ATMOSPHERIC CHEMISTRY

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Contents

Summary

The present level of air pollution is caused by natural and human-made emissions, with the exceptions of some purely anthropogenic chlorofluorohydrocarbons (CFCs). Since the industrial revolution, and especially since the 1950s, the anthropogenic sources exceeded by far the natural contributions for most air pollutants. Dependent on reactivity, transport and deposition, air pollutants are transported over hundred kilometers (ammonia), several thousands (aerosols) up to a truly global scale (carbon dioxide, CFCs).

Traffic can cause high concentrations of ozone and aerosols in cities. Ozone affects human health at concentrations over 200 μg m^{-3}. Recent investigations indicate that aerosol concentrations of 50 to 100 μg m^{-3} are harmful and in the Netherlands cause about 1500 deaths per year, same as traffic accidents. On a regional scale acid deposition, eutrophication (too high concentrations of nutrients like phosphate, ammonium and nitrate) and photochemical smog cause harm to vegetation. A truly

global problem is the destruction of stratospheric ozone by CFCs, resulting in an enhanced UV radiation at the Earth surface harmful for humans and marine ecosystems. Increased concentrations of greenhouse gases and aerosol change the radiative balance of the Earth, leading to climatic change.

The effect of air pollutants can be confusing as they can depend on the actual position in the atmosphere: Too high ozone concentrations at the surface are harmful for vegetation and at the tropopause enhance the greenhouse effect, but are beneficial in the stratosphere, filtering out more UV radiation.

Emission reductions are necessary to reach a sustainable situation. Remedies range from more efficient use of energy, to application of clean energy sources like wind and solar and balancing emissions of carbon dioxide by enhanced uptake through reforestation.

1. Introduction - What is Air Pollution?

In recent decades atmospheric chemistry has become an important subject, not only because of scientific fascination with a very complex subject but also because of the increased problems with air pollution since the middle of the twentieth century. Air pollution is somewhat difficult to define, as many air pollutants (at low concentrations) are essential nutrients for sustainable development of ecosystems. So air pollution could be defined as: ‘a state of the atmosphere which leads to exposure of humans and/or ecosystems to such high levels or loads of specific compound or mixtures thereof that damage is caused’. With a very few exceptions all compounds which are considered air pollutants have both natural as well as man-made origins.

Air pollution is not a new phenomenon; it was forbidden in mediaeval times to burn coal in London while parliament was in session. Air pollution problems have dramatically increased in intensity as well as scale due to the increase of emissions since the industrial revolution. All reports on air pollution in the nineteenth and early twentieth century indicate that the problems were local, in or around the industrial centers and the big cities. Even the infamous environmental catastrophes in the area of Liege in the 1930s or in London in the 1950s were essentially local phenomena. In the London smog episode, stagnant air accumulated such high sulfur dioxide and sulfuric acid concentrations (due to the use of coal) that several thousand inhabitants have died.

It is a feature of the second half of the twentieth century that the effects of air pollution were detected at regional (>500 km), continental and global scales. Acid deposition around 1960 caused the first observed effects on regional to continental scales. Lakes in Scandinavia as well as North America lost their fish populations as the lakes were acidified by acid deposition to the point that fish eggs would no longer produce young fish. About ten years later damage to forests, mainly loss of vitality of trees, was also attributed to acid deposition (see *Acid Deposition*).

Smog episodes in US cities such as Los Angeles were reported in the same period. Reactions of volatile organic compounds and nitrogen oxides produced high concentrations of ozone and peroxides, which are harmful for human beings as well as ecosystems. Around the same period the first high oxidant concentrations (the complex mixture of ozone, peroxides and other products of the reactions of organics and nitrogen oxides is called 'oxidants') were more and more frequently taking place in Europe during stagnant meteorological conditions (see *Formation and Effects of Smog*).

In the same period severe eutrophication (damage and changes in ecosystems due to availability of excess amounts of nutrients) was encountered. Deposition of ammonium and nitrate was shown to contribute substantially to high nutrient concentrations in soil and groundwater. Nitrate and ammonium are beneficial, even essential, for development in vegetation but in too high concentration they lead to loss of diversity, especially in oligotrophic (adapted to low nutrient availability) ecosystems. This problem was mainly encountered in The Netherlands, Belgium, and parts of Germany, Denmark and southern Sweden (see *Eutrophication and Algal Blooms*).

The next scale of air pollution is effects on global dimensions, such as the destruction of stratospheric ozone due to emissions of CFCs (chlorofluorocarbon compounds). This issue has attracted a lot of attention in the period 1985 to 1995, as it was revealed that the destruction of stratospheric ozone leads to higher UV light intensities and hence, for example, to skin cancer.

From 1990 onwards the increase of concentrations of radiation-active substances (compounds which alter the radiative balance of the Earth—greenhouse gases, but also aerosols and water in liquid form as clouds) and the connected climatic consequences, induced new research on air pollution. Greenhouse gases absorb long-wave infra red radiation emitted from the Earth, thereby retaining heat in the atmosphere and increasing the total radiative flux at the surface of the Earth. Aerosols and clouds reflect incoming short-wave sunlight and influence the optical properties of clouds towards more reflection of sunlight, and hence increasing concentration of aerosols leads to a decrease of the radiative flux at the surface.

Epidemiological research has quite recently shown significant effects of aerosols on the respiratory tract (inducing asthma and bronchitis). This evidence that aerosols increase mortality has prompted research on the composition and sources of aerosol, in order to find adequate control measures.

This sequence in time of air pollution problems could give the impression of sudden increases of air pollutant concentration, but that is probably not the case, as can be explained in the case of ozone. By carefully characterizing old methodologies, Volz-Thomas and Kley have been able to reconstruct ozone concentrations in the free troposphere (the air not directly influenced by processes taking place at the Earth's surface). From the latter part of the nineteenth century onwards, the ozone concentrations in Europe slowly increased at a rate of 1 to 2 percent per year from 10 ppb to over 50 ppb (ppb is a mixing ratio of 1 molecule of ozone in a billion molecules of air). It is well documented that the effects of ozone start at levels of about 40 ppb. So it is not surprising that the effects of ozone were detected in the 1970s as background continental ozone was already 30 ppb, and additional oxidant formation would increase the ozone concentrations both locally and regionally. But the increase had already been going on for a long time.

Ozone is a good example of a so-called secondary air pollutant. It is a product of a large set of atmospheric chemical reactions involving nitrogen oxides (NO_x) and volatile organic compounds (VOCs). These precursors—compounds which lead to a certain product, in this case ozone—are emitted by a wide variety of sources. In USA and Europe road traffic is the main emitter. These precursors are transported by air movement and will be involved in an intricate and very large set of atmospheric reactions under the influence of sunlight. Ozone is one of the products. The next stage is deposition of primary and secondary air pollutants. Deposition can take place by way of precipitation, air pollution is first incorporated in clouds or precipitation and hence transported to the Earth’s surface, or air pollutants are deposited directly on vegetation on the Earth surface: dry deposition (see *Trophospheric Ozone Pollution*).

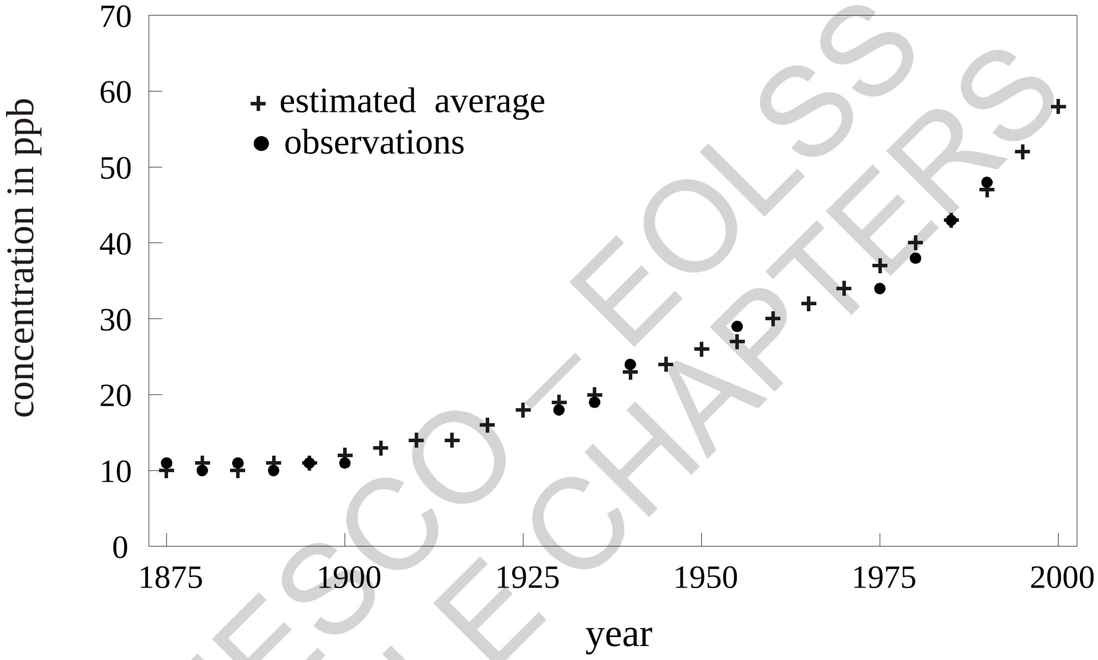

Figure 1. Historical trend of ozone concentration in free troposphere after Volz-Thomas and Kley.
Volz A., Kley D. (1988) Evaluation of the Montsouris series of ozone measurements made in the nineteenth century, *Nature* 332, 240-242.

The deposition loads of different products describe the total amount of air pollutants which reaches ecosystems. These are time integrated deposition fluxes per area unit. One popular, though not very logical, way of expressing loads is in moles per hectare per year. Effects caused by acid deposition and eutrophication are directly linked to the deposition loads of pollutants, as will be explained later. But other effects of pollutants, e.g. the effects of oxidants, are probably also tied in with the load of pollutants reaching the relevant parts of the vegetation. This connection has not yet, however, been demonstrated consistently (see *Air Pollution Damage to Vegetation*).

The removal of pollutants by chemical transformations and deposition processes is essential. If for instance sulfur dioxide emitted by natural causes like volcanoes would not be removed this way, a concentration of 1000 ppb or more will be reached in the atmosphere in a few months, and ecosystems and human populations would be endangered.

Once the effects of air pollutants are related to transgression of critical loads or concentrations, then it is possible to derive the necessary emission reductions using models describing the complete process from emissions, via transport, chemical conversions, to deposition and exposure, plus the effects.

2. Emissions

Most pollutants are emitted both by natural as well as anthropogenic sources. Natural sources are not influenced by humans, or human-induced activities. Volcanoes are a good example of this. A lot of emissions are biogenic, i.e. produced by living organisms, but these emissions are very often influenced by human activities. Nitrous oxide (N_2O) is a greenhouse gas which is for a large part emitted during nitrification and de-nitrification processes (the conversion of ammonium to nitrate and nitrate to N_2 and to ammonium respectively) taking place in the soil. But the highest N_2O concentrations are observed where nitrogen containing fertilizer is applied in agriculture.

The ratio between anthropogenic and natural emissions is very important as only the anthropogenic part can be influenced e.g. by abatement measures. The anthropogenic sources of sulfur dioxide (see Table 1) are much larger than the natural ones. In fact they exceeded the natural sources as early as 1950.

Sources	SO_2(IPCC)	**NO_x(Graedel and Crutzen)**
Industrial and utility activities	76	22
Biomass burning	2.2	6
Volcanoes	9.3	no data
Lightning	no data	5
Biogenic emissions from land areas	1.0	15
Biogenic emissions from oceans	24	no data
Total anthropogenic emissions	**78.2**	**27**
Total natural emissions	**34.3**	**21**
Total emissions	**112.5**	**48**

Table 1. Global natural and anthropogenic emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) in Tg per year

Adapted from Intergovernmental Panel on Climate Change and Graedel T.E., Crutzen P.J. (1993). *Atmospheric Change: An Earth System Perspective*, 446 pp. New York, USA: W.H. Freeman and Company.

The natural emissions of nitrogen oxides (NO_x) are, according to the estimate compiled by Graedel and Crutzen, of the same order of magnitude as anthropogenic emissions. NO_x emissions, together with the emissions of volatile organic compounds (VOCs) are responsible for the formation of oxidants like ozone, and peroxide acetyl nitrate (PAN). Some of the NO_x sources, especially natural, are quite uncertain, and the contribution of natural sources to ambient VOCs is not very well known either.

Sources	**Anthropogenic**	**Natural**
Fossil fuel use	45	not applicable
Biomass burning etc.	45	not applicable
Solvents	15	not applicable
Oceans	not applicable	25
Isoprene by vegetation	not applicable	350
Terpenes by vegetation	not applicable	480
Total	**105**	**855**

Table 2. Global emissions of volatile organic compounds (VOCs) in Tg of carbon per year

An overview of the emissions of VOCs on the global scale is given in Table 2 (data from *Hydrocarbons in the Atmosphere)*. These figures, especially the natural/biogenic emissions, have large uncertainties, but make clear that for the time being the natural VOC emissions are predominant. Nevertheless, near industrialized areas anthropogenic sources are often the most important ones. For detailed overviews of the emissions of sulfur, VOCs and nitrogen oxides check EOLSS contributions *Sulfur Dioxide and Sulfur Cycles*, *Hydrocarbons in the Atmosphere*, and *Reduced and Oxidized Nitrogen* respectively.

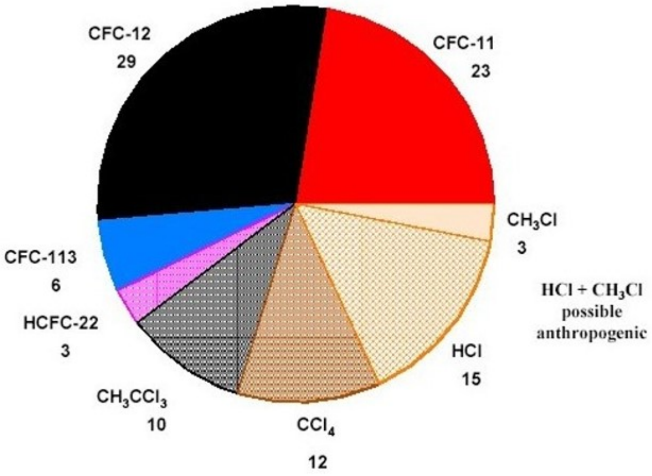

Figure 2. Origin of stratospheric chloride in percent after Intergovernmental Panel on Climate Change data

An extreme case is reactive chlorine (the main compound responsible for destroying stratospheric ozone) where at least 90 percent of the relevant emissions are anthropogenic (see Figure 2). After 1945 chlorofluorocarbons (CFCs) were widely applied until their use was restricted by the Vienna Convention and the Montreal protocol. No natural sources of these compounds are known.

In Figure 3, the atmospheric concentrations of the most important greenhouse gases (CO_2, methane (CH_4), CFCs and N_2O) have been plotted as fractions of the present global ambient concentration. If it is assumed (not completely true) that the ambient concentrations vary linearly with the emissions and that only natural emissions are responsible for concentrations before the year 1800, we can see that the ratio of natural versus anthropogenic sources varies greatly for the different greenhouse gases, being highest for N_2O and lowest for CFCs.

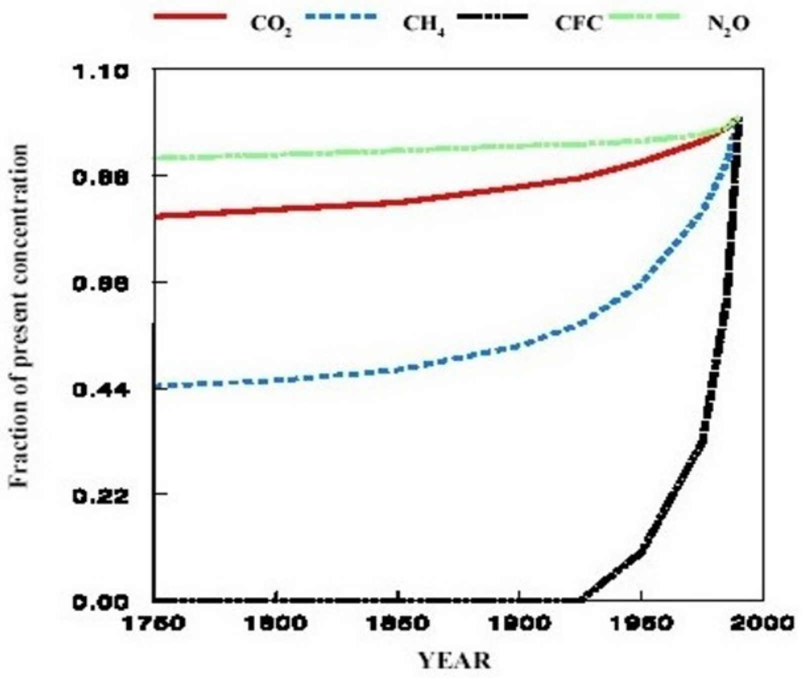

Figure 3. Relative concentrations of the principal greenhouse gases from 1750 to 1990 in fractions of present concentrations after Intergovernmental Panel on Climate Change data

A simplified overview of the emissions of greenhouse gases is given in Table 3. Natural sources are not regarded as large contributors to global atmospheric or carbon dioxide because the decay of biomass in fall and winter is in equilibrium with uptake during leaf formation and growth in spring and summer.

Emission type	Sources	**CO_2 (Tg of carbon)**	**CH_4 (Tg)**	**N_2O (Tg of nitrogen)**
Anthropogenic	Fossil fuel	5.5	100	cannot be quantified
	Biomass burning	1.6	40	cannot be quantified
	Ruminants	negligible	80	cannot be quantified
	Waste treatment	negligible	80	cannot be quantified
	Rice paddies	negligible	60	cannot be quantified
	Total	**7.1**	**360**	**4.4***
Natural	Wetlands/continents	120	6	cannot be quantified
	Ocean	10	2	cannot be quantified
	Other	20	negligible	cannot be quantified

	Total natural (carbon cycle)	**150**	**8**	**Very large**

Table 3. Overview of the annual emissions of greenhouse gases carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) after Intergovernmental Panel on Climate Change data. The sources of nitrous oxide cannot be quantified well.

Ambient aerosol concentrations are partly of primary and partly of secondary nature. Sea salt particles caused by waves and dust swept up by wind are examples of primary aerosol. A large part of the aerosol, however, consists of sulfates, and depending on the specific conditions, nitrate and organic compounds, which are formed by atmospheric conversion from sulfur dioxide, nitrogen oxides and VOCs as precursors (Figure 4).

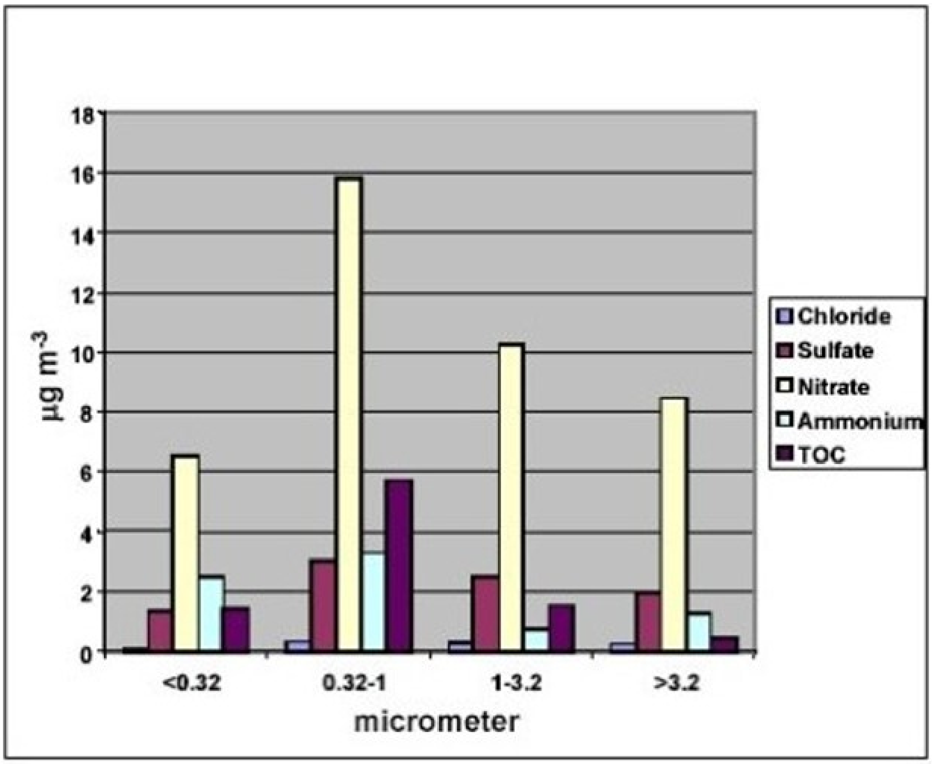

Figure 4. Composition of aerosol during an air pollution episode and under average conditions in the Netherlands based on data of Netherlands Energy Research Foundation (ECN), Petten, the Netherlands

Sulfate used to represent the largest fraction of anthropogenic aerosols but the present composition reflects a shift in emissions in especially in the developed countries since the early 1990s. Emissions of sulfur oxides have dropped in the developed countries, due largely to measures to reduce acid deposition. Emissions from traffic have remained stable or even increased, despite improved engine technology and the introduction of exhaust catalytic converters in cars. This is because the number of vehicles and the total distances driven per vehicle have clearly increased, particularly in USA and Europe. In many developing countries, for instance in eastern Asia and South America, the same shift in emissions is taking place right now. One could say that acid deposition problems are being exchanged for exposure to increased oxidant concentrations.

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www.emep.int [The reader can find a lot of general information on atmospheric chemistry, emissions in Europe, critical loads, etc. on the EMEP web site.]

www.ipcc.ch [This web site of IPCC offers the reader all relevant IPCC reports, on climatic change, emissions, scenarios etc.]

Biographical Sketch

Prof. Dr. Sjaak Slanina, born 22-4-1942 in Heerlen, The Netherlands, studied analytical chemistry at the University of Utrecht in the period 1962 to 1968. He held a position as scientist at the same university between 1968 and 1972 and obtained his PhD there.

He worked from 1972 to 2004 at the Netherlands Energy Research Foundation as project leader and head of the department of Environmental Research. He was from 1994 to 2005 a part-time full Professor at Wageningen University, The Netherlands, and holds now a Professorate in Air Pollution at Peking University, China.

Prof. Slanina has written over a hundred articles on air pollution problems, he has participated in scientific coordination of many international research projects and Dutch National Programs.