Tropospheric Chemistry and Transport

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Oxidation rates of trace gases in the troposphere depend on species-specific rate coefficients and are predominantly governed by the concentration of the hydroxyl radical (OH), the most important oxidizing molecule in the troposphere. The concentration of OH is in local photochemical steady state; it is, however, dependent on the concentration of trace gases such as ozone, water vapor, volatile organic compounds, and oxides of nitrogen. Diffusive and advective transport processes influence and change the concentrations of these trace gases. Oxidative and transport time scales are often of similar magnitude, which leads to coupling between tropospheric chemistry and transport.

The Earth's troposphere, which is the lowest 10 to 17 km (depending on latitude and season) of the atmosphere, acts like a chemical reactor in which huge quantities of volatile organic compounds (VOC) (equivalent to approximately 1 billion tons of carbon) and of other reduced trace gases that are emitted into the atmosphere annually from various biogenic and anthropogenic sources are transported by winds and turbulence, chemically processed, and converted to products. Photochemical degradation of VOC and other reduced trace gases starts with oxidation by the hydroxyl (OH) radical (*1*, *2*). Tropospheric VOC oxidation, at a typical tropospheric OH concentration of around 10^6 molecules per cubic centimeter, proceeds within less than 1 hour for highly reactive olefinic compounds to months for some of the less reactive alkanes and carbon monoxide and years for the slowly reacting methane. The lifetime of NO_2 with regard to oxidation by OH to nitric acid (HNO_3) is roughly 1 day.

In contrast to a well-stirred reactor, reactants and products are not homogeneously distributed in the atmosphere. Also, molecular diffusion is unimportant compared to other means of transport dynamics. The atmosphere transports and mixes trace gas constituents with a characteristic spectrum of time constants. Transport times in the troposphere are governed by wind speeds, large-scale and small-scale turbulence, planetary wave action, and slow residual circulations (*3*). Interhemispheric exchange is achieved in about 1 to 2 years; meridional transport across latitude belts takes months; and zonal transport in bands of constant latitudes is achieved in about 2 weeks. Vertical mixing in the troposphere takes about 1 month on average. However, vertical transport can occur within 1 hour when, during active deep convection, boundary layer air is lifted to the uppermost levels of the troposphere in the cores of cumulonimbus clouds.

The similarity of oxidation and transport time scales leads to coupling between transport and chemistry and generates principal and practical difficulties in the quest for a quantitative understanding of atmospheric chemistry. The examples below for the coupling between transport and chemistry in an urban setting and on the global scale illustrate some of these difficulties.

Large fluxes of VOC and NO_x (= NO + NO_2) from anthropogenic sources are emitted into the urban and suburban atmosphere (*2*). For a wide range of combinations of initial (early morning) mixing ratios of NO_x and of VOC, 12-hour mean OH concentrations have been calculated (Fig. 1) with the use of a zero-dimensional chemical (box) model (*4*). It can be seen that the OH concentration depends on the initial concentrations of the volatile organic compounds $(VOC)_0$, and of $(NO_x)_0$, and on the ratio $R_0 = (VOC)_0/(NO_x)_0$. High OH concentrations are the result of both efficient recycling and secondary production of OH. At high $(NO_x)_0$ values, the OH concentrations are low because of OH loss through the three-body reaction $OH + NO_2 + M \rightarrow HNO_3 + M$.

The city can be treated as a point source to consider the effects of dilution of city air with the cleaner environment on the oxidation rates of VOC and NO_x and the OH concentration. If spreading of the city plume into the clean surrounding air is fast or if there is no chemistry during the dilution, which happens at night, then, starting for example from a NO_x mixing ratio of 100 ppb and an R_0 of about 5, the polluted air is diluted as it spreads out, but R_0 will not change (*5*). Any point on the dilution line (curve 1 in Fig. 1) can thus be considered as a new initial value of $(VOC)_0$ and $(NO_x)_0$ at the moment at which the chemistry can be activated, for example at daybreak, which would lead to the indicated OH concentrations. However, chemical processes will result in steeper trajectories than that of the dilution line, because the oxidation of NO_x by OH proceeds at a faster rate than the oxidation of most VOC in city air. Thus, depending on the relative rates of mixing and dilution of polluted air masses with cleaner background air versus the chemical reaction rates, many points on the OH hypersurface below the dilution line can be reached. Such trajectories are indicated by curves 2, 3, and 4 in Fig. 1. Clearly, dilu-

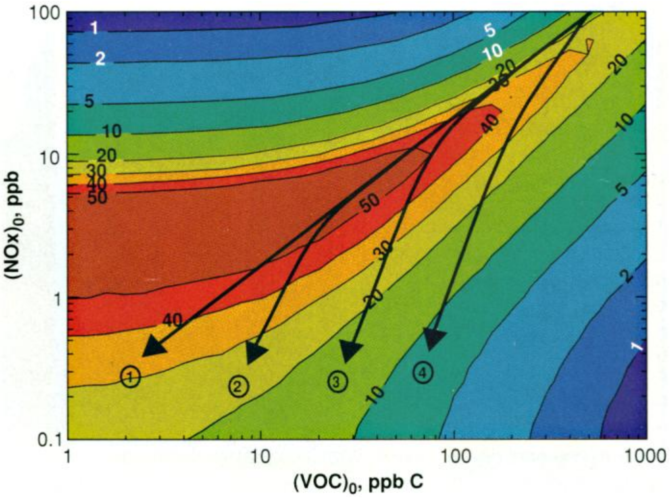

Fig. 1. Isolines of 12-hour mean concentrations of OH in units of 10^5 molecules per cubic centimeter for a wide range of initial $(VOC)_0$ and $(NO_x)_0$ combinations. A box model (*13*) and a VOC mix similar to that of Rome (*14*) were used. The origin of the straight line 1 is at $(NO_x)_0$ = 100 parts per billion (ppb) and $(VOC)_0$ = 500 ppb C, representative of initial conditions of polluted city air. Curves 2, 3, and 4 are illustrations of possible trajectories to new initial conditions that result from the simultaneous action, to different degrees, of chemistry and dilution on the trace gas composition.

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tion and mixing affect the complex nonlinear oxidation chemistry, depending on the relative importance of mixing and dilution compared to the chemical reaction rates.

Atmospheric chemistry is also affected by advective transport, which may import trace species that originated far away. Tropospheric ozone serves as an example. The chemical lifetime of ozone against photolysis-initiated destruction, which leads to OH production, depends on the stratospheric column density of ozone and on the concentration of water vapor (*1*). In the upper troposphere, the lifetime approaches 1 year, whereas in the boundary layer of the tropics the ozone lifetime is only a few days.

The tropical tropopause is the region where trace gases that originated at the Earth's surface can be transported into the stratosphere. Regardless of the details of the transfer processes across the tropopause (*3*), reduced compounds can only be transported to the stratosphere if, during their journey through the tropical troposphere, they escape oxidation by OH. Vertical, advective transport influences the oxidation capacity in the troposphere and therefore the concentration and vertical distribution of trace gases. The effects of convection on the tropical ozone distribution can be inferred from the large-scale meridional altitude-latitude cross section of the ozone mixing ratio, for example, as shown at 30°W in Fig. 2 (*6*). The ozone mixing ratio is at its minimum in the boundary layer in the central tropics near 10°N, which was the location of the Intertropical Convergence Zone (ITCZ) at the time of the measurement. These low ozone concentrations near the surface in the central tropics are caused by the combination of low stratospheric column density and high relative humidity at high tropical temperatures, a condition that leads to rapid destruction of ozone. The photochemical lifetime of ozone under these conditions is only about 5 days (*7*). In the ITCZ, deep convection lifts air from near the sea surface to the upper troposphere typically within 1 hour. The associated vertical mass flux is compensated for by horizontal convergence. The boundary layer evacuation time is also about 5 days (*8*), and therefore the strong ozone sink in the boundary layer in the ITCZ acts like a flow-through processor of ozone, continuously destroying ozone while the air passes through it. The combined effect of ozone destruction in the marine boundary layer and vertical uplift also leads to low mixing ratios in the middle and upper troposphere (Fig. 2).

Because ozone is the precursor of the OH radical, the fast convective transfer of low ozone to the middle and upper troposphere described above has implications for the oxidation capacity of the troposphere. The accompanying decrease of the OH concentration is mitigated by an increase of relative humidities at all altitudes during convection. However, screening by large anvil clouds during active convection decreases the ultraviolet actinic light flux, which reduces the OH production and causes low overall OH concentrations (*9*). Low OH concentrations and short residence times of reduced substances in boundary-layer air during convection conspire to allow highly reactive, reduced gases to reach the upper tropical troposphere. Kley *et al.* (*9*) suggested that substantial amounts of dimethylsulfide [(CH)$_2$S] and methyliodide (CH$_3$I), which originate in seawater (*1*), can escape oxidation in the marine boundary layer and reach the upper troposphere where their oxidation products may form aerosols and cloud condensation nuclei.

Figure 2 illustrates also that the large convective cell, located in the ITCZ, extends into the upper troposphere and is accompanied by sinking air on either side, as can be inferred from the high ozone mixing ratios that originate in the upper troposphere, some 10° of latitude to the north and south of the convective cell. In the meridional cross section of Fig. 2, this ozone-rich air is sinking, and some of it is entrained into the convection near an altitude of 5 km (*10*). This upper tropospheric air, which is advected as filamentary structures within a few days (*11*), should have a trace gas composition similar to that of the region from which it originated, but this has not been verified so far. It seems possible, however, that air from the lower stratosphere can be advectively transported and entrained in the tropical convection on the potential temperature surface around 315 to 320 K, which isentropically connects the troposphere to the stratosphere in the subtropics (*12*). This air should then contain enhanced concentrations of nitrogen oxides from the stratosphere, which, after entrainment in the convection, would provide a source of NO$_x$ for the upper tropical troposphere. NO$_x$ is of critical importance for tropospheric chemistry, and therefore investigations of this type of advective transport should have high research priority.

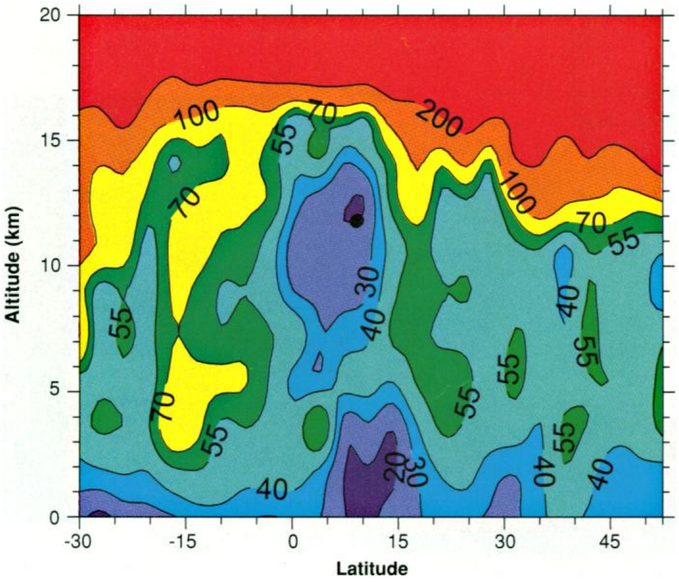

Fig. 2. Meridional altitude-by-latitude cross section of the ozone mixing ratio at 30°W during September and October 1988 (*6*). The low mixing ratios in the lower troposphere near 10°N are the result of photolytic ozone destruction during advective flow from higher latitudes into the ITCZ. The large cell with low mixing ratios in the upper troposphere is caused by convective transport of boundary layer air to the upper troposphere. Subsidence at latitudes north and south of the convective cell transports ozone-rich dry air to the middle troposphere. Some of this air is advected and entrained in the convective cell at altitudes near 5 km (*10*, *11*).

REFERENCES AND NOTES

1. M. O. Andreae and P. J. Crutzen, *Science* **276**, 1052 (1997).
2. B. J. Finlayson-Pitts and J. Pitts, *Science* **276**, 1045 (1997).
3. J. D. Mahlman, *Science* **276**, 1079 (1997).
4. A box model is a chemical model that allows calculation of the change of concentrations of reactants, products, and intermediate species as a function of time without consideration of the effects of molecular diffusion or macroscopic transport.
5. It is assumed that the VOC and NO$_x$ concentrations of the surrounding air, into which the diluting air masses spread, are negligibly small.
6. H. G. J. Smit, S. Gilge, D. Kley, *In Physico-Chemical Behaviour of Atmospheric Pollutants*, G. Restelli and G. Angeletti, Eds. (Kluwer, Dordrecht, Netherlands, 1990), pp. 630–637.
7. S. C. Liu, M. McFarland, D. Kley, O. Zafiriou; B. Huebert, *J. Geophys. Res.* **88**, 1360 (1983).
8. The boundary layer evacuation time T_{ev} is the approximate residence time of air in the ITCZ with regard to vertical displacement to the free troposphere by deep convection. T_{ev} can be estimated from $T_{ev} = M_{bl}/(N_{st} \times \Phi_{st})$, where M_{bl} is the boundary layer

mass of the ITCZ, Φ_{st} is the vertical mass flux per storm, and N_{st} is the number of active storms. [H. Riehl and J. M. Simpson, *Contrib. Atmos. Phys.* **52**, 287 (1979)].
9. D. Kley *et al.*, *Science* **274**, 230 (1996).
10. D. Kley *et al.*, *Q. J. R. Meteorol. Soc.*, in press.
11. A. R. Numaguti *et al.*, *J. Meteorol. Soc. Jpn.* **73**, 267 (1995); B. E. Mapes and P. Zuidema, *J. Atmos. Sci.* **53**, 620 (1996).
12. Potential temperature (Θ) is defined as $\Theta = T (1000/p)^{\kappa}$, where T is the temperature, p is the pressure, $\kappa = R/mc_p$, R is the gas constant, m is the molecular weight of dry air, and c_p is the heat capacity of air at constant pressure. Θ is the temperature that an air parcel would attain after adiabatic compression from given values of T and p to a pressure of 1000 hPa.
13. W. R. Stockwell and D. Kley, *Ber. Forschungszentrum*, **Jülich. Jül**, 2868 (1994).
14. D. Brocco *et al.*, *Atm. Environ.* **31**, 557 (1997).

Tropospheric Air Pollution: Ozone, Airborne Toxics, Polycyclic Aromatic Hydrocarbons, and Particles

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Tropospheric air pollution has impacts on scales ranging from local to global. Reactive intermediates in the oxidation of mixtures of volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) play central roles: the hydroxyl radical (OH), during the day; the nitrate radical (NO_3), at night; and ozone (O_3), which contributes during the day and night. Halogen atoms can also play a role during the day. Here the implications of the complex VOC-NO_x chemistry for O_3 control are discussed. In addition, OH, NO_3, and O_3 are shown to play a central role in the formation and fate of airborne toxic chemicals, mutagenic polycyclic aromatic hydrocarbons, and fine particles.

Tropospheric air pollution has a long and storied history (*1, 2*). From at least the 13th century up to the mid-20th century, documented air pollution problems were primarily associated with high concentrations of sulfur dioxide (SO_2) and soot particles. These problems are often dubbed "London Smog" because of a severe episode in that city in 1952. However, with the discovery of photochemical air pollution in the Los Angeles area in the mid-1940s, high concentrations of O_3 and photochemical oxidants and their associated impacts on human health have become a major issue worldwide.

In this article we discuss recent research on air pollution on scales ranging from local to regional, although analogous chemistry occurs on a global scale, as discussed in the accompanying articles by Andreae and Crutzen (*3*) and Ravishankara (*4*). Thus, an increase in tropospheric O_3 has been observed globally over the past century (*5–11*), an example of which is seen by comparison of O_3 levels measured at Montsouris in France from 1876 to 1910 to those at a remote site on an island in the Baltic Sea (Arkona) from 1956 to 1983 (Fig. 1). Surface concentrations of O_3 found in other remote areas of the world now are similar, ~30 to 40 parts per billion (ppb) (1 ppb = 1 part in 10^9 by volume or moles), as compared with ~10 to 15 ppb in preindustrial times. This increase has been attributed to an increase in NO_x emissions associated with the switch to fossil fuels during the industrial period.

The potential effects of a global increase in O_3 and other photochemical oxidants are far-ranging. Ozone is a source of the hydroxyl radical (OH) (see below), which reacts rapidly with most air pollutants and trace species found in the atmosphere. Hence, increased concentrations of O_3 might be expected to lead to increased OH concentrations and decreased lifetimes of globally distributed compounds such as methane. Because both O_3 and methane are greenhouse gases, this chemistry has implications for global climate change. In addition, because O_3 absorbs light in the region from 290 to 320 nm, changes in O_3 levels can affect the levels of ultraviolet radiation to which we are exposed.

Inextricably intertwined with the formation and fate of O_3 and photochemical oxidants in the troposphere are a number of closely related issues, such as the atmospheric formation, fate, and health impacts of airborne toxic chemicals and respirable particles. Understanding these issues is key to the development of reliable scientific risk assessments (*12, 13*). In this context, we give an overview of the chemistry of tropospheric air pollution involving O_3 and associated species and give examples of applications to strategies for control of O_3, airborne toxic chemicals, polycyclic aromatic hydrocarbons, and respirable particulate matter. We emphasize the key roles played by a remarkably few reactive species, such as OH. The chemistry of SO_2 and acid deposition is closely linked with this chemistry, but that topic is beyond the scope of this article.

Ozone and Other Photochemical Oxidants

The term "photochemical" air pollution reflects the essential role of solar radiation in driving the chemistry. At the Earth's surface, radiation of wavelengths 290 nm and greater—the so-called actinic region—is available for inducing photochemical reactions. The complex chemistry involving volatile organic compounds (VOCs) and NO_x (where $NO_x = NO + NO_2$) leads to the formation not only of O_3, but a variety of additional oxidizing species. These include, for example, peroxyacetyl nitrate (PAN) [$CH_3C(O)OONO_2$]. Such oxidants are referred to as photochemical oxidants. We concentrate here on O_3, recognizing that a variety of other photochemical oxidants are associated with it.

Sources of O_3. The sole known anthropogenic source of tropospheric ozone is the photolysis of NO_2

$$NO_2 + h\nu\ (\lambda < 420\ \text{nm}) \rightarrow NO + O(^3P) \qquad (1)$$

followed by

$$O(^3P) + O_2 \xrightarrow{M} O_3 \qquad (2)$$

(M in Eq. 2 is any third molecule that stabilizes the excited intermediate before it

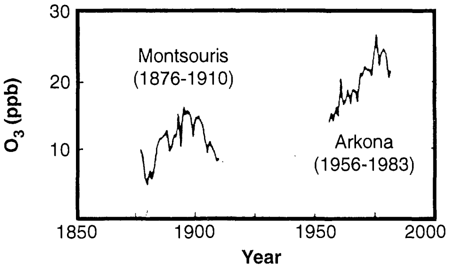

Fig. 1. Mean annual O_3 concentrations in Montsouris (outside Paris) from 1876 to 1910 and at Arkona from 1956 to 1983, showing increasing O_3 levels on a global scale [reprinted with permission from *Nature* (*8*), copyright 1988, Macmillan Magazines Ltd.].

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