

A 3-DIMENSIONAL MODEL OF THE TROPOSPHERE FROM THE PRE-INDUSTRIAL TO THE PRESENT

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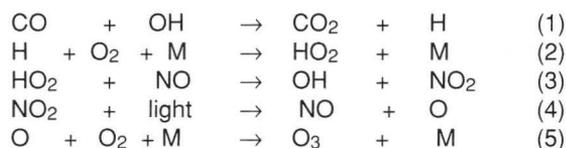
The composition of the Earth's atmosphere plays a key role in the world climate system. Radiatively active gases which influence the Earth's radiation budget include chemically inert gases such as water vapor and carbon dioxide, but also several less abundant species whose concentrations are partly or completely controlled by photochemical processes taking place in the atmosphere. The subject of our study is the investigation of the role and time-evolution of the chemically active species influencing the climate system.

Among these trace gases, ozone (O₃) and methane (CH₄) are of particular interest, because their concentrations in the troposphere are known to increase in time, at higher rates than carbon dioxide: about 1%/year for methane, between 0 and 2 %/year for ozone. They are called "greenhouse gases" because, as carbon dioxide and water vapor, they trap some fraction of the infra-red radiation emitted by the Earth's surface which would otherwise be emitted to space. The basic reason for the increase of the concentration of ozone, methane and many other compounds is the rise in the human-controlled emissions of various gases to the atmosphere. Methane, for example, is released as a result of e.g. coal mining, natural gas exploitation, and anaerobic microbial production in rice paddies sediments.

1. Tropospheric ozone

Ozone is not emitted at the Earth's surface. It is, however, a secondary pollutant produced by the light-triggered oxidation of primary pollutants. The combustion of fossil fuel accounts for a substantial fraction of the emissions of the primary pollutants, such as the nitrogen oxides, sulfur oxides, hydrocarbons and carbon monoxide. Deforestation and the burning of savanna and forests for the purpose of agriculture is a major source of the same species in the Tropical regions. For these reasons, the atmospheric concentrations of these species are believed to have dramatically increased since the beginning of the industrial era. We'll see in a following section that this assumption is supported by numbers of experimental and modelling results. The relevance of these com-

pounds arises from the fact that the tropospheric oxidation of carbon monoxide and hydrocarbons is known to produce ozone when the mixing ratio of nitrogen oxide is sufficiently high (typically, more than about 10 pptv of NO). A typical chemical cycle responsible for this production of ozone is



As can be seen, the net result of these reactions is (besides the oxidation of carbon monoxide, CO) the production of ozone. More complex, but still similar reaction cycles follow the OH-oxidation of methane and other hydrocarbons. The presence of NO is crucial with respect to the ozone photoproduction. In low-NO environments, the hydroperoxyl radical HO₂ will mainly react with ozone (instead of reaction (3)); the CO oxidation will in this case destroy ozone. Due to the short lifetime of nitrogen oxides in the troposphere, the distribution of their concentration is characterized by a very high degree of variability: the NO+NO₂ mixing ratio exceeds parts per billion (ppbv) near the surface above polluted areas, whereas it can be as low as a few pptv over remote areas such as the Tropical ocean. Note that, although the stratosphere is characterized by generally higher mixing ratios of nitrogen oxides than in the troposphere, their presence does not favor ozone production, due to the very different photochemical conditions prevailing in the stratosphere.

In addition to being a so-called "greenhouse gas", tropospheric ozone is also important for two other reasons. First, surface-level ozone is directly harmful to plants and to human health, and constitutes the central component of the so-called photochemical smog. Surface ozone mixing ratios larger than about 90-120 ppbv are considered above-norm in most industrialized countries. Photochemical smog is however frequent in polluted areas during summer anticyclonic episodes, when the conjunction of high radiation levels (cfr. reaction (4)) and stable meteorological conditions (favoring the accumulation of pollutants) allows a very efficient build-up of ozone and other harmful pollutants.

Finally, ozone plays a key role in the oxidizing capacity of the troposphere. Indeed, the photodissociation of ozone producing excited oxygen,



is the principal mechanism for hydroxyl radical production, through the reaction of excited oxygen with water vapor:



In turn, and despite its extremely low atmospheric concentration, OH is the main oxidant of a large number of chemical species emitted at the Earth's surface, including methane, the non-methane hydrocarbons (NMHC), CO, the hydrochlorofluorocarbons (HCFC), etc. Hydroxyl levels are controlled by ozone, CO, hydrocarbons, nitrogen oxides and light through complex mechanisms. There is therefore a concern that Man's polluting activities might perturb the OH chemistry and so alter the oxidizing capacity of the atmosphere. We'll see later below that OH actually seems pretty stable and uneasy to change on the global scale.

2. Modelling the chemistry of the troposphere

The quantitative assessment of the physical and chemical mechanisms governing the chemical composition of the troposphere is not an easy task. The problem is global : for example, the tropospheric composition of even the most remote areas of the planet is affected by the emissions of trace gases occurring in the source regions, thousands of kilometers away. The problem is four-dimensional : the composition of the troposphere varies strongly in the three spatial dimensions as well as in time. For the purpose of computational convenience, the atmosphere is divided into a given number of model boxes, and the concentration of each species in each model box has to be calculated as a function of time, given specified initial conditions and boundary conditions at the model borders. Moreover, the chemical system that has to be solved is known to be "stiff" (i.e., ill-conditioned), because the lifetimes of the species vary from microseconds to decades. Long-lived species like methane requires years of integration to reach equilibrium, whereas short-lived compounds exhibit strong diurnal variations. Finally, the troposphere is deeply influenced by its interaction with the Earth's surface (emissions, deposition) which need to be accurately parameterized. In addition to this, number of important processes are still poorly known, and are very crudely represented in the models.

Despite these difficulties, a hierarchy of models has been developed by the scientific community to investigate tro-

pospheric chemistry at various scales and with varying degrees of realism. In our study, a global, three-dimensional model of tropospheric chemistry has been developed in collaboration with the National Center for Atmospheric Research (Boulder, Colorado). The atmospheric sulfur cycle has also been introduced in the model, in collaboration with the Service d'Aéronomie of the Université Paris VII. This model, called IMAGES (Intermediate Model for the Annual and Global Evolution of Species), has an horizontal resolution of 5° in latitude as in longitude and include 25 levels in the vertical, between the Earth's surface and the lower stratosphere (50 mb). The model is able to represent the diurnal behavior of the species as well as the seasonal evolution of their concentrations. The chemical species calculated by the model include all the major species determining the oxidation capacity of the atmosphere, namely, the hydrogen (OH, HO₂, H₂O₂), oxygen (O₃, O, O(¹D)), nitrogen (NO, NO₂, NO₃, N₂O₅, HNO₄, HNO₃ and several organic nitrates), carbon (CO, CH₄, several other hydrocarbons, and their oxygenated oxidation products) and sulfur species. The geographical distribution of the pollutants release at the Earth surface has been determined from a detailed inventory of the different contributions to the trace gases emissions, including the vegetation, biomass burning, fossil fuel burning, the soils and the oceans. Surface deposition velocity maps for several trace gases were also constructed from ecosystem and climatic datasets. The results of this inventory showed that the human activities are responsible for two thirds or even a larger fraction of the emissions of nitrogen oxides, sulfur oxides, carbon monoxide and methane.

IMAGES includes about 120 chemical reactions and photodissociations describing the sources and sinks of about 50 chemical species. Surface deposition of chemical compounds as well as precipitation removal of water-soluble gases are considered. Washout is determined using the observed precipitation rate and the climatological distribution and frequency of cloud occurrence determined by the International Satellite Cloud Climatology Program (ISCCP). The photodissociation coefficients of 20 species are interpolated at each time step and each point of the grid from tables giving these coefficients for discrete values of the altitude, the solar zenith angle, the ozone column above the point and the albedo of the underlying surface. This table was calculated using a one-dimensional radiative transfer model based on the discrete ordinates method.

The long-lived species are transported by winds, diffusion and cloud (Cumulo-nimbus) convection. In this "intermediate" model, the effect of short-term variability of the winds is simulated as an eddy diffusion process. The advective transport is performed using monthly mean winds taken from the climatological analysis of the European Centre for Medium-Range Weather Forecasts (ECMWF). Other fields such as the atmospheric temperature, the water mixing ratio and the precipitations are

also taken from climatological datasets. A semi-lagrangian scheme has been adopted to calculate the advective transport of the species, allowing the use of relatively large timesteps. Vertical convection in cumulo-nimbus clouds is parameterized as a one-dimensional process, using the ISCCP climatology.

The purpose of the model is to calculate the three-dimensional distributions and the global budgets of the most important chemically active trace gases in the troposphere. IMAGES is an ideal tool to assess, e.g., the impact of human activities on the chemical structure of the atmosphere and to understand the role played by chemically active trace gases in such concerning problems as the greenhouse effect and the photochemical smog. The model has been validated by an extensive comparison with available observations of CH₄, CO, NO_y, O₃ and other species. Although IMAGES cannot represent properly the real short-term variability of the atmospheric composition, the comparison shows its ability to reproduce the large-scale features and climatological budgets of the major tropospheric compounds. In particular, the oxidizing capacity of the atmosphere appears to be correctly calculated by the model, since the simulated lifetime of methane (whose main sink is the reaction with hydroxyl) is in good agreement with the recent estimates based on methylchloroform budget constraints.

3. The impact of industrialization on the composition of the troposphere

As a consequence of the substantial amounts of pollutants injected into the atmosphere due to human activities, it can be expected that the composition of the troposphere has changed since the last century. The retrieval of ancient air composition from ice cores in Antarctica and Greenland supports this conclusion, at least for some species. Methane, in particular, was about 2.5 times less abundant in the preindustrial era than it is today. Nitrous oxide increased much less by comparison, as this gas is mainly biogenic. Little information is however available on the past mixing ratios of the less abundant trace gases such as carbon monoxide, nitrogen oxides, and the non-methane hydrocarbons. This is the reason why the use of comprehensive models is clearly necessary to assess theoretically the impact of industrialization on tropospheric composition.

For this purpose, the IMAGES model has been run with surface boundary conditions corresponding to the pre-industrial era (ca. 1800). The pre-industrial emissions associated with fossil fuel burning, mining activities and industry were assumed to be negligible. To represent the fact that human population in the Tropical regions were much lower than it is today, the emissions associated with biomass burning were reduced by a factor three. As the world's climate, the terrestrial biosphere and the ocean

have only slowly varied since the last century, they were assumed to be identical to what they are today in our simulations. Moreover, the preindustrial methane budget being particularly difficult to establish (the uncertainty on the main biogenic sources of methane are around a factor of three), we chose to specify the ice-core measurements of methane as surface mixing ratio at pre-industrial times.

The results of this simulation show that the NO_x, CO and hydrocarbon concentrations were much lower than they are today. For example, the nitrogen oxides surface mixing ratio over continental areas was lower by a factor of 5 on global average and by 1-2 orders of magnitude at the Northern mid-latitudes. The atmospheric burden of CO is found to be 3 times lower than its present value. CO was more abundant in tropical regions (40-60 ppbv) than in the mid-latitudes (30-40 ppbv), because the biogenic sources of CO (microbial production, oxidation of hydrocarbons) are mostly concentrated in the Tropics. The resulting changes in the ozone abundance are substantial and most pronounced in the Northern Hemisphere, mostly during the summer. Figure 1a-b illustrates the net ozone production integrated over the entire troposphere in June, for present-day and pre-industrial conditions. The effect of the fossil-fuel emissions (over continental mid-latitudes) and biomass burning (over tropical regions) are clearly seen, the maximum values of the ozone production being about 3 times larger at present time than before the industrialization. The change in the zonally averaged ozone concentration (referred to pre-industrial conditions) reaches more a factor of two in the summer Northern Hemisphere. The predicted surface ozone changes over Western Europe (a factor of 3 in summer) are consistent with the evolution of observed surface ozone concentrations in Europe since the end of the 19th century. The seasonal cycle was less pronounced than it is today, because the nitrogen oxides levels were too low to allow a significant photochemical production of ozone during summer. The averaged surface ozone changes over the continents (a factor of 2) imply a mean increase rate of about 1%/year since the beginning of the industrial revolution. The oxidation capacity of the atmosphere, however, was less affected by industrialization. The photochemical lifetime of methane and carbon monoxide were about 10% and 5% lower than their present values. These small changes result from two compensating effect: the increase of OH (compared to present) in tropical regions, due to the lower CO and CH₄ concentrations, and the decrease of OH at midlatitudes, where NO_x and O₃ changes were most pronounced. These results are consistent with previous studies performed using less detailed models of tropospheric chemistry.

O₃ INTEGRATED NET PRODUCTION

(a) PRESENT-DAY



(b) PRE-INDUSTRIAL

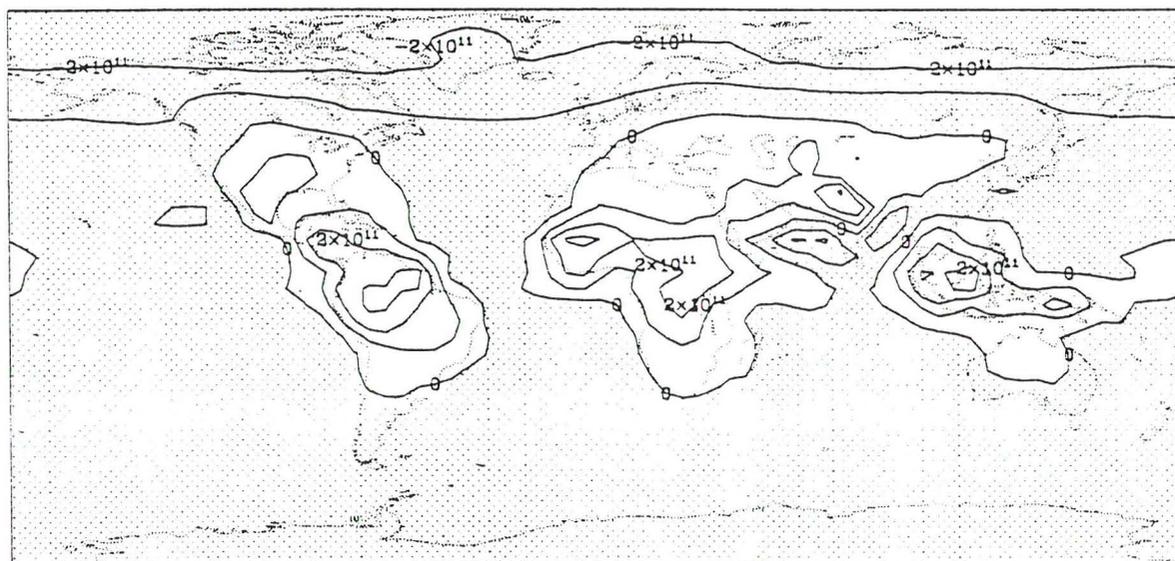


Figure 1 : Column-integrated net ozone production predicted by the model in June, (a) at present time, and (b) during the pre-industrial period. Units: molec./cm²/s

4. Conclusion

We have presented a three-dimensional chemical-transport model which has been developed to study the global distributions and budgets of trace constituents in the troposphere. From the transport point of view, the model is "intermediate" between highly parameterized approaches such as those used in one-dimensional models and fully explicit representations such as those provided by tracer models coupled to General Circulation Models (GCM). IMAGES provides a mathematical tool which requires a factor of 10 less computer resources than 3-d chemistry models coupled to GCMs because it has been designated to be integrated with long time steps, while accounting for the diurnal variation in solar insolation. Although the model doesn't produce the high frequencies found in the observed time series of tracer concentrations, it provides climatological evolutions and spatial distributions which are generally in good agreement with the available observations.

This model has already been applied to the study of the pre-industrial atmosphere, as shown above, but also to the investigation of the role of subsonic aircrafts, and on the sulfur cycle and the sulfate/climate relationship. A future study will focus on the impact of the possible future

increase in CO₂ concentration, with its implications on the climate, the biosphere, the trace gas emissions and the chemistry of the troposphere.

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