although precipitating hydrometeors (e.g. rain drops) also fall down due to gravitation force, we call this process *wet deposition*. As already mentioned in foot note 1, the trace species dissolved in hydrometeors come from the CCN and gases via cloud formation and processing (*in-cloud scavenging*), finally ending with falling rain drops (*sub-cloud scavenging*). A third deposition process is called *dry deposition*, an efficient removal process for gaseous components and particulate matter from the accumulation mode (0.1-1 μm). When the species are in contact with the Earth surface (water, soil, vegetation, material etc.) they might be sorbed (physically and and/or chemically) resulting in a concentration gradient above the surface and subsequent vertical turbulent transport downwards. Thus, dry deposition is a complex process depending from the properties of the surface, the trace species and the meteorological status of the atmospheric boundary layer.

*acidity* is a budget figure in terms of the difference between acids and bases. Simplified (when the pH of the system is less than 6) we can describe the acidity with the concentration of free hydrogen ions ( $H^+$ ). However, things are much more complicated<sup>4</sup> and we have to take into account also weak acids (and bases) as well as precursors (e.g. anhydrites like  $SO_2$ ). To make it even more complicated, the resulting acidity in soils (and lakes) after deposition might shift from the atmospheric acid deposition, due to interactions with the soils compartments. Ammonia ( $NH_3$ ) being the only gaseous base in atmosphere will quickly produce ammonium ( $NH_4^+$ ), an extremely weak acid. After its deposition it will be oxidized by micro-organisms (*nitrification*) making free protons, i.e. acidifying the soil.

We see, these important impacts like oxidative stress, acidification, contamination will result to effects only after deposition of related trace species (pollutants). In contrast, increase of UV(B) and climate forcing are atmospheric processes due to interaction between trace species and radiation. The atmospheric effects (warming, cooling, UV) will have subsequent impacts (feedbacks) on the atmosphere, such as photochemistry, pollutants transport, cloudiness, precipitation etc. On a subsequent “impact level” (cf. Fig. 4 in Introduction) there are effects concerning human health, vegetation, land use etc., being the *real* problem.

Impacts due to deposition have a geographic component, thus depend from the site. Therefore not the concentration (mass per volume) of pollutants is the relevant parameter for describing the effect but the time-related matter input (exposure or dose). In pharmacology *dose* is defined being the incorporated quantum. In ecotoxicology normally the product of concentration and time (dimension e.g. ppb·h, see later the definition for AOT-40) is the impact parameter to be quantified. Besides, it is useful to define a *specific* deposition (in sense of incorporated quantum per time).  $F_{\text{spec}}$  is the amount of pollutant per square a (leaf surface, soil etc.):

$$F_{\text{spec}} = \frac{1}{a} \frac{dn}{dt}. \quad (1)$$

Due to the diurnal and seasonal variation of  $F_{\text{spec}}$  it should be averaged (integrated) over time and we get a dose:

$$\text{dose}_{\text{spec}} = \int_0^t F_{\text{spec}} dt. \quad (2)$$

Without detailed explanation it is believed that the same specific deposition on a tree will have different effects in winter and in summer. An *intelligent*<sup>5</sup> air pollution control (and management) must therefore include a time-related aspect.

Injures on plants, animals and humans might result directly from specific properties of pollutants (toxicity) but also from integral characteristics (oxidative stress, acidification) as well as indirectly via changes of living conditions (soil and water quality, nutrients, feed, food, climate). Broad vegetation damages, documented with *Waldsterben* (forest decline)<sup>6</sup> in Saxonia (Osterzgebirge – “eastern ore mountains”) at the beginning of the 1970s destroyed the whole ecosystem and can influence the local climate and water cycle. Indeed, in most

<sup>4</sup> See my paper „Acid Rain – Gone?“ on the homepage [www.luft.tu-cottbus.de](http://www.luft.tu-cottbus.de).

<sup>5</sup> Behind an intelligent air pollution control I understand a strategy not fixed primary on (mostly politically) agreed emission abatement but orientated on preventable effects.

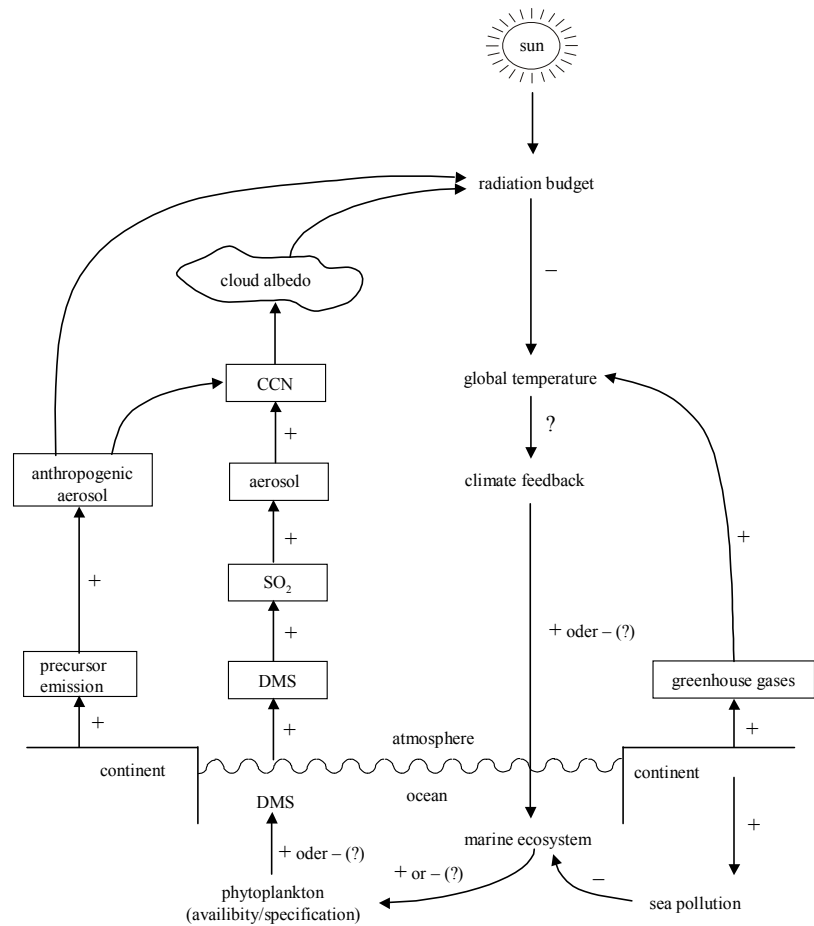
<sup>6</sup> The German word „Waldsterben“ has been used as a technical term for „new-type forest decline“, observed in the 1970s. Waldsterben (forest disease), i.e. forest (ecosystem) death and not only injuries, however, was only observed in forests with direct influence of primary pollutants ( $SO_2$ ), so-called classical forest decline; see subchapter 4.2.2.

cases other environmental impacts than air pollution will result in the total loss of vegetation, e.g. forest burning, forest clearing and contamination). Contamination may be increased by atmospheric deposition of heavy metals and POPs (persistent organic pollutants).

The interaction between plants and atmosphere is very impressively demonstrated by the cycle shown in Fig. 2. This cycle, known as the GAIA hypothesis, involves the CCN formation from sulphur emitted by oceanic plankton. Marine clouds initiate the global water cycle. Clouds generally act as climate adjusters. Within certain variation, the cycle is positively or negatively coupled back by temperature. Perturbation of this controlling mechanism exists at several sites. Pollution of sea water (e.g. iron pollution) negatively influences the plankton activity. Atmospheric warming by greenhouse gases positively affects the plankton growth but also the water cycle. Finally, man-made emissions might increase the CCN number and consequently cloudiness (see Fig. 3). We do not know where the threshold lies when breaking up the self-controlling cycle. Emphasizing that it is a hypothetical cycle and reality is much more complex, it illustrates as an example the close interaction between biosphere and atmosphere.

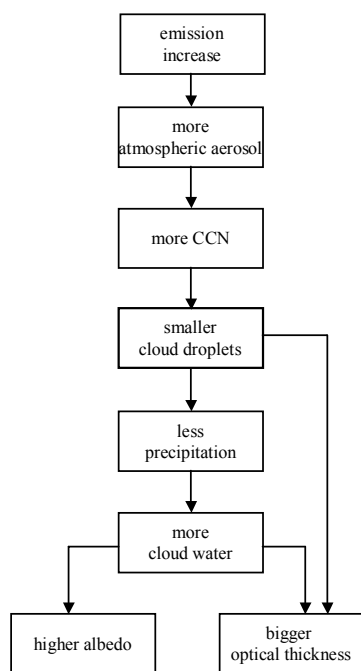
**Fig. 2**

Connection between marine DMS emission and climate including feedbacks (GAIA hypothesis); changed after Charlson et al. (1987)



Damages of building materials (corrosion) lead to economic losses in the order of a few percent of the net social product. However, secondary factors, esp. natural stress by weather and improper constructions play an important role; the interested readers should have a look at special textbooks dealing with that matter. Many regrettable cultural losses arose on historical buildings and sculptures in Europe due to air pollution by acid corrosion of marble and sulphatization of sandstone surfaces leading to instabilities.

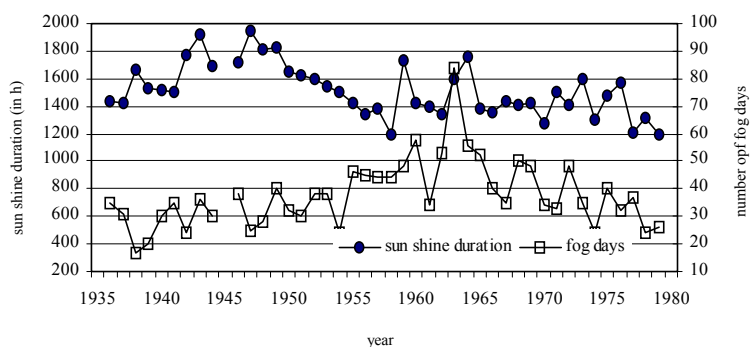
Today we believe climate change to be the most serious environmental problem. The question whether climate change is possible or not is no longer discussed – under discussion is only the quantity of change. By influencing the direct solar radiation (e.g. increase of UV-B due to stratospheric ozone depletion, back scattering by atmospheric aerosol) and terrestrial radiation (greenhouse effect) primarily the temperature will be changed and secondary all other climate elements (esp. cloudiness, precipitation, wind).

**Fig. 3**

Relationship between emission, atmospheric aerosol, clouds and precipitation (*Twomey-effect*)

Another problem concerning increased particulate matter loading of the atmosphere is the reduction of *visibility*. Formation of *haze* by small (sub- $\mu\text{m}$ ) wetted particles scatters sun light and significantly reduces the visibility. Even the formation of fog - when the atmosphere becomes oversaturated with water - can lead to drastic consequences for traffic security. From the data collected at weather monitoring stations it is not simple to deduct on reduced visibilities. Such observations have been made in some heavy industrialized areas, like Bitterfeld in central Germany (Fig. 4). With increasing abatement of particle producing gaseous precursors (esp.  $\text{SO}_2$  and NMVOC) these impacts have been reduced. Reducing visibility is also known as a natural phenomenon from many forested warmer areas in the world being *blue haze*, where biogenic NMVOC (probably terpenes) via oxidation by ozone and OH produce particles in the range

between 10 and 100 nm. A visibility trend analysis has been done in the US (1980-1995) based on 298 synoptic meteorological stations (by human observers) showing a significant decline ( $\sim 10\%$ ) in haziness throughout the eastern United States as well air basins of California (Schichtel et al., 2001). Despite the  $\text{SO}_2$  emission decline of about 10%, a causality has not been established. Based on measurements of extinction coefficients, gaseous and particulate pollutants in Hong Kong, it is concluded that sulphate scattering mostly contributes to visibility degradation (Lai and Sequeira, 2001).



**Fig. 4** Trend of annual sun shine duration (in h) and number of fog days in Bitterfeld 1936-1979. The decreasing sun shine duration since 1945 is obvious (from 1800 to 1200 h), number of fog days increased between 1936 until 1960 ( $y = 0,912x + 22,87$ ,  $r^2 = 0,49$ ) with  $\bar{x} = 30 \pm 7$  and decreased from 1961 until 1979 ( $y = -1,61x + 57,46$ ,  $r^2 = 0,41$ ) with  $\bar{x} = 41 \pm 13$ , after Möller (1984), unpubl.

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## 4.2 Principles of toxicological effects

One distinguishes between damaging impacts on plants (*phytotoxicology*), humans (*humantoxicology*), animals and ecosystems (*ecotoxicology*)<sup>7</sup>. However, on a cellular level there exist many similar and even same mechanisms of the impacts. In the classical toxicology (e.g. *occupational medicine*) many impacts of air pollutants have been described,

<sup>7</sup> *Toxicology* is the science of impacts of harmful substances on living organisms. This term originates in *toxicon* = toxin and *logs* = world/teaching. Important elements were introduced in the 16<sup>th</sup> century by *Theophrastus Bombastus von Hohenheim*, also called *Paracelsus*. He said: “*Was ist das nit giftt ist, alle ding sind giftt, und nichts ohn giftt. Allein die dosis macht, daß ein ding kein giftt ist*“ (What is not a toxin, all things are toxins, and only the dose makes it that a thing is not a toxin)

however, with concentrations (doses) being several orders of magnitude larger than in atmosphere. Thus, for atmospheric pollutants one has to consider that

- concentrations are very small (not clinically investigated)<sup>8</sup>,
- always different pollutants will impact together,
- mostly exists a simultaneous impact of particulate and gaseous pollutants,
- always additional cofactors must be considered (living conditions of the organisms).

The harmful effect might be established due to short-time high dose (acute injury) and/or through long-term impact by accumulation and contamination. A monocausal cause-impact relationship can be excluded in most cases. Consequently, impacts are often *synergetic*, that is, the observed effect of concurring factors is different from that by summarizing of single effects. Concerning air pollution control it must be concluded that the determining impact factors can only be identified by a complex analysis of all stress factors. According to the principle that the effect must be reduced or even be avoided, this may be successfully and economically done only by consideration of selected impact factors (causes) which possibly be other than air pollution (e.g. water pollution, nutrition, social factors etc.).

#### 4.2.1 Oxidative stress

In life systems a permanent struggle in cells exists, between the attack of oxidants (oxygen radicals like  $O_2^-$ , hydroxyl radical OH and peroxides like  $HO_2$  and  $H_2O_2$ ) and antioxidative defense mechanisms. Radicals are produced due to irradiation (solar, radioactive) but also through chemical reactions (Sies, 1986; Halliwell and Gutteridge, 1995). Many trace gases (e.g.  $O_3$ ,  $NO_2$ ,  $SO_2$ ) can form radicals in aqueous phase, being harmful themselves or subsequently producing other radicals damaging cell constituents. These are natural processes and therefore each organism developed *antioxidants* (vitamines and enzymes) in its evolution. On the other hand, radicals are an important vital factor for establishing the immune system and respiratory chain. Only with very high oxidant concentration acute injuries, esp. on membranes and surface receptors, have been observed. During the life process there is a shift in the equilibrium between oxidative injuries and antioxidative repairing to irreversible damages, called the normal process of aging, finally ending with the death of the organism. Consequently, with increasing oxidation capacity of the atmosphere there must be a tendency to increase irreversible injuries (e.g. leaf necroses, skin cancer), expressed as an accelerated aging and finally a reduced life time. It should be noted that for humans many other factors are more harmful but also may be compensating (medical treatment for example). Vegetation, which exists mostly by exchange of air with the surrounding, will likely be more sensitive against oxidative stress.

#### 4.2.2 Vegetation injuries

Influencing plants by air pollutants happens via two channels:

- air → leaf (direct pathway)
- air → soil → root (indirect pathway).

<sup>8</sup> Indications medically stated below a given threshold are non-specific and not quantifiable. The physician is talking about confused (irritative) effects (that means "all and nothing"). Also vegetation injuries have been investigated in gas and open-top chambers with increased concentrations.

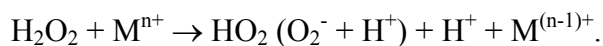
Gaseous trace species are incorporated via assimilation organs (esp. stomata) together with CO<sub>2</sub>. A small part also may be incorporated through epidermis and bark after preceded surface adsorption. The incorporated species will be dissolved in cellular liquid, transported and react according to its specific chemical and biochemical properties. Particulate substances are deposited on leaves and may change the surface (mechanically injures, warming by light absorption, reducing the photosynthetic active radiation). They can also be dissolved during dew formation and when precipitation occurs, and penetrate diffusive into the organisms and washout out nutrients from the leaves. Most of them will be washed off by rain (*leaching*) and deposited into soil; the intermediary storage on leaves is called *interception*. Fixed pollutants on plants will be harvested together and get into feed/food of animals and humans.

Pollutants deposited onto soil can change the offer of nutrients (deficit or excess), may be incorporated via roots into plants and liberate toxic metals (*bioavailability*). Input of phytotoxic substances and its accumulation have been discussed to be playing a major role in forest decline. Two type of impacts will be distinguished (Däßler, 1991):

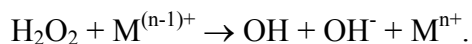
small concentration over long time → chronic damage (not visible) →  
pollutant accumulation → reducing growth,

high concentration → acute damage (visible) → Necroses (irreversible  
discoloration) → cell decease → death of plant.

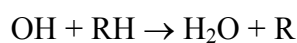
Nowadays it is assumed that gaseous pollutants initiate oxidative stress in cells mostly by blocking the enzymatic system. A key role is played by the superoxide radical O<sub>2</sub><sup>-</sup> (Matschke et al., 1988). It is formed via electron transfer onto oxygen: O<sub>2</sub> + e<sub>aq</sub><sup>-</sup>. This process occurs via photolytic exciting of electron donators in chloroplast. It is also produced in reactions between hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and transition metal ions (M<sup>n+</sup>):



On the other hand H<sub>2</sub>O<sub>2</sub> is a source of OH radicals due to the *Fenton* reaction:



OH radicals directly attack biomolecules (RH) by abstraction of H atoms



which leads to serious damages. The organic radical R again reproduces HO<sub>2</sub>/O<sub>2</sub> in subsequent reactions, and finally a radical chain process has been established. In this context Möller (1989) suggested that H<sub>2</sub>O<sub>2</sub> may play a crucial role in new-type forest decline.

Incorporated trace species will partially be assimilated within the metabolism, e.g. SO<sub>2</sub> will be oxidized to sulphate, but also reduced to H<sub>2</sub>S and re-emitted or accumulated. NO<sub>x</sub>, which in contrast to SO<sub>2</sub> will not lead to damages at small concentrations, will be reduced to NH<sub>3</sub> in cells and metabolized to amino acids. Increased nitrogen deposition, however, will result in a higher need of other nutrients and consequently in nutrition defects. Beside SO<sub>2</sub> as a “classical” primary pollutant fluorine compounds (esp. HF) also lead to plant damages. Ammonia (NH<sub>3</sub>) will damage vegetation in high concentrations (nearby stock-houses) only.

So-called *new-type* forest decline has been observed first in the end of the 1970s in forests at middle altitudes (800 until 1000 m) in Central and Western Europe, in a distance between 100 and 300 km from larger industrial areas (Krause et al., 1983, 1985; Brehlow and Kirch, 1984; Schütt and Cowling, 1985; Wentzel, 1985; Prinz, 1987). Damages dispersed quickly

over larger areas showing a “typical” damage picture: assimilation organs (needles) discoloured from year to year into lemon yellow from the inner to the outer parts of the tree. Later the needles became brown and were lost, leaving the tree stand naked. Beside these visible damages a magnesium deficit has been found – Mg loss and the yellow colouring were called the *Waldschaden syndrome*.

Many hypothesis (more than 100) have been proposed to explain the Waldschaden, but until the end of the financed research in Germany in the end of 1989 no hypothesis was able to fully explain the syndromes. Most favorized was the idea that first “acid rain” leached the leafs or needles to make the plant more sensitive for uptake of gaseous pollutants. Simultaneously the soil showed a loss of nutrients and liberates metals (aluminium toxicity) due to acidification (Ullrich, 1985). Finally, photooxidants were the triggering factor in damaging the leaf tissue (Prinz, 1987; Krause und Köllner, 2000). As a photooxidant, only ozone has been regarded in that time (Ashmore et al., 1985). However, already in the 1980s it has been found that O<sub>3</sub> at measured ambient concentration causes no direct verifiable damages (Skeffington and Roberts, 1985; Metzner, 1987). Until present, the quest for the initiating species remains unanswered. Damages even increased over time: from 300000 probes from different pines in 32 European countries the needle loss was estimated as following (in % after Krause and Köllner (2000):

1989: 10-20  
1998: 17-27.

Based on the observations where Waldschaden occurred the following conclusions concerning the primary factor may be drawn:

- the damaging species is not primary emitted but secondary produced in atmospheric chemical reactions,
- the concentration of the damaging species must be higher in damaged forests than in areas near to man-made sources, i.e. at higher primary polluted sites,
- the concentration of the damaging species must have passed a phytotoxic threshold within a short time period.

Indeed, ozone has higher concentrations in rural than in urban areas and also shows an increase with altitude. Its general concentration increase since 1950 has been similar to the increase of primary emitted pollutants (1-2 % a<sup>-1</sup>). However, there is no evidence that ozone at concentrations around 30 ppb (found in that time in forests) results in plant damage<sup>9</sup>. There is much more believe that H<sub>2</sub>O<sub>2</sub> fulfils all mentioned conditions; in subchapter 4.2.4 the nitrate radical (NO<sub>3</sub>) will propose to be another possible damaging species. Plant damages by H<sub>2</sub>O<sub>2</sub> have been described already many years ago (Masuch et al., 1985; Metzner, 1987).

**Tab. 1** Standards of WHO resp. UN/ECE for protection the vegetation against ozone (1996)

type	AOT-40 (in ppm-h)	periode (in month)
agricultural culture (crops)	3	3 (growing periode)
forest trees	10	6 (phase of highest sensitivity)
plant communities	3	3 (growing periode)

According to our present knowledge it is believed that higher O<sub>3</sub> concentrations with same dose based on smaller concentrations will have a higher damage potential with increasing

<sup>9</sup> In past, however, the maximum O<sub>3</sub> concentrations and the number of days with exceedence of mean values were much higher then present. The conclusion whether acute injuries from such “high ozone events” passed to Waldschaden is not validated.



exposure. Therefore the UN/ECE (UN *Economic Commission for Europe*) proposed the AOT-40 (accumulated exposure over a threshold of 40 ppb) being an accumulated stress parameter (Table 1).

AOT-40 figure considered all exceedences above 40 ppb based on hourly means which will be summed up. It corresponds to an ozone dose. According to the German law (22. BImSchV, §1a) the ozone thresholds amount for vegetation:

$$\begin{array}{ll} 1 \text{ h} & 200 \mu\text{g m}^{-3} \\ 24 \text{ h} & 65 \mu\text{g m}^{-3}. \end{array}$$

A mean O<sub>3</sub> concentration of 40 ppb (uncertainty 25-75 ppb) over the growing season is considered to be damaging the vegetation on a long-term base (Krause and Köllner (2000)).

Damages on horticulture and agriculture have been widely investigated (Däßler, 1991; Weigel and Bender, 2000), but remain not well quantified. For agricultural plants the main questions in connection with air pollution are

- yield,
- quality (composition of plants) and
- accumulation of pollutants (esp. heavy metals and POPs).

#### 4.2.3 Humans health damage<sup>10</sup>

In the introduction has been mentioned that in medicine most investigations were carried out at workplaces (*occupational medicine*), under much higher pollutant concentrations. These results can not be transferred to ambient damages (*environmental sanitation*).

The World Health Organisation (WHO) defined health as “*a state of complete physical, mental and social well-being and not merely the absence of disease or infirmity*”. This very complex definition characterizing an ideal status is essentially more than the absence of disease. Remarkable that there is no definition of disease. In the western world normally it is answered in that way: *Disease is a disturbance of live processes impairing the general performance of the individual and can be measured due to detectable changes of the body*<sup>11</sup>.

Causes of diseases are extensively called and subdivided into outer (food, physical and chemical impairments) and inner (genetic factors), not to forget the life style of the individual (smoking, drinking, working, sport, stress, etc.). The definition of disease is based on the social conception. Demokrit<sup>12</sup>, a skeptic philosopher flouted: „*People entreat the gods to give them good health but that it lies in their own hand to achieve it they don't realize*”.

The so-called *winter smog* episodes shown in Fig. 5 are past now. In that time a statistical significant relation between excess daily mortality and short-time air pollution has been found. During the episode in December 1962 about 1000 persons more than statistically expected diseased. In 1952 more than 4000 persons diseased in excess (in that time no measurements have been done) – this event stimulated the sulphur pollution research and

<sup>10</sup> Impacts of air pollutants – not described in this chapter – are impairments (odours) and influences on well-being (live quality). Life quality is reduced by dust deposition (dirt), reduced visibilities but also by damaged nature (Waldsterben). Smell-intensive emissions and dust depositions were the only effects directly detected (sensible and visible) by humans (smell and see) and stimulated already in early time demands for air pollution control.

<sup>11</sup> Statement by Prof. Dr. Bruno Müller-Oerlinghausen (Chairman of the drug commission of German physicians), press conference on the occasion of Medica, November 20, 1998 in Düsseldorf.

<sup>12</sup> Demokritos of Abdera (460-371 BC), who also said: „One should cultivate much thought but not much knowledge“.

named such episodes winter smog or London smog<sup>13</sup>. The question is whether concentrations of about 3 mg m<sup>-3</sup> (considering the “normal” concentration of 0,4 mg m<sup>-3</sup>) lead to serious health damage. Fig. 6 shows a historical record (calculations based on economic activities) of air pollution in London. Thus, the mean SO<sub>2</sub> concentration ranged from 0,6 to 0,9 mg m<sup>-3</sup> between 1700 and 1900. In that time the life time of humans was mostly limited by other constraints: hygienic conditions, bad nutrition and missing medical treatment.

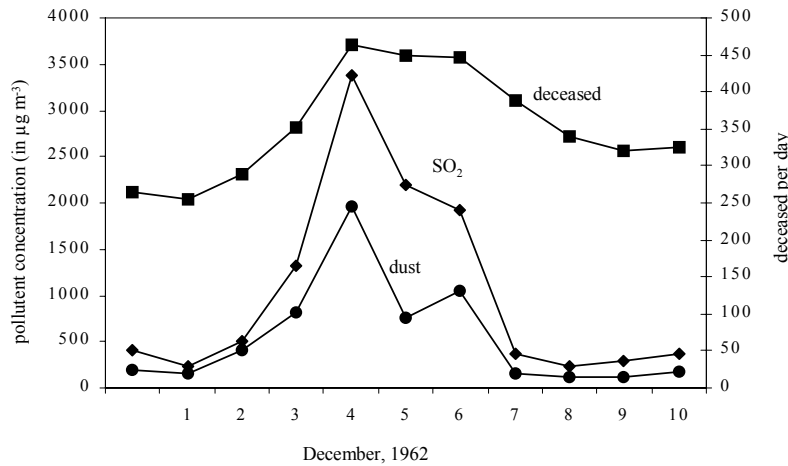


Fig. 5 Winter smog episode in London, December 1962, after data from Ito and Thursten (1996)

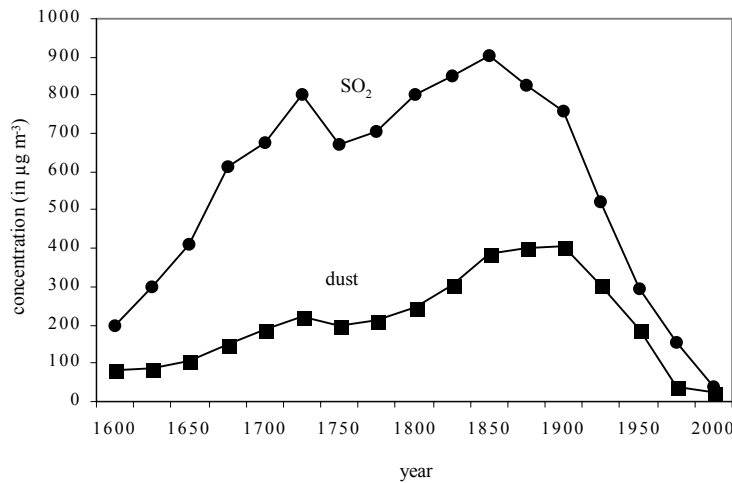


Fig. 6 Historical air pollution in London, after Lomborg (2001)

Without any doubt, a combination of dust particles and high SO<sub>2</sub> concentration will have a synergetic effect, that is, be more damaging than each single component. It is also likely that a changing concentration in short time (cf. Fig. 5), i.e. a large gradient, will produce more health stress than constantly high concentration levels due to adaptation (Auermann, 1985). For example, in Leipzig (Eastern Germany) the highest mean SO<sub>2</sub> concentrations have been measured in winter to be around 1,5 mg m<sup>-3</sup>. Smog episodes are characterized by concentrations an order of magnitude higher (Table 2) where esp. ailing persons (asthma, bronchitis) become sensitive against increasing air pollution, which may result in acute mortality.

<sup>13</sup> In 1905 term *smog* at the Hygienist Congress in London was defined, combined from smoke and fog.

**Table 2** Air pollution in London in  $\mu\text{m m}^{-3}$  (from data in Fig. 5 and 6)

period	smog diseased	smog episode		annual mean	
		dust	SO <sub>2</sub>	dust	SO <sub>2</sub>
1850-1900	-	-	-	400	900
1952	4000	-	-	150	300
1962	1000	1000	2500	50	180
2000	-	-	-	25	35

Several studies show that long-time exposure leads to chronic damage (Dab et al., 2001). Most epidemiologic studies were focused on correlation with particulate matter (PM). A general finding is that mortality increases by 1,5% and more than 10% with an increase of  $10 \mu\text{g m}^{-3}$  PM<sub>2.5</sub> (Morgan et al., 1998; Dockery et al., 1993). These results must not be overestimated as many questions concerning natural mortality variation and accompanying factors remain unanswered. A study on influencing declining ambient air pollution on lung function (expiratory flow by spirometry) of more than 3000 children in Linz (Austria) provides the first evidence that improvements of air quality are correlated with health benefits (Neuberger et al., 2002)<sup>14</sup>. On the other hand, this study suggest that adverse effects on lung function related to air pollution are reversible before adulthood.

An assessment of air pollution impact on human health is made by the *relative risk*

$$\text{relative risk} = \frac{A(A + B)}{C(C + D)} \quad (3)$$

and an *odd ratio*

$$\text{odd ratio} = \frac{A \cdot D}{B \cdot C}, \quad (4)$$

where the parameter are the number of diseased (A, C) and healthy humans (B, D) in polluted (A, B) and unpolluted areas (C, D), respectively.

It is very likely that gaseous pollutants at concentration levels observed in urban and rural areas have do not have any humantoxicological relevance. This conclusion may not only be valid for the air pollution of today but also for past. It is also likely that some of the thresholds given by national laws (In Germany: maximale Immissionskonzentration, MIK) are unreasonable (what sense does an O<sub>3</sub> limitation with  $240 \mu\text{g m}^{-3}$  make, when “damages” to humans will be observed only at above  $400 \mu\text{g m}^{-3}$ ?).

Nowadays the impact of fine particulate matter (PM<sub>2.5</sub>) lies within the focus of human health effects. The principal damage effects of some particulate matter, e.g. by soot (carcinogenic), quartz dust (silicoses) and asbestos fibres (asbestoses) are well known. But again, the key question targets the concentration level, which for PM may be expressed in mass per volume and number per volume. For inhalation depth the particle size is essential, particles with diameters larger than  $5 \mu\text{m}$  will be removed in nose and throat sphere, whereas smaller particles can penetrate to the bronchial sphere and even smaller ( $< 1 \mu\text{m}$ ) to the alveolus in lung. It is not yet clear whether a mechanical and/or chemical impact is decisive. A chemical effect (toxicological) is given by the chemical composition of the PM.

<sup>14</sup> In the City of Linz TSP (total suspended matter) and SO<sub>2</sub> declined elsewhere in the period regarded but NO<sub>2</sub> changed at one site from  $77$  to  $42 \mu\text{g m}^{-3}$  and at other site from  $65$  to  $55$  (“unchanged”)  $\mu\text{g m}^{-3}$ . Only the children living in the NO<sub>2</sub> “changed” area showed an increase in endexpiratory flow rate (about 15%). I feel that the correlation to air pollution is very weak.

In air polluted areas not more asthmatics will statistically be found than in remote areas. PM has found not to be correlated with asthma but with cough, bronchitis and wheeze. From Dutch studies can be concluded (Buringh, 2001) that

- causal factors of impacting PM are still unknown,
- a high air pollution correlates with affecting health,
- high daily and episodic PM pollution show a smaller effect than long-term exposure,
- the non-reactive fraction of PM (water, sea-salt, sulphate and nitrate of ammonium, non crystalline minerals) show no toxic effects and sum-up 1/3 of total PM mass.

Today the impact of air pollution on allergenic diseases are discussed, but an evidence is not found (Björkstén, 1994).

Effects of heavy metals are well-known<sup>15</sup>. They play an important role, esp. with occupational exposure. In the past lead (Pb) and cadmium (Cd) pollution initiated serious damages, esp. in Japan. In the former GDR with its high air pollution the mean elemental uptake has been assessed being smaller than the WHO recommendation (excluding Zn and Cu where at the WHO level), suggesting that airborne heavy metals seems to have a toxicological relevance near sources only (see Table 3).

**Table 3** Budget of mean elemental uptake (in  $\mu\text{g d}^{-1}$ ) by population, after Fiedler and Rösler (1993)

element	uptake			need	WHO recommendation
	air	water	food		
Pb	4-15	4-30	150	187 <sup>a</sup>	430
Cd	0,06-0,23	0,1-2	42	30 <sup>a</sup>	57-712
Zn	10-50	50-1700	14670	2000-10000	1700-2100
Mn	1-4	20-220	4400	3000-5000	-
Cu	10-30	10-40	2250	1500-2000	300-400
Cr	0,08-0,5	1-4	127	50-200	-
Hg	1-5	2-6	29	21	40
F	40-160	100-600	200-1300	1500-2500	8000-10000

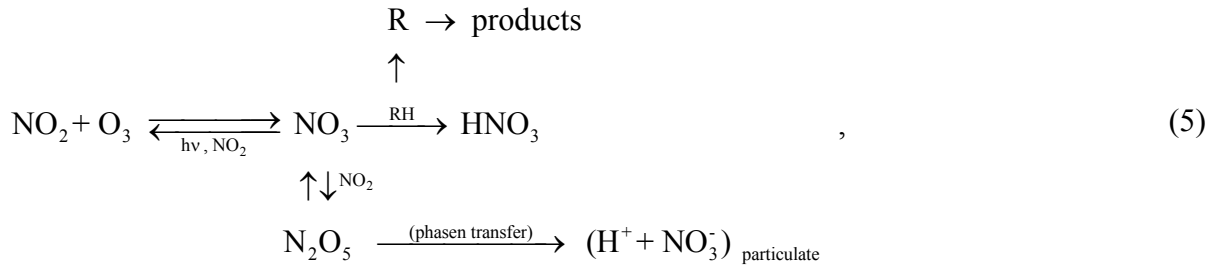
<sup>a</sup> Necessity not evidenced

In analogy to heavy metals, the atmosphere provides a medium for dispersion of persistent organic compounds (POPs).

#### 4.2.4 New-type effects by the nitrate radical ( $\text{NO}_3$ )

In subchapter 4.2.1 we described that oxidative stress is a natural phenomenon and caused mainly by OH radicals destroying organic molecules. The same effects may be given by  $\text{NO}_3$  via H abstraction, however, the specific reaction rates are about by a factor 100 less, but the  $\text{NO}_3$  concentration (only nocturnal) is much higher than that of OH, which may result in comparable rates. Additionally (in contrast to the OH effect) nitric acid ( $\text{HNO}_3$ ) is produced which can lead to acidic cauterising.

<sup>15</sup> Uptake of heavy metals dominates via food (91-99%). Drinking water contributes up to 0,3-5% and breath air to 0,1-4% (Fiedler and Rösler, 1993).



Nocturnal  $\text{NO}_3$  concentrations could be significant (few ppt, maximum up to 85 ppt); daytime it is fast photolysed. Mean residence times have been estimated to 92 s (5-615 s); Geyer et al. (2001). No seasonal variation of the concentration but of the residence time has been found, suggesting a seasonal variation of its sinks. In summer it quickly reacts with monoterpenes emitted from forests, and in winter the uptake by particles dominates. From the scheme (5) an expression for the stationary concentration is derived:

$$[\text{NO}_3] = \frac{k_1}{k_2 [\text{RH}] + k_3 [\text{NO}_2]} [\text{O}_3] [\text{NO}_2], \quad (6)$$

i.e. the  $\text{NO}_3$  concentration is proportional to those of  $\text{O}_3$  and  $\text{NO}_2$ .

An essential indication of  $\text{NO}_3$  impacts was found by the synergetic effects of a mixture of  $\text{O}_3$  and  $\text{NO}_2$ . The effects of  $\text{O}_3$  are much smaller without  $\text{NO}_2$  (see next chapter). Thus it is to assume that the impacting species is  $\text{NO}_3$ , produced from  $\text{O}_3$  and  $\text{NO}_2$ . Simultaneous influence of  $\text{O}_3$  and  $\text{NO}_2$  on humans shows effects similar to those resulting from X-rays (Stockinger, 1962), an indication of radical attack. On the other hand inhalation of a mixture of  $540 \mu\text{g m}^{-3} \text{NO}_2$  and  $940 \mu\text{g m}^{-3} \text{O}_3$  over 4 h did not show an essential effect on the lung function for healthy men (Hackney, 1975).

It is not unlikely that the Waldsterben (new-type forest decline) was initiated by  $\text{NO}_3$  radicals. Impacting  $\text{NO}_3$  produces acidity and oxidative stress simultaneously. The sum of  $\text{O}_3$  and  $\text{NO}_2$  concentration shows a spatial pattern according to the appearance of Waldschaden (altitude and distance from urban sites):

- $\text{O}_3$  concentrations in urban areas are significantly smaller than at rural sites,
- $\text{O}_3$  concentration increases with altitude,
- $\text{NO}_2$  concentration decreases with high (dilution effect),
- $\text{NO}_2$  concentration is approximately constant (due to  $\text{NO} \rightarrow \text{NO}_2$  transfer) in a distance of few hundreds of kilometres; only in larger distances without new sources it decreases due to  $\text{NO}_2 \rightarrow \text{NO}_y$  transfer and subsequent deposition.

This hypothetical example emphasized that an *intelligent* air pollution control must include into assessments of cause-effect-relation not only non-linear emission-concentration relationships but also different spatial effects (geographic conditions) and time relations (seasonal variations, trends etc.).

### 4.3 Impacts of ozone

The characteristic odour from flashes of lightning was already known in antique time and called „sulphur smelling“<sup>16</sup>. *M. van Marum* observed<sup>17</sup> a reduce in volume and strong odour

<sup>16</sup> Mohr (Pogg. Ann. 91, 1854, pp. 625-627) based on four examples from *Homers Odyssee* and *Ilias*.

<sup>17</sup> Beschreibung einer ungemein großen Elektrisiermaschine (Description of an unusual large electrizing machine), Vol. 1, Leipzig 1786, p. 25

while flashing in a closed gas volume above water, which he relates to the „electric material“. Later this smell also was found during electrolysis of sulphuric acid and described by *W. Cruickshank*<sup>18</sup> “chlorine-like”. Only *C. F. Schönbein*<sup>19</sup> identified this odour in 1840 because of a new unknown matter, calling it ozone (greek: οξείν = smell). More than 130 years ago many scientists already expressed that ozone despite its small concentration in air must have an important function in nature and regulates it (Wilmot, 1998).

Bleaching and germicidal properties of O<sub>3</sub> have been realized early but for an application the complicated formation process was limited (end of 19<sup>th</sup> century hydrogen peroxide was preferred for such application form). In contrast ozone was carried for water sterilization (Fonrobert, 1915). Fast disease of bacteria under ozone influence stimulated experiments in that time to use O<sub>3</sub> for an improvement of air quality (!). *Schwarz* and *Münchmeyer*<sup>20</sup> found that H<sub>2</sub>S and SO<sub>2</sub> will partially be oxidized by O<sub>3</sub>. Fonrobert (1915) stressed the question whether O<sub>3</sub> is harmful for humans with the comment:

*Da aber Ozon nachgewiesenermassen auf Tiere in konzentrierter Form nachteilig einwirkt, so ist nicht recht einzusehen, weshalb nicht beim Menschen dasselbe der Fall sein soll, wenn er auch hier nur geringe Ozonkonzentrationen, aber viel längere Zeit hindurch, einatmet*

(Because there is evidence that ozone is harmful for animals it is hard not to assume why the same should be invalid for humans even at small concentrations but inhaled over longer time).

The mortality doses for rats, cats and dogs have been estimated to be 15-20 ppm. In smaller concentrations it was believed to be refreshing for humans and even useful for persons with lung damages (see citation in Fonrobert, 1915). Effects of ozone in dentistry were positively assessed<sup>21</sup>.

Damage on plants by ozone were shown by *Sigmund*<sup>22</sup>. Unfortunately, no information about the used concentrations exists; we can only assume experiments to be carried out with large concentrations ( $\gg 1$  ppm). In the 1920s ozone has been shown to be harmful to humans “already” at concentrations of  $> 1$  ppm. In medical experiments, using pure ozone, however, this threshold was shifted to  $> 20$  ppm, and it was found that small contamination of nitrogen oxides reduces the impact level down to about 1 ppm (see discussion in previous subchapter concerning NO<sub>3</sub> radical). It is likely that in almost all experiments with O<sub>3</sub> other trace gases were present and the effects were the result of synergetic impacts<sup>23</sup>.

A mortality dose is given by 1000 ppm (1 Vol-%) for humans; permanent residence in X-ray laboratories containing about 3500  $\mu\text{g m}^{-3}$  (1,25 ppm) ozone resulted in a general bad feeling but without any damage to lung functions (Gmelin, 1943). There is no reason to query this historical finding and it is more astonishing that today ozone in its ambient concentrations is regarded harmful to human health. Modern clinic experiments show reversible effects (irritations) only for  $> 400 \mu\text{g m}^{-3}$  and it remains a question whether this already is a toxicological threshold. Therefore, the toxicity of ozone is summarized here as:

- a) With ambient concentrations there is no effect on human health. In context of diseases reported in connection with air pollution it is likely that other species (where O<sub>3</sub> is a possible precursor) are impacting.

<sup>18</sup> Gilb. Ann. 7 (1801) 88-113

<sup>19</sup> Christian Friedrich Schönbein (1799–1868), Prof. for chemistry, University Basel.

<sup>20</sup> Z. Hyg. 75 (1914) 81

<sup>21</sup> E. A. Fisch (1936) Dtsch. zahnärztl. Wochenschr. 39, 943-946 und 971-976; Zahnärztl. Rdsch. 45, 857-860

<sup>22</sup> C. Bakt. 14 (1905) 400, 494 and 627; C (105 II) 839

<sup>23</sup> The role of NO<sub>x</sub> belonging to the O<sub>3</sub> toxicity recently has been described in reaction with lipids and formation of NO<sub>3</sub> (Friedman et al., 2000).

- b) Present mean rural O<sub>3</sub> concentrations already are in the range of phytotoxic relevance; there is strong evidence that it still increases in future

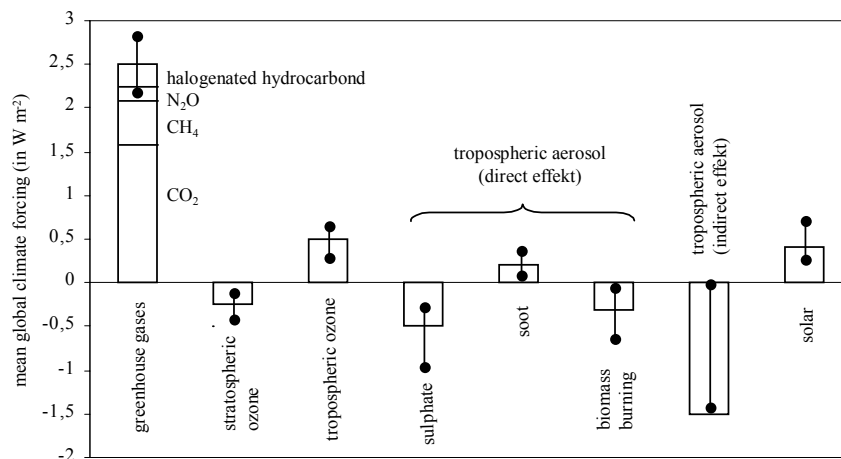
#### 4.4 Climate change

Possible impacts of air pollutants on climate basically pass via direct and indirect influencing of the radiation budget. Most important parameter is *climate forcing*, measured in  $\text{W}\cdot\text{m}^{-2}$ , i.e. changing radiant flux density (intensity) and irradiance, being positive or negative. Positive forcing results into warming (temperature increase) and negative forcing into cooling (temperature decrease). *Direct* climate forcing is called an interaction between radiation and trace substance (absorption, reflection, scattering on molecules and aerosol particles). Thus the solar or terrestrial radiation is immediately influenced by changing temperature being a primary climate element. Other climate elements will subsequently be influenced (cloudiness, precipitation, humidity, wind etc.). Essential are two effects of direct climate forcing:

- aerosol forcing (cooling) and
- greenhouse effect (warming).

We speak of *indirect* climate forcing when changes of radiation budget do not immediately occur but via a process chain already linked with energetic interactions (in the sense of climate, not on molecular level). Among them clouds play a huge role due to their albedo<sup>24</sup>. Other indirect climate factors are changes in the water cycle and surface albedo. Cloud processes (as a part of the water cycle) are essentially influenced through atmospheric aerosol. In this context, particulate matter can result in positive (via clouds) and negative (via direct scattering) forcing. Earth surface albedo<sup>25</sup> can drastically be changed by soot deposition on snow covers (e.g. in alps) and warm up the surface. With an increase of cloudiness albedo rises and it follows a cooling of sub-layers. An increase of the number of CCN can lead to the

*Twomey* effect (see Fig. 3). All effects work together in atmosphere and it remains very difficult to quantify single effects (Fig. 7).



**Fig. 7**

Contribution of different effects to climate forcing, after IPCC (1996)

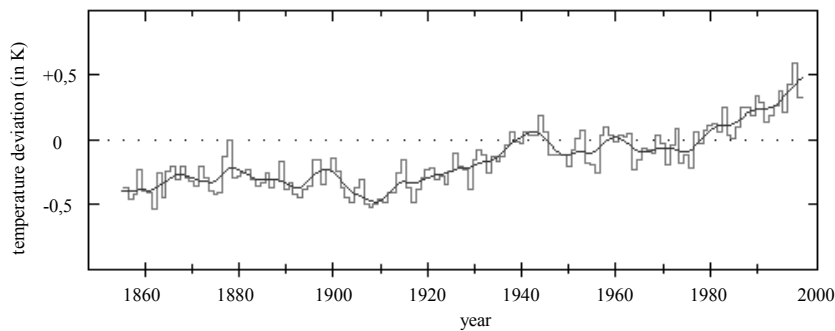
It is misleading to talk about compensation between positive and negative effects; better is the statement that the negative aerosol forcing is *masked* by (positive) greenhouse effect and vice versa (Charlson and Heintzenberg, 1995). It is important to note that the residence time of PM is in the order of only two weeks whereas life time of greenhouse gases is between 10 and more than 100 years. Assuming hypothetically that all aerosol precursors (e.g. SO<sub>2</sub> as the

<sup>24</sup> Albedo is the ratio between light reflection and absorption resp. passing through.

<sup>25</sup> It should be noted that land use changes may have larger impacts on albedo and water cycle (evaporation, accumulation).

most important one) are reduced in short time by one order of magnitude (which is technically not the problem – but economically) than the atmospheric warming would increase due to the resulting net effect.

It is no doubt that the global temperature rose within the last 100 years (Fig. 8) and there are also no questions that this is a consequence of man-made activities, mainly by so-called greenhouse gases. The temperature increase until the end of 21<sup>st</sup> century is assessed between 2 and 8 K<sup>26</sup>. The *Kyoto* protocol<sup>27</sup>, even when it will be realized, will have an effect of only 0.1 K temperature decrease (Schellnhuber, 2001). With other words, there is no effect in sense of air pollution control<sup>28</sup>! Probably the global CO<sub>2</sub> emission must be reduced by more than 50% within a few years – a very little realistic target, even when the political will exists<sup>29</sup>.



**Fig. 8**

Trend of global mean temperature, after P. D. Jones, T. J. Osborn and K. R. Briffa (Univ. East Anglia, Norwich, UK) as well D. E. Parker (Met. Office, Bracknell, Berkshire, UK), internet information

A particularity is the increase of surface UB(B) due to stratospheric ozone depletion. As a consequence changes of tropospheric photochemistry and damages on biota are discussed. The following subchapters will describe climate effects in more detail.

#### 4.4.1 UV-B

Ultraviolet solar radiation (UV) has been considered as an important environmental parameter due to its impact on all biota. Ozone in the stratosphere is basically absorbing nearly all radiation within the range 242-300 nm (below 242 nm oxygen is absorbing radiation). Thus solar radiation only larger about 300 nm is penetrating into the troposphere and available there for photochemical processes. Ozone also absorbs solar radiation in the range 300-700 nm, thus triggering tropospheric photochemistry due to formation of oxygen radicals. Only a very small percentage of wavelengths shorter than 300 nm reaches the Earth surface. This percentage, however, has been increasing for about two decades due to the reduction of the stratospheric ozone level. Stratospheric ozone depletion is caused by so-called “ozone-depleting substances” (ODS) which are able to interact with the O<sub>3</sub> regeneration cycle:



<sup>26</sup> IPCC assessment from 1996 considered 2 K (1.0 to 3.5 K) until 2100, the biggest warming within the last 10000 years. Mean sea level will rise by 50 cm (15 to 90 cm); a 50 cm increase would banish millions of humans from flat delta regions and many islands.. IPCC assessment from 2000 considered 5K (±3K).

<sup>27</sup> *Kyoto protocol to the United Nations framework convention on climate change*, established on December 11, 1997 in Kyoto and signed until March 15, 1999 by 84 countries; based on the climate convention accepted on May, 9, 1992 in New York by the UN.

<sup>28</sup> The political signal of global understanding should not be underestimated.

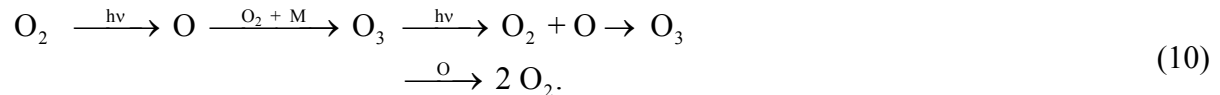
<sup>29</sup> The government of the Federal Republic of Germany resolved on December 13, 2001 the non-invertible exit from nuclear power. One could agree with this decision with the guaranty that the energy deficit is closed by solar energy. Indeed, that is still impossible and the gap will be closed partially by using fossil fuels and (imported) nuclear electricity.



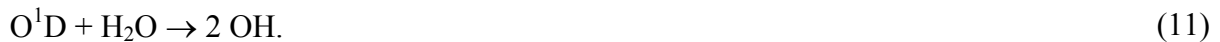
This is a “catalytic” cycle, regenerating back the depleting substance X, which may be halogens (Cl, F) but also NO and “natural” species of the stratosphere (OH); XO would be ClO, FO, NO<sub>2</sub> and HO<sub>2</sub>. The net effect of this simple cycle is the destruction of ozone:



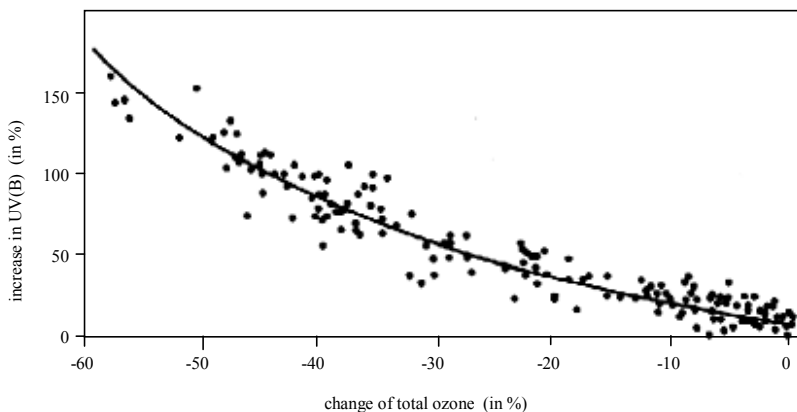
The ozone cycle represents a small number of reactions only, photolysis of O<sub>2</sub> (< 242 nm) and O<sub>3</sub> where the O radical (exactly: only the triplet O<sup>3</sup>P) recombines with O<sub>2</sub> forming O<sub>3</sub>. The following scheme summarized the principal reactions:



The OH radical is produced from the singlet oxygen (O<sup>1</sup>D), which is the photolysis product of O<sub>3</sub> with radiation < 320 nm



Halogens and NO in stratosphere are of man-made origin. The precursors are halogenated hydrocarbons used as spray gases, in electrical isolations and esp. in refrigerators (world-wide banned with the Montreal protocol in 1992) in past. Those substances are chemically extremely stable in the troposphere but will be photolysed in stratosphere releasing free halogen atoms. It is calculated that one chlorine atom can pass 100000 cycles before irreversibly removed from the stratosphere. Due to its long residence time of 100 and more years it will still react over the next decades according to the cycle (7-8). NO mainly is a degradation product of N<sub>2</sub>O, an important emission from agriculture. Also airplanes near the tropopause directly emit NO and may contribute to ozone depletion. The effect of lowering the stationary O<sub>3</sub> concentration is reversible: just when removing or even decreasing the ODS ozone is re-establishing in its previous concentration.



**Fig. 9**

Relation between UV(B) increase and decrease of ozone column density based on measurement at South pole, after Booth and Madronich (1994)

The amount of UV radiation getting to Earth surface can be calculated, using optical models of radiation transfer with knowledge of radiant flux at the top of the atmosphere, but also be measured. Direct measurements are preferred, but they are not easily done with high quality – therefore only limited data exist. However, with such data models have been validated and now model calculations for each site on the Earth are available to simulate past and future development. The relation between reducing total atmospheric ozone and increasing UB(B) is nowadays well estimated by laboratory tests and fields measurements (Madronich et al., 1995), see for example Fig. 9. According to this relation, the amount of UV(B) increases by

2% with each 1% decrease of O<sub>3</sub> (WMO, 1995). 2% increase in UV(B) result in an increase of skin cancer by 2-6%. Yearly 500000 new skin cancers are registered in the USA. Beside skin damage UV also damages the human immune system and plants, esp. oceanic plankton which is the basis of the marine food chain. It has been assessed that the yearly loss due to injured agricultural plants amounts billions of USD.

During significant (but short-time) ozone changes observed during large volcanoes eruption (e.g. Mt. Pinatubo) a direct UV(B) increase has been measured. Long-time measurements are sparse and show large variations due to clouds, local air pollution and other factors; thus trends can not be derived yet from measurements.

**Table 4** Expected increase of yearly UV dose and frequency of skin cancer due to stratospheric ozone depletion between 1979 and 1992 (averaged over the 14 years, in % based on 1979), after Madronich and de Gruijl (1993)

latitude	total ozone	erythema (dose)	DNA damage (dose)	skin cancer (dose)	frequency of normal cell carcinoma	frequency of scaly cell carcinoma
85 N	-8,8±3,2	7,1±1,7	14,8±3,6	10,6±2,5	15,1±5,6	28,5±11,2
75 N	-9,0±2,9	7,6±1,7	14,9±3,3	10,8±2,4	15,4±5,8	29,1±11,5
65 N	-7,4±1,7	7,6±1,7	14,1±3,2	10,3±2,3	14,7±5,6	27,7±11,0
55 N	-7,4±1,3	7,2±1,7	12,9±3,2	9,5±2,3	13,5±5,3	25,4±10,3
45 N	-6,6±1,2	6,5±1,7	10,9±3,0	8,1±2,2	11,6±4,7	21,6±9,0
35 N	-4,8±1,4	5,0±1,8	8,2±3,0	6,1±2,2	8,6±4,0	16,0±7,6
25 N	-2,7±1,5	3,0±1,9	4,8±3,1	3,5±2,2	5,0±3,5	9,0±6,4
15 N	-1,5±1,1	1,7±1,4	2,6±2,3	1,9±1,6	2,7±2,4	4,8±4,4
5 N	-0,6±1,6	0,7±1,9	1,2±3,0	0,8±2,2	1,2±3,1	2,1±5,5
5 S	-1,1±1,4	1,2±1,7	2,0±3,0	1,4±2,0	2,0±2,8	3,6±5,2
15 S	-1,9±1,3	2,2±1,5	3,5±2,4	2,5±1,7	3,6±2,6	6,5±4,8
25 S	-2,6±1,6	3,1±1,7	5,0±2,4	3,6±1,9	5,1±3,1	9,2±5,8
35 S	-4,0±1,6	4,8±1,6	7,9±2,6	5,7±1,9	8,1±3,6	14,9±6,8
45 S	-5,6±1,4	7,2±1,6	12,5±2,7	8,9±1,9	12,7±4,8	23,9±9,2
55 S	-9,0±1,5	10,9±2,0	19,7±3,6	14,2±2,6	20,4±7,4	39,3±15,1
65 S	-15,0±2,0	16,3±3,0	30,5±5,8	21,9±4,1	31,9±12,2	64,0±26,6
75 S	-19,5±2,6	24,1±5,4	49,8±12,0	34,0±7,7	50,6±21,4	107,7±52,0
85 S	-21,1±3,0	31,0±6,8	72,0±17,6	46,5±10,5	70,6±31,2	159,6±83,6

The spectral radiant flux density is the fundamental parameter, characterizing the intensity  $I(\Theta, \varphi, \lambda)$ , it depends from solar zenith angle  $\Theta$ , azimuth  $\varphi$  and wavelength  $\lambda$ . Another important parameter is the spectral irradiance  $E(\lambda)$  above flat square, the figure directly measured in  $W m^{-2}$ . For large changes in O<sub>3</sub> a good correlation to irradiance has been found (Madronich and de Gruijl, 1993):

$$E \sim (Ozon)^{-RAF}, \tag{12}$$

where RAF represents a radiation amplification factor, defined as the percentage increase of weighted irradiance with 1% O<sub>3</sub> increase, cf. Fig. 9. From wavelength depending figures integral parameter have been derived often, reflecting biological sensitivities, for example the UV index (WMO, 1994):

$$UV \text{ index} = 40 \int E(\lambda)B(\lambda)d\lambda, \tag{13}$$

where  $B(\lambda)$  represents a figure for erythema (skin burning); McKinlay and Diffey (1987). Increase of UV however is connected non-linear with biological effect (Table 4). It has been found that frequency of normal skin cancer is strongly correlated with UV(B) according to following relation (Kricker et al., 1993):

$$\text{frequency} \sim E^{-\text{BAF}}, \quad (14)$$

where BAF means a biological amplifying factor estimated empirically to be  $1.4 \pm 0.4$  for normal and  $2.5 \pm 0.7$  for scaly skin cancer.

The increase of UV(B) is partially compensated due to the increase of tropospheric ozone and aerosol (Table 5)

**Table 5** Total change of UV-B (annual DANN weighted dose) since pre-industrial time until 1992, after Madronich et al. (1995)

effect	UV(B) change (in %)
Northern hemisphere, middle industrialized latitudes	
stratospheric ozone depletion	+5 to +15
sulphate increase	-5 to -18
tropospheric ozone increase	-3 to -10
net:	-23 to +7
Northern hemisph, remote areas	+5 to +15
Tropics	+1 to +5 <sup>a</sup>

<sup>a</sup> uncertain

#### 4.4.2 Cooling by scattering aerosol

On a global average Earth is covered 60% by clouds. Only the cloud-free sector may influence radiation via scattering through aerosol particles. Particles show two competing processes: scattering and absorption<sup>30</sup> of solar radiation. On a global scale only scattering is of importance. This is supported by the fact that large parts of Earth surface have small albedo. Particle scattering increases planetary albedo and subsequent cooling. Such effects were measured after volcanoes eruptions. Sulphate is considered as a prototype of scattering PM. Also, organic particulates and mineral dust contribute to scattering. Thus, the reduction of direct solar radiation reduces absorption at surface with the consequence of cooling the air, reducing the convective latent and sensitive heat fluxes and possibly convective precipitations.

Important properties of PM are size and water content. Table 6 lists important optical properties of atmospheric particles, which may be related to single particles and aerosol as a whole. More information may be found in Horvath (1999). In this script we will only describe the scattering summarizing by Equation (15), which presents the decrease of radiant flux density  $I$  through the layer  $dz$  (after Friedlander, 1977):

$$-dI = I \sigma_e dz = I \left[ \int_0^{\infty} \frac{\pi d_p^2}{4} K_e(x, m) n_d(d_p) d(d_p) \right] dz, \quad (15)$$

where  $n_d(d_p)d(d_p) = dN$  number of particles with a diameter between  $d_p$  and  $d_p+d(d_p)$ ,  $K_e$  extinction efficiency (ratio between scattered and absorbed radiation to irradiated energy<sup>31</sup>),  $x = \pi d_p/\lambda$  optical sizes (dimensionless parameter) and  $m$  refractive index. Last one represents a parameter specific for the substance, depending from chemical composition (Table 7), defined as the ratio of phase light speeds in vacuum and material.

<sup>30</sup> Only absorbing substance in PM is soot.

<sup>31</sup> In Table 5 this coefficient has been named as the ratio of radiant fluxes (energy per time and square).

**Table 6** Symbols and dimensions of optical properties of aerosol

parameter	symbol (dimension)	definition
scattering coefficient	$\sigma_s = -\frac{1}{\Phi} \frac{d\Phi}{dx}$ (in $m^{-1}$ )	percentage of radiant flux lost by PM scattering per unit of thickness
absorption coefficient	$\sigma_a = -\frac{1}{\Phi} \frac{d\Phi}{dx}$ (in $m^{-1}$ )	percentage of radiant flux lost by PM absorption per unit of thickness
extinction coefficient <sup>a</sup>	$\sigma_e = -\frac{1}{\Phi} \frac{d\Phi}{dx}$	percentage of radiant flux lost by PM per unit of thickness
single scattering albedo	$\tilde{\omega} = \frac{\sigma_s}{\sigma_e}$ (dimensionless)	ratio of scattering to extinction coefficient
absorption number	$\tilde{\alpha} = \frac{\sigma_a}{\sigma_e}$ (dimensionless)	ratio of absorption to extinction coefficient
transmittance	$\delta = \frac{\Phi}{\Phi_0}$ (dimensionless)	ratio between incoming radiant flux $\Phi_0$ and the layer penetrating radiant flux $\Phi$
optical depth	$\tau = -\ln \frac{\Phi}{\Phi_0}$ (dimensionless)	negative decadic logarithm of transmittance

<sup>a</sup> called also attenuation coefficient

**Table 7** Refractive index  $m$  of different materials, after Horvath (1992)

H <sub>2</sub> O	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	NH <sub>4</sub> HSO <sub>4</sub>	NH <sub>4</sub> NO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	CaCO <sub>3</sub>	SiO <sub>2</sub>	OC
1,333	1,528	1,482	1,559	1,430	1,586	1,478	1,44 bis 1,60

From Eq. (15) one can see the meaning of the extinction coefficient  $\sigma_e$ . As already mentioned, absorption can be neglected for most materials, thus extinction = scattering ( $\sigma_e = \sigma_s$ ). Regarding volume related scattering, the scattered radiant flux density in volume  $dV$  within the spatial angle  $d\Omega$  in direction of the scattering angle  $\Phi_s$  is

$$dI = E \gamma(\Phi_s) dV d\Omega, \quad (16)$$

where  $\gamma(\Phi_s)$  is a volume scattering function with a dimension of  $m^{-1} sr^{-1}$ . Integrating over the whole spatial angle, we get the scattering coefficient being

$$\sigma_s = \int_{4\pi} \gamma(\Phi_s) d\Omega. \quad (17)$$

Finally, by integrating the extinction coefficient over an atmospheric layer  $dz$  we get the *optical thickness*  $\tau$ :

$$\tau = \int_{z_1}^{z_2} \sigma_e dz, \quad (18)$$

which describes the solar extinction in a vertical column by aerosol. Table 8 summarized typical figures of optical properties of the lower troposphere.

**Table 8** Typical figures (ranges) of observed optical parameters in the lower troposphere (scattering and absorption coefficients in  $\text{m}^{-1}$ , other parameters dimensionless), after Mészáros (1999)

	polluted continent	remote continent	remote ocean
optical thickness $\tau$	0,2-0,8	0,02-0,1	0,05-0,1
single scattering albedo $\tilde{\omega}$	0,8-0,9	0,9-0,09	close 1
scattering coefficient $\sigma_s$	50-300	5-30	5-20
absorption coefficient $\sigma_a$	5-50	1-10	0,01-0,05
back scattering/total scattering	0,1-0,2	n.a. <sup>a</sup>	0,15

<sup>a</sup> not available

Because the transmittance of air is equal to  $e^{-\tau}$ , an optical thickness of 0.1 means that about 90% of solar radiation penetrate through the layer. Data from Table 8 show that only scattering essential contributes to extinction. Figure of single scattering albedo is larger in remote areas where particles mostly consist from ammonium sulphate whereas in polluted areas soot has a small share due to absorption. Finally only a small fraction is directly scattered back because particles scatter dominantly in *Mie* range, where forward scattering dominates.

#### 4.4.3 Warming by absorbing gases (greenhouse effect )

Belong the six greenhouse gases resp. groups called in the *Kyoto* protocol are  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , chlorinefluorhydrocarbons (CFC's), perfluorcarbons (PFC's) and sulphur hexafluoride ( $\text{SF}_6$ ). The “greenhouse effect”<sup>32</sup> is a natural property of the atmosphere. Without the greenhouse effect on Earth there would be no life, as the temperature would only measure about 155 K (33 K less) assuming the same albedo. The difference (warming) is given by same gases absorbing in the infrared (IR) range of terrestrial radiation. Those gases are called greenhouse gases. Among them the most important natural one is water vapour.

The increase of several gases since the industrial revolution in the middle of 19<sup>th</sup> century in the atmosphere amplified the greenhouse effect and thereby the warming of the atmosphere. However, as mentioned in the previous chapter, some other processes of scattering and reflection “smooth” this effect by cooling.

Greenhouse gases absorb IR radiation (Fig. 10) from Earth surface in different wavelength ranges according to the specific quantum mechanical properties (vibrational-rotational bands). Practically, radiation below 8  $\mu\text{m}$  is quantitatively absorbed. Water vapour is responsible for quantitative absorption of IR above 18  $\mu\text{m}$ . Water in atmosphere is basically not (yet) influenced by mankind; however, due to possible climate change a change of the dynamic equilibria between evaporation, condensation and transportation may result. Thus it is an important component in climate feedbacks. Carbon dioxide is the second important greenhouse gas; it absorbs in the range from 15 to 18  $\mu\text{m}$  and has a dominant absorption around 15  $\mu\text{m}$ . The wave length range from 8 to 12  $\mu\text{m}$  is called *atmospheric window* because there is little absorption by trace gases. However, most non- $\text{CO}_2$  greenhouse gases ( $\text{O}_3$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , CFCs) show strong absorption in this atmospheric window (Fig. 10). Therefore, small increase of those gases may stronger contribute to the greenhouse effect than an increase of

<sup>32</sup> The opponents of the greenhouse effect always stress the argument that within a greenhouse other effects play a role. Within going to the differences (they do not play any role for the further discussion), the term “greenhouse effect” is in analogy to “acid rain” an expression for the *problem*, in this case for warming the atmosphere by IR absorbing substances. It also does not play a role to separate between a natural and man-made effect. With the exception of most halogenated compounds all other substances have natural as well as anthropogenic sources. Only the total concentration determines the absorption capacity. Important is only the further increase and its (non-linear) contribution to the greenhouse effect. Calling it “greenhouse effect” is totally unimportant. The *effect* is proved scientifically to be true, its quantification, however, is different according to the models used and to our knowledge of complex processes.

CO<sub>2</sub>. With extreme concentrations (this is the case only for CO<sub>2</sub> and H<sub>2</sub>O) some wavelength ranges are totally absorbed (*wavelength saturation*) – further increase of atmospheric concentration will not lead to more warming. That is the case for the 15 μm band (Wuebbles, 1995). Further climate forcing by CO<sub>2</sub> is about proportional to the natural logarithm of its concentration. A doubling of atmospheric CO<sub>2</sub> will have a climate forcing of 4.6 W m<sup>-2</sup>. CH<sub>4</sub> (around 1600 ppb) and N<sub>2</sub>O (around 550 ppb) also exist in high concentrations; its further increase is proportional to the square root of its concentration. Generally climate forcing of gases is negligible at wavelength where water absorbs. Only CFCs show absorption bands far away from saturation, thus climate forcing is linear with its concentration increase.

Another important effect which must be considered for calculation of the net effect is the so-called *band overlapping*. For example, CH<sub>4</sub> and N<sub>2</sub>O simultaneously absorb at several bands with the result that the total effect (absorption) is smaller than the sum of individual absorption.

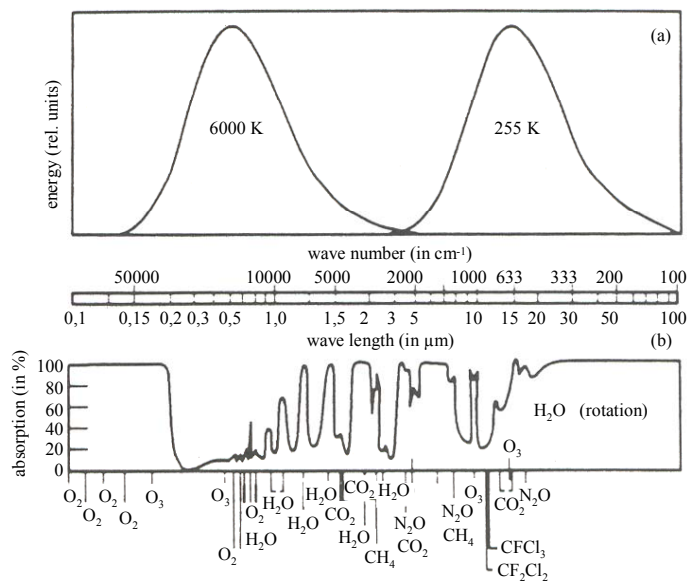


Fig. 10

(a) Black body curve of emitted radiation with wavelength typical for Sun (6000 K) and Earth (255 K) and

(b) percentage of atmospheric absorption. Note the relative small absorption in the range 8-12 μm (called atmospheric window)

In the system Earth-atmosphere exists a balance between incoming solar radiation and outgoing infrared radiation. From 100% solar radiation (343 W m<sup>-2</sup>, called *solar constant*) only 55% (189 W m<sup>-2</sup>) will be absorbed by Earth surface. A part is reflected by Earth surface (4% global albedo) and clouds (20%) as well as air molecules and particles (6%). Another part is absorbed by clouds (3%) and gases, esp. water vapour (16%). Thus from the incoming energy within the range from 300 to 2500 nm about 30% are directly radiated back into space. The remaining energy is emitted in higher IR and radiated back (2.5 to 40 μm), see also Fig. 10.

A significant part of the radiation absorbed by Earth surface is transferred into latent heat due to evaporation of water into atmospheric vapour (27%) and upward transported by turbulence as sensitive heat (4%). The remaining energy deficit (19%) covered the IR radiation of Earth surface (*terrestrial radiation*), to a large degree absorbed by (greenhouse) gases (and water vapour) and finally dissipated in higher IR ranges into all directions. Thus it comes partially back to Earth surface entering a cycle. Finally it will be radiated back to space. The difference of 151 W m<sup>-2</sup> between radiative emission of Earth (15% + 99% = 114% = 391 W m<sup>-2</sup>) and total IR irradiation into space (15% + 20% + 35% = 70% = 240 W m<sup>-2</sup>) represents the “greenhouse effect”. The relative percentage of different gases is shown in Table 9.

**Table 9** Percentage of different gases to the global greenhouse effect (in %) and temperature increase per decade and for the total period (specific for substance), after Nisbet (1994)

gas	1850-1960	1960-1970	1970-1980	1980-1990	1850-1990	$\Delta T$ (°C) <sup>b</sup>
CO <sub>2</sub>	68	58	53	52	56	+ 0,70
CFC	-	17	23	21	19	+ 0,41
CH <sub>4</sub>	20	10	10	14	12	+ 0,15
O <sub>3</sub>	12	9	10	9	10	+ 0,07
N <sub>2</sub> O	-	6	4	4	3	+ 0,08
$\Delta T$ (°C) <sup>a</sup>	+ 0,034	+ 0,076	+ 0,126	+ 0,153	+ 0,39	+ 1,40

<sup>a</sup> after Nisbet (1994)

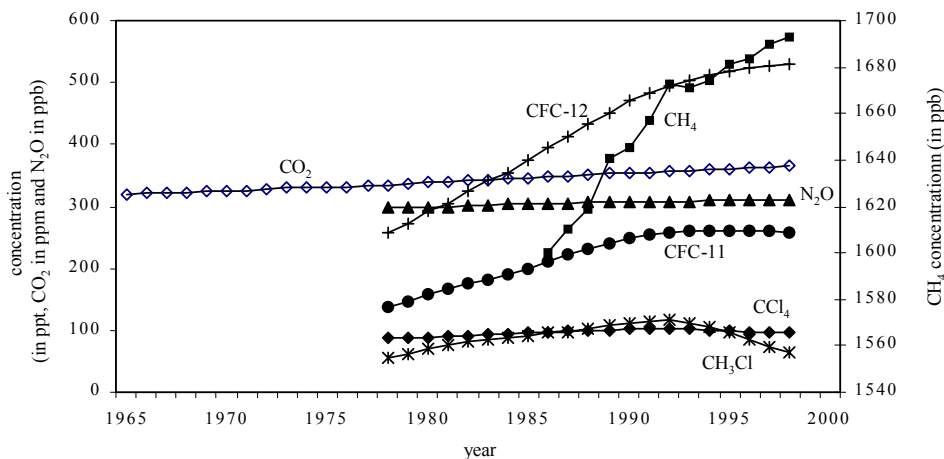
<sup>b</sup> after Schneider (1991)

A consequence is the warming of the Earth's surface and the lower atmosphere. Only radiation with wavelengths where no absorber exists in atmosphere is radiated back into space. The resulting energy balance is combined with a certain temperature. Highest uncertainty in quantification of the budget results from clouds.

CO<sub>2</sub> remains the most important greenhouse gas, despite CFCs have increased significantly in past. Relative importance of CO<sub>2</sub> slightly decreased whereas that of CH<sub>4</sub> increased. With the worldwide stop in use of CFCs its share will sink in future, but very slowly. Table 9 also shows how different scientists assessed the contribution to warming: Nisbet (1994) believed a total effect of about 0,4 K and Schneider (1991) about 1,4 K. Last estimation is more reliable when comparing with real temperature increase and taking into account the masking (cooling) effect of aerosols. The global temperature is believed to have increased by 1 K since (cf. Fig. 8) 1860. This corresponds to a cooling effect by aerosols of 0.4 K.

Concentration of „classical“ greenhouse gases increased each year on average by (see also Table 10 and Fig. 11):

- CO<sub>2</sub>        1-2 ppm
- CH<sub>4</sub>        ~ 3 ppb
- N<sub>2</sub>O        ~ 0,5 ppb.



**Fig. 11** Trend of greenhouse gas concentration, after WIR (2001)

Concentration of „non-classical“ greenhouse gases (ozone depleting substances) reached a maximum or are even decreasing due to control measures. Within the last 100 years, CO<sub>2</sub> concentration rose by 25% and that of CH<sub>4</sub> doubled. Surface-near ozone concentration is at values twice as high as in 1950. May this concentration pattern reflect the temperature curve? Obviously not in detail. The temperature curve in Fig. 8 shows many fluctuations and several periods with different trends, suggesting that the system is highly complex, i.e. temperature is controlled by many factors.

**Table 10** Historical trend in greenhouse gas concentration, after Lelieveld et al. (1998)

year	CO <sub>2</sub> (in ppm)	CH <sub>4</sub> (in ppb)	N <sub>2</sub> O (in ppb)
1850	287	750	260
1900	296	970	292
1960	316	1270	296
1990	354	1720	310
1995	360	1730	312
$\tau$ (in a)	50-200	7,9	120

**Table 11** Development of greenhouse gas emission in European Community (in Mt CO<sub>2</sub> equivalent a<sup>-1</sup>), after EEA (2000)

substance	1990	1992	1994	1996	1998
CO <sub>2</sub>	3320	3269	3217	3359	3328
CH <sub>4</sub>	440	414	387	374	367
N <sub>2</sub> O	399	377	375	392	360
CFC	- <sup>a</sup>	-	-	58	-

<sup>a</sup> unknown

To make statements on the relation between climate and emission changes without application of complex climate models, the *global warming potential* (GWP) has been defined (IPCC, 1990). It is defined for a homogeneous mixed gas being the time-integrated change of climate forcing  $\Delta F_R$  as the consequence of emission of 1 kg of trace species  $i$  relative to emission of 1 kg CO<sub>2</sub>:

$$\text{GWP} = \frac{\int_0^{t_a} \Delta F_{R,i}(t) dt}{\int_0^{t_a} \Delta F_{R,\text{CO}_2}(t) dt} \quad (19)$$

Using a linear approximation, where  $a_i$  is the radiation forcing due to the emission of the trace species  $i$  and  $n_i$  is concentration as well as  $t_a$  is the time horizon and  $\tau$  an *effective* residence time we get

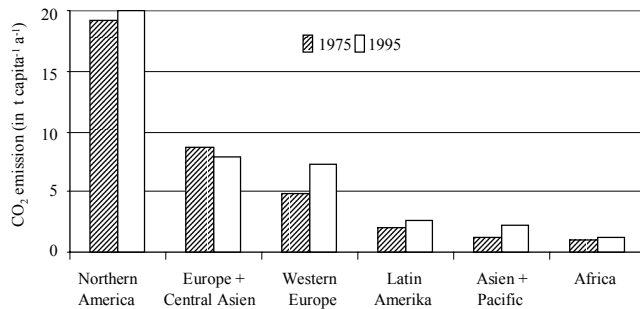
$$\text{GWP} = \frac{\int_0^{t_a} a_i n_i(t) dt}{\int_0^{t_a} a_{\text{CO}_2} n_{\text{CO}_2}(t) dt} = \frac{a_i \int_0^{t_a} e^{-\frac{t}{\tau_i}} dt}{a_{\text{CO}_2} \int_0^{t_a} e^{-\frac{t}{\tau_{\text{CO}_2}}} dt} = \frac{a_i \tau_i}{a_{\text{CO}_2} \tau_{\text{CO}_2}} \frac{1 - e^{-\frac{t_a}{\tau_i}}}{1 - e^{-\frac{t_a}{\tau_{\text{CO}_2}}}} \quad (20)$$

Selection of the time horizon requires the knowledge of characteristic times of climate changes. Thus, the atmospheric CO<sub>2</sub> reservoir (pool) is influenced by the emission rate from transfers between different reservoirs within the biogeochemical cycling. The effective residence time of CO<sub>2</sub> has been estimated to be 120 years (Maier-Reimer and Hasselmann, 1987) in contrast to 40-50 years in case of constant CO<sub>2</sub> concentration.

To quantitatively express the percentage of different greenhouse gases to the effect, the *greenhouse gas equivalents* factors have been introduced (IPCC, 1996), which represent the weighted share to GWP over 100 years: 1 (CO<sub>2</sub>), 21 (CH<sub>4</sub>), 310 (N<sub>2</sub>O), 6000 (CFC) and



23900 ( $\text{SF}_6$ )<sup>33</sup>. In this way GWP emissions can be expressed in tons of  $\text{CO}_2$  equivalent directly showing the contribution to warming (Table 11).



**Fig. 12**

$\text{CO}_2$  emission per capita and year in different regions of the world, after GEO (2000)

The key question remains: the future increase of  $\text{CO}_2$  and its GWP. Prognosis of its emission are uncertain, strongly depending on future energy scenarios. It is likely that  $\text{CO}_2$  increase is even larger than the highest IPCC scenario (see Module Chapter 2: Trend in Air Pollution). Based on emission in 1990 it would be the following factors: 3 (2025), 5 (2050), 8 (2075) and 10 (2100). A doubling in atmospheric  $\text{CO}_2$  (present 366 ppm) would increase the temperature by 2,5 K (1,5-4,5) after IPCC (2000). IPCC (1996) assessed that stabilization of 550 ppm means a global average of only 5 t  $\text{CO}_2$  per capita including a reduction until 2100 to 3 t. 1995 the range amounts from 1 t (Africa) to 20 t (Northern America). It seems very unlikely that such target is realistic.

In a warmer world agricultural production would increase in higher latitudes in Northern and Southern Hemisphere whereas in tropics and subtropics – where a deficit in food production already exists – bioproductivity decreases. All ecosystems change its biodiversity, esp. fresh water quality will decrease and dangerous insects (esp. mosquitos) rise and disperse over wide areas (IPCC, 1998).

Hurricanes are another climate change effect with huge damages. Statistically significant is the increase of storms within the last 10-15 years, but no correlation with warming has been validated. It is believed that there are natural variations (with periods of several decades) in frequency (Bengtsson, 2001).

Of largest uncertainty, but also of highest social meaning are feedbacks, i.e. a climate change (warming) may amplify this effect (positive feedback). Present models show an amplifying factor of 1-3 (IPCC, 1990). Most important effect are changes of the  $\text{H}_2\text{O}$  greenhouse contribution, ice albedo, cloud feedbacks and ocean-atmosphere coupling. Recently it has been reported that the Gulf current has been weakened by 20% (Rahmsdorf, 2001). In discussion are changes of frequency and intensity of El Niño, influencing large parts of the Earth in its climate.

<sup>33</sup> Recently a new greenhouse gas has been identified in antarctic ice,  $\text{SF}_5\text{CF}_3$  probably a degradation product of  $\text{SF}_6$ , which was absent before 1960 in air; its residence time is extreme with several thousands of years (W. Sturges, Science, 289, 2001, p. 611).