

# GAS-PHASE (PHOTO) CHEMICAL PROCESSES IN THE TROPOSPHERE

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## Summary

The Earth's troposphere is an efficient oxidizing and "cleansing" medium. Its capacity to remove carbon-based trace species and pollutants, biogenic and anthropogenic, is determined by a number of chemical and photochemical processes, initiated mainly by hydroxyl radicals ( $\bullet\text{OH}$ ) and depending on the levels of nitrogen oxides ( $\text{NO}_x$ ). An overview is presented on the major tropospheric (photo)chemical reactions, involving mainly hydroxyl ( $\bullet\text{OH}$ ) and peroxy ( $\text{HO}_2\bullet$ ) radicals, nitrogen oxides ( $\text{NO}$  and  $\text{NO}_2$ ), ozone ( $\text{O}_3$ ), nitrate ( $\text{NO}_3\bullet$ ) radicals and halogen atoms, and organic peroxy and oxy radicals. The  $\bullet\text{OH}$  radical is the most important reactive species in the troposphere, since it is formed in large amounts and because it reacts with the majority of the chemical compounds emitted into the atmosphere from the biosphere. The chemical

reactions that govern the complex interrelations between hydroxyl and peroxy radicals ( $\text{HO}_x$ ), nitrogen oxides ( $\text{NO}_x$ ) and ozone are discussed too. Photochemical production of tropospheric ozone is also addressed, and gas-phase tropospheric processes involving biogenic and anthropogenic volatile organic compounds (VOC) are presented. Finally, in relation to Global Change issues, the major factors are addressed that control the oxidizing capacity of the atmosphere and the (potential) changes thereof as a result of anthropogenic influences.

## 1. Introduction

The atmosphere is the gaseous envelope that surrounds our planet, from the Earth's surface up to altitudes of more than 100 km. This chapter covers that part of the atmosphere called troposphere, the lowest atmospheric layer extending from the Earth's surface up to the tropopause, i.e. the boundary between the troposphere and the stratosphere. The troposphere is a region of turbulence and mixing. The decreasing temperature with increasing altitude, due to the heating effect at the Earth's surface by the absorption of visible and near-UV solar radiation, leads to a large convection (because less dense warm air rises and is replaced by the cooler air from higher altitudes), resulting in a rapid mixing of gases inside the troposphere. In this way, compounds emitted from the Earth's surface are able to reach the upper parts of the troposphere in a few days to several weeks.

With the exception of variable amounts of water vapor (below 1 %), our atmosphere consists of more than 99 percent by volume of molecular nitrogen ( $\text{N}_2$ ), molecular oxygen ( $\text{O}_2$ ) and argon (Ar). Of the remaining 0.1 %, roughly half is accounted for by the three gases carbon dioxide ( $\text{CO}_2$ ), neon (Ne) and helium (He). The remaining minute fraction is composed of a complex mixture of hundreds of trace gases, the most abundant being methane ( $\text{CH}_4$ ), nitrous oxide ( $\text{N}_2\text{O}$ ), carbon monoxide (CO) and ozone ( $\text{O}_3$ ). Of the mentioned species, water vapor,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{O}_3$  absorb infrared light. Such infrared-absorbing gases are of vital importance to our biosphere, as their combined “greenhouse-effect” raises the temperature at the earth's surface to an average of  $15^\circ\text{C}$ ; in their absence the average temperature would be about  $-17^\circ\text{C}$ .

The concentrations of the major constituents,  $\text{N}_2$  and  $\text{O}_2$ , have been determined by geological and biological processes that have operated over timescales of hundreds of millions of years, and human activity cannot directly affect their concentration to any significant degree. However, the human activities can increase (directly or indirectly) the emissions and concentrations of many of the trace gases, most of which are shorter-lived, such as CO,  $\text{CH}_4$ ,  $\text{O}_3$ , nitrogen oxides ( $\text{NO}_x$ ), volatile organic compounds (VOC) and their partly oxidized intermediates such as formaldehyde, acetone and peroxy acetyl nitrate ( $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ , or PAN). All of these species react with hydroxyl radicals. Human activity can also release gases in the atmosphere that are not naturally present, such as halogenated hydrocarbon gases commonly known as freons and halons.

These trace gases are of great importance for the chemistry and the oxidizing capacity of the atmosphere and also for the radiation budget of the Earth-atmosphere system, and thus for our planet's climate. Substantial effects of human activities have arisen only during the last two centuries. The changes that are occurring now have their origins in the industrial revolution and the expansion of technology, and are therefore directly related to human activities.

The major objective of atmospheric and specifically tropospheric chemistry studies is to understand the chemical composition of the natural, pristine atmosphere, the way chemical species in the atmosphere interact with each other and with the Earth's surface and the biosphere, and how human activities may be changing the chemical and physical characteristics of the atmosphere and the interactions mentioned (see *Atmospheric Chemistry*). There are very important natural sources of both hydrocarbons and nitrogen oxides ( $\text{NO}_x$ ) to the atmosphere. Soils emit  $\text{NO}_x$  as a product of nitrification and denitrification (see *Soil Chemistry*). Lightning and natural biomass burning also produce nitrogen oxides. Hydrocarbons are also naturally emitted (see *Hydrocarbons in the Atmosphere*). Biogenic volatile organic compounds (also referred to as BioVOC), in particular, are a group of hydrocarbons and oxygenated hydrocarbons emitted to the atmosphere from surface vegetation, soils, and oceans, in vast quantities. The most important source is considered to be vegetation, mainly forests. Biogenic VOC emissions far dominate over anthropogenic ones on a global scale, and they can even dominate in some industrialized areas. Thus, BioVOC are of great importance to the chemistry of the global atmosphere, and this is why the atmospheric chemistry of these species is receiving particular attention. In addition, somewhat less than half of the present global emissions of methane and carbon monoxide (see *Oxides of Carbon*) are of natural origin. These very large amounts of reduced carbon compounds (i.e.: all VOC, methane and carbon monoxide), emitted by the natural biosphere into the atmosphere, are oxidized *in situ*, and therefore imply an important oxidation capacity, which resides for the greater part in the lowest and most dense layer, i.e. the troposphere. The naturally emitted methane and carbon monoxide and the BioVOC determine the oxidative capacity of the atmosphere to a large extent; they also contribute greatly to tropospheric ozone production, in the boundary layer as well as in the free troposphere (see *Tropospheric Ozone Pollution*). It is the basic chemistry underlying and governing this oxidizing or “cleansing” power of the troposphere that constitutes the main subject of this chapter.

Much of the human impact on the atmosphere is related to emissions of a variety of pollutants, mainly carbon monoxide, hydrocarbons and nitric oxide. When built-up at sufficiently high levels, which occurs frequently in the boundary layer of urbanized/industrialized areas, these anthropogenic species initiate photochemically driven chain reactions that may finally lead to photochemical smog (see *Formation and Effects of Smog*), acid rain (see *Acid Precipitation*) and high levels of ozone (see *Tropospheric Ozone Pollution*), a powerful toxic agent that can cause damage to human health, forests and agricultural crops (see *Air Pollution Damage to Vegetation*). The role of  $\text{NO}_x$  in such photo-oxidant production in the (urbanized/industrialized) boundary layer is crucial, as it acts as a catalyst (see *Oxidized and Reduced Nitrogen in the Atmosphere*). Since the  $\text{NO}_x$  lifetime in the troposphere is very short (about one day),

these species are removed close to the sources and are therefore highly unequally distributed in the troposphere. Even if within a local urban area the levels of most pollutants are usually dominated by the contributions for which man himself is responsible, BioVOC can nevertheless in some instances be of great importance also to the chemistry of local and regional pollution problems.

$\text{NO}_x$ -catalyzed boundary layer photo-oxidant production from (mainly) VOC, anthropogenic as well as biogenic, is also examined in this chapter. Finally, we will address the crucial Global Change issue of the impact of anthropogenic emissions of carbon monoxide, methane and VOC on the oxidizing capacity of the global atmosphere (see *Greenhouse Gases and Global Warming*).

## 2. Tropospheric Chemical and Photochemical Reactions

Despite the relatively inert molecules that compose the bulk of our planet's atmosphere, the troposphere is anyway an efficient oxidizing medium. This is due to the fact that it contains also free radicals and other species that are reactive toward CO,  $\text{CH}_4$  and VOC, the most important of which are  $\text{HO}_x$  ( $\bullet\text{OH}$  and  $\text{HO}_2\bullet$ ), followed by the nitrate radical ( $\text{NO}_3\bullet$ ), ozone ( $\text{O}_3$ ), and halogen species. The hydroxyl ( $\bullet\text{OH}$ ) radical is the major oxidizing agent in the troposphere. It is the only oxidant that can attack  $\text{CH}_4$  and CO, which are the principal reduced carbon compounds in the free troposphere;  $\bullet\text{OH}$  is also the major oxidant of volatile organic compounds (VOC) during daytime. The  $\text{NO}_3\bullet$  radical plays an important role at night in polluted areas of the planetary boundary layer. It is formed from the reaction between nitrogen dioxide ( $\text{NO}_2$ ) and ozone, but during daylight it is quickly photolysed (to  $\text{NO}_2 + \text{O}$  and to  $\text{NO} + \text{O}_2$ ). The nitrate radical and ozone are the most important oxidants of VOC at night. Halogen species, such as chlorine (Cl) or bromine (Br), are relevant to the chemistry in the marine boundary layer and to that above ice sheets in polar regions during early spring.

### 2.1. Basic Chemical and Photochemical Processes in the Troposphere

In this subsection, the basic (photo-)chemical reactions will be discussed that control the production and loss of the major reactive species in the troposphere, as well as the reactions by which these species oxidize carbon monoxide and methane, and so produce photochemical ozone when nitric oxide is present. Also, the complex interrelations between the major actors in tropospheric chemistry,  $\text{HO}_x$ ,  $\text{NO}_x$  and ozone, will be discussed in some detail.

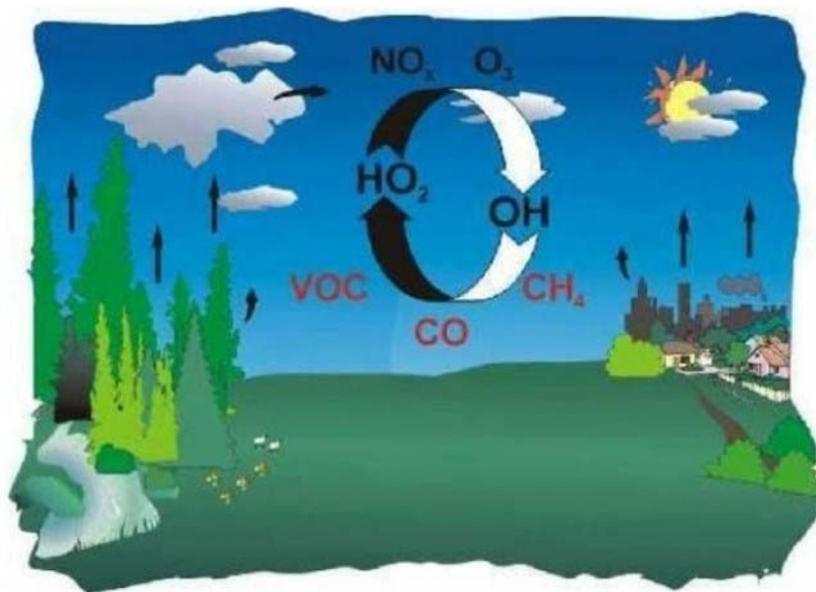


Figure 1: The main sources of CO, CH<sub>4</sub> and VOC, and the major actors in tropospheric chemistry

### 2.1.1. The Hydroxyl Radical and Other “Odd Hydrogen” Species

The hydroxyl radical ( $\bullet\text{OH}$ ) is the most important reactive radical in the troposphere, both because it is formed in large amounts and because it can react with most of the (reduced) carbon compounds that the biosphere — including mankind — releases into the atmosphere. Due to its high reactivity with respect to a wide range of species,  $\bullet\text{OH}$  is often referred to as the “detergent” of the atmosphere. Hydroxyl is involved in catalytic cycles, leading to steady-state diurnal atmospheric concentrations of about  $10^6$  molecule  $\times$  cm<sup>-3</sup>. In the troposphere,  $\bullet\text{OH}$  radicals are usually formed from photolysis of ozone ( $\text{O}_3$ ) or nitrous acid ( $\text{HONO}$ ), or from the reaction between the hydroperoxy radical  $\text{HO}_2\bullet$  and  $\text{NO}$ . Nitrous acid, present at its maximum concentration in the nighttime urban troposphere, is rapidly photolysed during daytime to  $\bullet\text{OH}$  and  $\text{NO}$ . If  $\text{HONO}$  accumulates overnight, then its photodissociation can become important in the morning before other sources of  $\bullet\text{OH}$  radicals become dominant.

Reactions of  $\bullet\text{OH}$  radicals with  $\text{CO}$ ,  $\text{CH}_4$  or  $\text{VOC}$  molecules give rise to other radical species, “peroxy radicals” ( $\text{HO}_2\bullet$  or  $\text{RO}_2\bullet$ , see below), which by further reactions may result directly or indirectly in the regeneration of  $\bullet\text{OH}$ , at least in part. Thus, in such a catalytic oxidation cycle,  $\bullet\text{OH}$  radicals are not necessarily lost, but often only temporarily “cycled” into other kinds of radicals, of which the most important is the hydroperoxy radical  $\text{HO}_2\bullet$  (others being organic peroxy radicals and organic oxy radicals). Thus, generally the oxidation processes of reduced compounds in the troposphere have a (radical) chain reaction character. In particular for quantitative chemical kinetics descriptions of such processes, it is most useful to consider the sum of concentrations of various radicals involved, rather than only the concentration of  $\bullet\text{OH}$

radical. Therefore, one often groups  $\bullet\text{OH}$  and  $\text{HO}_2\bullet$  together in a pool of “odd hydrogen” radicals, denoted as  $\text{HO}_x$ .

Of much importance are those (photo)chemical reactions that result in a net production or a net loss of  $\text{HO}_x$  radicals. Globally, the most important  $\text{HO}_x$  source is the photodestruction of ozone occurring at wavelengths below 320 nm, and forming oxygen atoms in the excited state ( $\text{O}({}^1\text{D})$ ) that can further react with water vapor, in competition with their deactivation by collisions with nitrogen or oxygen molecules, which results in ozone regeneration:



For reaction (1),  $h\nu$  refers to an ultraviolet photon. In the planetary boundary layer, the fraction of the excited oxygen atoms  $\text{O}({}^1\text{D})$  that reacts with water vapor to form two  $\bullet\text{OH}$  is of the order of 10 percent. This process is by far the largest  $\text{HO}_x$  source in the lower troposphere. It becomes less important with altitude due to the decrease of the water vapor mixing ratio with height, as a result of the decrease in temperature. In the cold upper troposphere (UT), above 6-8 km of altitude, other sources of  $\text{HO}_x$  can become important and even dominant. In particular, several partially oxidized organic compounds, formed in the planetary boundary layer from VOC precursor species, can be transported into the UT and be photolysed there to produce  $\text{HO}_x$ . These species are mainly acetone ( $(\text{CH}_3)_2\text{CO}$ ), formaldehyde ( $\text{CH}_2\text{O}$ ), and methyl hydroperoxide ( $\text{CH}_3\text{OOH}$ ). For acetone and methyl hydroperoxide, one of the products of the photo-oxidation is formaldehyde, which is further rapidly photolysed to produce  $\text{HO}_2\bullet$ . Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is another, but less important source of  $\bullet\text{OH}$ ; its high solubility in water results in an almost equally rapid scavenging by precipitation as its photolysis by ultraviolet sunlight. As the major  $\text{HO}_x$  sources are photolytic, the  $\bullet\text{OH}$  and  $\text{HO}_2\bullet$  concentrations typically increase during daytime.

Another, only recently recognized source of  $\text{HO}_x$  in the planetary boundary layer is the ozonolysis of alkenes, which has been found to yield substantial amounts of  $\bullet\text{OH}$ . Yields from such reactions range between 0.1 and 0.8 radicals formed per alkene molecule consumed by ozone. This  $\text{HO}_x$  source is of much importance in rural areas and in forests (both tropical and boreal), as vegetation emits vast amounts of biogenic

alkenes, such as isoprene and the terpenes, which readily react with ozone. Alkene ozonolysis is probably the main nighttime HO<sub>x</sub> -source.

•OH is the fragment of the very stable water molecule, to which it can revert by abstraction of hydrogen from an organic molecule. A very great percentage of emitted molecules have one or more hydrogen atoms, and once a molecule has been attacked, it is headed for partial oxidation and concomitantly increased aqueous solubility and thus more rapid scavenging from the atmosphere.

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### **Biographical Sketches**

**Jozef Peeters**, born on Jan 4, 1941 (Borsbeek, Belgium), took degrees of Master of Arts in chemistry at the University of Toronto, Canada, in 1965, and of Doctor of Sciences at the University of Leuven, Belgium in 1967. In 1968 he obtained a Postdoctoral Research Mandate of the Belgian National Fund for Scientific Research. First in that capacity, he carried out his research at the University of Leuven (KULeuven), at which he became a lecturer in 1971, and at which he presently holds a full professorship. He is teaching or has taught undergraduate courses in: advanced experimental methods in physical chemistry (1969 - ), basic principles of general chemistry (1971 - 1997), chemical kinetics (1972 - ), atmospheric chemistry (1990 - ), instrumental methods in analytical chemistry (1998 - ), as well as a graduate course in unimolecular reaction theory (1995 - ). Since over thirty years, his research activities have been focused on the chemical kinetics and mechanisms of radical reactions in the gas phase, initially directed mainly to combustion chemistry, but during the past decade increasingly more to atmospheric chemistry and chemical processes in the interstellar medium, bringing to bear advanced experimental techniques as well as cutting-edge theoretical methodologies. The past 5-years, 2001 - 2005, he co-authored 48 papers in peer-reviewed international journals.

**Gaia F. S. Fantechi**, born on September 28, 1972 (Sorengo, Switzerland), took degrees of Master of Science in chemistry at the Free University of Brussels, Belgium, in 1994, and of Doctor of Sciences at the Catholic University of Leuven, Belgium, in 1999. During her Ph.D., she worked as a researcher in atmospheric chemistry at the Environment Institute of the Joint Research Centre (JRC) of the European Commission, Italy. Her main field of interest, in which she has been involved already for several years, is atmospheric chemistry, in particular the development of degradation mechanisms and kinetic studies of biogenic hydrocarbons and (mono)terpenes as well as their degradation products. Upon receiving her Doctorate, she worked for the Air Quality Unit-Environment Institute of the JRC of the European Commission, Italy. Since 1996, she has authored and co-authored several publications in peer-reviewed international journals and in proceedings of international meetings. Currently living in Belgium, she carried out Post-Doctoral research in the group of Prof. J. Peeters at the Catholic University of Leuven, 2001 – 2002, and since 2003 she holds a permanent scientific staff position at the food agency of the European Commission.