

Annex 1: Modeling

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1 Introduction

2 The chemistry of the atmosphere is controlled by a large number of
3 complex chemical and physical processes. The study of such a complex
4 system requires the use of numerical models which have increasingly
5 developed over the past 10 years. These models are mathematical
6 representations of the main physical and chemical processes controlling the
7 spatial and temporal distribution of trace gases. The models have been
8 developed in order to test our understanding of the atmospheric processes, to
9 identify key variables and important interactions, and to interpret local,
10 regional and global observations. Additionally, they can be used to predict the
11 evolution of the chemical state of the atmosphere in response to natural or
12 anthropogenic perturbations, and to help policymakers define emission
13 reduction policies.

14 Over the last decade, efforts to improve our understanding of atmospheric
15 processes have pushed the development of a hierarchy of models. Box models
16 continue to be excellent tools to illuminate our understanding of chemical
17 processes. They can now take into account several hundreds of chemical
18 species linked by a few thousands chemical reactions. As many tropospheric
19 chemical species are short-lived and exhibit large spatial and temporal
20 heterogeneities, the use of regional and global three-dimensional chemistry-
21 transport models has become more common. Considerable progress has been
22 made over the last 10 years on the development and application of these
23 sophisticated global three-dimensional models. The salient features of several
24 of these models are listed in Table xx.1. As shown in this table, present day
25 global tropospheric chemical transport models typically have horizontal
26 resolutions of 250-500 km, and include a reasonably complex representation
27 of chemistry, taking into account in many instances non-methane
28 hydrocarbons chemical schemes of varying levels of complexity.

29 Key advances in numerical techniques and computer power have benefited
30 models over the past decade. These improvements have enabled refined
31 temporal and spatial resolution of the models and more accurate

1 parameterizations of subgrid processes, allowing the scientific community to
2 use the models for many applications, as seen in Chapters 3 and 4. Section 2
3 will discuss the model developments over the last decade, Section 3 will
4 discuss model evaluations and intercomparisons with regard to specific
5 scientific problems. Section 4 presents a few new model developments such as
6 the development of coupled earth system models, or the use of large satellite
7 datasets in data assimilation and inverse modeling.

8

9 **2 Model developments**

10 **2.1 Box / Lagrangian models**

11 Major advances in understanding atmospheric chemistry have resulted
12 from the detailed analysis of individual processes. For this purpose, zero-
13 dimensional or box models, which consider a box in which the air mass is well
14 mixed, are commonly used. Box models are used to analyze observations of
15 selected species, to study tropospheric chemistry under specific conditions and
16 to simplify complex chemistry schemes. These models are also used to
17 evaluate and parameterize subgrid processes such as the fast chemistry
18 occurring near source areas with time scales shorter than the characteristic
19 transport times in large scale models, resulting in an „effective" source, for
20 instance in the boundary layer, with significantly different chemical
21 composition from the initial emissions.

22 Eulerian models which have fixed spatial grids differ from lagrangian or
23 trajectory models in which chemistry is calculated along the air parcel
24 trajectory. In these models, source and sink terms vary as the air parcel moves
25 into different spatial regions. Lagrangian and trajectory models, which allow a
26 detailed consideration of chemistry, are often used for local or regional scale
27 studies. Both types of models have the intrinsic difficulty that they do not
28 include mixing processes, which makes the validity of these models on longer
29 time scales questionable.

1 Tropospheric models also must take into account a significant number of
2 chemical reactions to simulate accurately tropospheric chemistry. The
3 parameterization of chemical processes in models is discussed in section 2.3.
4

5 **2.2 Parameterization of the transport of chemical compounds**

6 **2.2.1 Advection schemes**

7 The implementation of transport in chemical transport models is normally
8 separated into resolved or large scale advection and subgrid-scale processes,
9 usually subdivided into moist and dry mixing. In the real atmosphere, of
10 course, this separation of scales does not play a role and the different
11 parameterized processes occur simultaneously.

12 Advection by the resolved scale winds is theoretically a straight-forward
13 process, but deciding how to numerically implement this process in a transport
14 model requires compromise. The qualities desirable in an advection scheme
15 include: computational efficiency, accurate solutions, movement of tracer
16 should occur locally and in the downwind direction, solutions should be
17 monotonic (i.e., no new extrema should be introduced without divergence in
18 the flow), and mass conservative'. So far numerical solutions to the advective
19 transport have had to compromise on one or more of these traits. For example,
20 the semi-lagrangian transport schemes were not by nature conservative, so that
21 a mass fixer had to be introduced, which caused the transport to be slightly
22 non-local (Rasch and Williamson, 1990). The second order advection schemes
23 use a slightly higher memory and computational cost to obtain accurate, mass
24 conserving solutions (e.g., Russel and Lerner, 1981). New formulations of
25 mass flux schemes (Lin and Rood, 1996; Rasch and Lawrence, 1998) appear
26 to have improved stability and accuracy while being computational efficient
27 and mass conserving. They have been implemented in various forms in
28 chemical transport models and general circulation models. A very accurate
29 algorithm, recommended for coarse resolution grids, has been proposed by
30 Prather (1986): in this formulation, the tracer concentration inside a grid box is
31 represented by second-order polynomials and its spatial distribution by

1 second-order moments. This method, characterized by small numerical
2 diffusion, requires a large computation time. Reviews of the different
3 advection schemes used in chemistry-transport models are given for example
4 in Rood (1987), Hov *et al.* (1989), Chock (1991), and Brasseur *et al.* (1999).

5 **2.2.2 Subgrid processes: convection scheme**

6 Mixing processes, especially vertical mixing, often occur at scales smaller
7 than those resolved by chemical transport or general circulation models. These
8 models generally distinguish between mixing in the presence or absence of
9 moisture. In the former case they are referred to as moist cumulus convection
10 or simply convection and in the later case they are often referred to as
11 boundary layer mixing or turbulent diffusion. Moist convective mixing
12 processes have the capability of moving a boundary layer parcel to the
13 tropopause during an intense event, such as a thunderstorm, and the inclusion
14 of this process in models appears to significantly contribute to the simulated
15 vertical transport (e.g. Mahowald, *et al.*, 1997). Currently, there appears to be
16 no best way to include cumulus convection in either chemical transport or
17 general circulation models. Moist convective mixing parameterizations vary
18 from simple increased diffusion in areas of moist convective instability (Levy
19 *et al.*, 1982) to complicated physically based schemes based on convective
20 available potential energy (Pan and Wu, 1995). Currently available
21 observational data are insufficient to judge which of the very different vertical
22 profiles resulting from the different schemes is more realistic (e.g. Jacob,
23 *et al.*, 1997).

24 Dry convective mixing occurs when the boundary layer or other layers are
25 statically unstable and is often parameterized using a simple diffusive
26 approach based on local instability such as Louis (1979). This approach may
27 simulate somewhat too little mixing in the boundary layer under highly
28 unstable (daytime) regimes, which led to the development of non-local
29 schemes such as Holtslag and Boville (1993). Comparisons of models such as
30 Jacob *et al.* (1997) or Rasch, *et al.* (in press) suggest that the local Louis
31 schemes may produce too little mixing but the non-local schemes may mix

1 slightly too much. Since many species have surface sources, and many
2 observations occur at the surface, improvements of parameterizations for the
3 boundary layer have a high. Unfortunately, observations that can be used to
4 unambiguously evaluate these parameterizations are scarce.

5 Many chemical transport models are off-line models, in which the winds
6 and temperature are input to the model, and have been derived from another
7 model, either a general circulation or a forecast center model. Recently,
8 chemical transport models have added the ability to explicitly treat moisture in
9 order to better capture the moist convective mixing and precipitation events
10 which control especially soluble species in the atmosphere (e.g. Rasch *et al.*,
11 1997). In this case, the temperature and humidity are predicted (using surface
12 flux and radiative flux fields from the driving model) including the effects of
13 moist convection and stratiform precipitation. These offline models are thus
14 capable of simulating specific events using forecast center winds such as the
15 NCEP or ECMWF winds and capturing the hydrological cycle (Lawrence,
16 *et al.*, 1999a + *other references*). Another approach which allows the
17 simulation of specific events is to use an online model which is 'nudged' to the
18 "observed" meteorology from forecast center analyses (Jeuken *et al.*, 1996).
19

20 **2.2.3 Transport of chemical species from the stratosphere to the troposphere**

21 An important process that must be represented in studies of tropospheric
22 oxidant chemistry is the downward transport of ozone (and to a lesser extent
23 of NO_x) from the stratosphere. To do this accurately, one must realistically
24 simulate stratospheric chemistry, downward transport in the stratosphere, and
25 the space-time distribution of stratosphere-troposphere exchange events. The
26 current generation of tropospheric chemistry models does not include a
27 explicit an rigorous treatment of stratospheric chemistry. In the recent IPCC
28 (1999) report on the impact of aircraft on the atmosphere, 2-D models were
29 used to simulate stratospheric processes, while 3-D models were used for the
30 troposphere, and the results were combined to obtain a global picture. This
31 was recognized as a major weakness in the analysis of model results. It should

1 be noted however that though models simulating both tropospheric and
2 stratospheric chemistry are currently under development within a few
3 modeling groups.

4 In almost all current models, the concentrations of O₃ and related species
5 are prescribed at some level in the stratosphere, usually at or below 10 hPa.
6 Exceptions are the Harvard-GISS and MOGUNTIA (table xx.1) models which
7 use an alternative parameterization by prescribing flux boundary conditions at
8 the tropopause. An additional consideration is that the vertical (and in some
9 cases horizontal) model resolution is often rather coarse and calculation of the
10 relevant transport processes in the middle atmosphere is missing in most
11 models, so that there are significant uncertainties in model-calculated
12 stratospheric dynamics as well as in the dynamics of stratosphere-troposphere
13 exchanges. While the global cross-troposphere flux of O₃ is constrained to
14 some extent by budget considerations, there is a considerable range in the
15 "simulated" cross-tropopause O₃ flux in various models. Furthermore, the
16 differences in the models can lead to large differences in the context of the
17 stratospheric contribution to tropospheric O₃ at particular locations and time-
18 periods.

19

20 **2.3 Parameterization of chemical processes**

21 The representation of chemical processes in tropospheric models is
22 strongly limited by computing time. In the global background marine
23 troposphere, it seems reasonable to consider a simplified chemistry scheme
24 based on O_x/NO_x/CH₄ and CO photochemical reactions. However, natural
25 emissions of organic compounds from oceans (mainly alkenes and dimethyl-
26 sulfide (DMS)) might significantly affect the marine boundary layer
27 chemistry. The possible role of halogens on the ozone budget in the marine
28 atmosphere has recently been discussed by Dickerson *et al.* (1999). Over
29 continental areas, both under clean and polluted conditions, chemistry is much
30 more complicated. Consideration of non-methane hydrocarbons chemistry
31 oxidation in the troposphere is improving the agreement between model

1 results and observations for species such as carbon monoxide and ozone
2 (Houweling *et al.*, 1998; Wang *et al.*, 1998c). A very large number of
3 chemical reactions and species are involved in the oxidation chains of
4 hydrocarbons. Therefore, a number of techniques were developed in the past
5 years to provide „reduced" chemistry schemes. Reduction of the chemical
6 reaction schemes introduces inaccuracies in the computation of chemical
7 species which are evaluated by comparison i) with field and smog chamber
8 observations, ii) with other reduced and iii) with detailed "master" chemical
9 mechanisms (the most known being the NCAR (Madronich and Calvert, 1989)
10 and University of Leeds (Jenkin and Hayman) master mechanisms) containing
11 several thousands of reactions that may be relevant in the troposphere.
12 Unfortunately, most reactions have not been measured since most laboratory
13 data concern the rates and the first generation product yields of the compounds
14 of interest. As expected, the level of mechanism reduction is not the same for
15 local and regional pollution model as for global models. Among the best
16 known reduced are the Carbon Bound IV (Gery *et al.*, 1988), the Lurmann
17 (Lurmann *et al.*, 1986), the Carter (Carter, 1990; Carter and Atkinson, 1997),
18 the RADM – RACM (Stockwell *et al.*, 1986) and the EMEP (Simpson *et al.*,
19 1993) mechanisms. Although most are based on the same laboratory kinetic
20 data, they differ by the techniques and assumptions used to represent and
21 simplify the organic chemistry.

22 Two main reduction or lumping techniques are, first, the structural
23 approach, in which the molecular structures or functional groups within the
24 hydrocarbon molecules are the lumping category. The second category
25 considers the molecular lumping approach, where the numerous emitted
26 organic compounds are represented by a limited number of species, each of
27 them representing a certain class of compounds. The principal requirement for
28 this is that the behavior of the individual compounds that are lumped must not
29 depart too much from the average behavior of the category. The disadvantage
30 of the lumped mechanisms is that they depend on the laboratory kinetic data
31 set used to produce them. Any change in the reactions or in the reaction rates
32 requires the development and the reevaluation of a new mechanism, based on

1 the initial reduction procedure. As expected, the results of models using
2 different chemical mechanisms are not the same. It is important to evaluate
3 and take into account uncertainties in the representation of the chemistry.
4 Thus, for the past years, since NMHCs have been shown to be important for
5 regulating oxidant levels, recommendation of kinetic data has been extended
6 to the still limited NMHCs oxidation chemistry and intercomparison exercises
7 have been performed on an international level (see section 3.1).

8 Recent improvements of chemical schemes in the models which will
9 continue in the near future concern for example the incorporation of HONO
10 chemistry and its impact on OH, and the improvement of parameterizations of
11 gas/particles interactions.

12 Careful evaluation and minimization of uncertainties and errors in CTMs
13 is requested to enable their application to the study of observed changes in
14 ozone as low as a few percent. Current models simulate absolute ozone
15 concentrations within 20 to 50 percent. Calculated changes in ozone
16 distributions as a result of perturbations, such as changes in surface emissions,
17 could however be more accurate. Over the past years, several studies (mainly
18 based on Monte Carlo simulations) focused on the evaluation of the sensitivity
19 of oxidant levels to various chemical reactions to identify crucial processes for
20 error minimization. Chemical reaction rates are also uncertain: for instance, in
21 the early 90's, determination of the reaction rates of CH_4 and CH_3CCl_3 with
22 OH suggested that these reactions were about 20% slower than previously
23 estimated. Similarly, the reaction between OH and NO_2 , which is an important
24 sink for NO_x in the troposphere, has been recently measured at 10-30 percent
25 lower than previous estimates (Donahue *et al.*, 1998; Brown *et al.*, 1999;
26 Dransfield *et al.*, 1999). Temperature dependence of reaction rates can also
27 introduce a 20-40% uncertainty in concentrations of chemical species such as
28 ozone in the troposphere (Stewart and Thompson, 1995).

29 An other equally important source of uncertainties in chemical calculations
30 is related to the computation of the rates of photodissociation reactions, which
31 are the driving force of photochemistry in the atmosphere. These rates depend
32 on the zenith angle, surface albedo, presence of clouds and aerosols (size

1 distributions and optical properties) and of distribution of chemical species.
2 Discrepancies in the photolysis rates computed by various methods, as
3 discussed below, result from the use of different input parameters.
4 Fundamental methods for radiative transfer calculations such as the Matrix-
5 Operator method require too much computer time to be practical in global
6 CTMs. Therefore, approximate methods have been developed for three-
7 dimensional chemistry-transport models. The most commonly used are the
8 two-stream methods. There are a variety of such methods. The basic
9 differences between various two-stream methods are the choice of
10 fundamental scattering parameters. Recently, new approximations for on-line
11 calculations of photolysis rates in sophisticated CTMs have been developed
12 (Landgraf and Crutzen, 1998, Berntsen *et al.*, 1997a, and NCAR, Irvine
13 groups, Krol and Van Weele, 1997), to allow computationally efficient
14 consideration of feedbacks between chemistry and photochemical rates in the
15 models. Another approach to overcome computing limitations is the use of
16 look-up tables wherein photolysis rates are precalculated from accurate
17 radiative transfer models over a range of a limited number of controlling
18 parameters. The accuracy of such calculations is particularly limited by the
19 number of parameters that can be taken into account and by corrections for the
20 impact of clouds and aerosols, whose distributions and optical properties
21 remain poorly documented. Furthermore, uncertainties in parameters such as
22 the $O_3 \rightarrow O(^1D)$ quantum yield dependence and HNO_3 cross sections directly
23 affect the calculated tropospheric OH, and thus the lifetime of many
24 tropospheric constituents.

25 Over recent years, growing attention has also been focused on the
26 importance of heterogeneous reactions in the troposphere. On the basis of
27 extremely limited laboratory studies and numerous assumptions, it has been
28 calculated that scavenging of compounds such as NO_2 and N_2O_5 followed by
29 reaction in clouds or/and on to aerosols can be crucial for the oxidant levels in
30 the troposphere (Dentener and Crutzen, 1993). However, contrary to the
31 situation for gas phase tropospheric chemistry, a reference scheme for
32 heterogeneous chemistry does not exist nor does any recommended kinetic

1 data. Finally, although present CTMs include parameterizations of
2 heterogeneous chemistry, no intercomparison has been performed to evaluate
3 consistency of their results.

4 Aside the missing knowledge on the physical and chemical processes
5 involved in the heterogeneous reactions, the complexity of the problem is
6 increased by i) the interactions of chemistry and transport which lead to
7 differences in the result of box models considering only chemical processes
8 and the CTMs taking simultaneously into account transport processes and
9 particularly convection in the atmosphere, ii) the pH dependence of
10 cloud/liquid phase chemistry and iii) the non uniform distribution of aerosols
11 in composition, density and surface. Indeed, based on their chemical
12 composition, tropospheric aerosols can be divided in the following 6 main
13 categories: sulfuric aerosols (mainly SO_4^-), black and organic carbon aerosols,
14 mineral dust, sea-salt and NO_3^- aerosols. However, in the troposphere, we
15 commonly observe aerosols which are a mixture of the above mentioned
16 chemical components and have thus chemical and optical properties
17 depending on the specific chemical mixture. For simplicity reasons, the
18 approach adopted in most of the earlier studies was to measure and model
19 each aerosol component as well as the impact of its presence on heterogeneous
20 chemistry, considering a chemically uniform particle of one of the above
21 mentioned major chemical components. Distributions, sources and sinks of
22 these "pure" particles are therefore studied individually based on observations
23 and model results. Recently, efforts have been made to characterize the
24 chemical composition of aerosols, understand the mechanisms of their
25 formation and parameterize the internal mixture of the various chemical
26 components of the aerosols. Further work is needed to acquire the required
27 knowledge for understanding nucleation and condensation processes, and
28 accurately modeling the formation, growth, and hygroscopicity of the
29 internally mixed aerosols taking into account their mass and size distributions,
30 together with their chemical and optical properties.

31 The hydrological cycle scheme used in the CTMs for chemistry is of great
32 importance for the calculation of the abundance of the soluble species and for

1 the OH radical distributions, since the amount of H₂O regulates the chemical
2 production of OH, and washout has been shown to be crucial for the levels of
3 oxidants (Refs.). The parameterization of these processes is highly variable
4 from one model to the other. The simplest parameterization of washout is
5 based on the use of a reaction rate, and more detailed parameterizations are
6 based on observed or calculated precipitation rates and Henry's Law constants
7 for the different species considered. It has been shown that gravitational
8 settling and evaporation of cloud droplets and ice particles can induce a
9 significant downward flux of HNO₃ and H₂O₂ affecting trace compounds such
10 as OH and NO_x (Lawrence and Crutzen, 1998). The omission of this process
11 could explain the overestimation of HNO₃ in the upper troposphere by most
12 CTMs. Recently, Tabazadeh *et al.* (1999) argued that precipitating cirrus may
13 not be a key player in removing HNO₃ from the upper troposphere. An
14 accurate simulation of the hydrological cycle remains a challenge, and recent
15 parameterization are developed in order to calculate on-line and consistently
16 the hydrological cycle in CTMs by connecting cloud dynamics and
17 precipitation distributions as discussed in section 2.2.2. It should be noted that
18 in most current models where the hydrological cycle is simulated, it is
19 assumed that the cloud fraction is essentially a function of the relative
20 humidity (Slingo, 1987).

21

22 **2.4 Surface emissions and dry deposition**

23 Chemistry-transport model calculations require specification of the
24 conditions that exist at the boundaries of the spatial domain. These boundary
25 conditions represent the impact of the external environment on the considered
26 domain and are often representative of complex processes at the interface
27 between different components of the Earth system. Their estimation can be a
28 difficult problem, as these conditions depend on several factors such as
29 biological processes and human activities.

30 The development of the CTMs has pushed the development of global
31 inventories of both natural and anthropogenic emissions. The first simulations

1 using chemical-transport models were generally based on emissions data bases
2 developed by the modellers at the resolution used by each model (Muller,
3 1992, and other groups). As the number of models and model studies
4 increased, there has been a need for consistent surface emissions, at a high
5 resolution. The IGAC/GEIA (Global Emissions Inventory Activity) activity
6 was created in order to establish a framework for developing and evaluating
7 high resolution global emission inventories at a high resolution. A large group
8 of scientists voluntarily contributed to this effort, which resulted in a large set
9 of data set that is currently available (Table xx.2). The file format is kept
10 uniform, for a better use of the different inventories. Most of the data sets
11 correspond to annual averages, except for the emissions of nitrogen oxides
12 from soils and anthropogenic activities, anthropogenic emissions of sulfur
13 dioxide, natural emissions of volatile organic compounds (isoprene, terpenes,
14 and other hydrocarbons), as well as black carbon from biomass burning, which
15 are also available on a monthly average basis. Emission inventories for species
16 such as CO or methane are currently under development.

17 The EDGAR (Emission Database for Global Atmospheric Research: ftp
18 info.rivm.nl) data base (Olivier *et al.*, 1996), available through internet,
19 provides an estimate for 1990 of the annual emissions of several compounds
20 per sector of human activity, on a 1x1 degree grid basis, and a 1km altitude
21 resolution for aircraft emissions. The database has been constructed using the
22 same approach for all species, i.e. emissions were first calculated on a country
23 basis by multiplying activity levels with emission factors per compound. The
24 selection of main source categories and spatial resolution was based on
25 available statistical data and quality and consistence of these data. The list of
26 inventories available within the EDGAR data base, as well as the global
27 source strength for each species is given in Table xx.3. An update of these
28 emissions (typical of year 1995) is currently under way.

29 It should be noted that the estimates of surface emissions and exchanges of
30 chemical constituents between the surface and the atmosphere rely in most
31 cases on field observations or on laboratory experiments. These measurements
32 are generally performed in a very small area and, due to the very high

1 variability of the processes responsible for the emissions, the extrapolation of
2 these local measurements to broader areas remains a major problem, and the
3 uncertainties on global emissions of compounds resulting both from
4 anthropogenic and natural processes are large.

5 As chemistry-transport models are used to simulate both the evolution of
6 the atmosphere over the last decades or centuries, as well as its future
7 evolution, there is currently a major need to develop historical anthropogenic
8 sources inventories as well as future inventories. Work has already been done
9 in estimating the evolution of the emissions of several gases over the last
10 century (Dignon *et al.*, 1989; Bertnsen *et al.*, 1996 and *other references*),
11 using estimations of the evolution of fossil fuel consumption. However,
12 realistic estimations of past and future emissions of trace gases resulting from
13 biomass burning are urgently needed.

14 Several gases such as ozone, CO, nitrogen and sulfur compounds, etc.
15 undergo irreversible absorption at the Earth's surface. The downward flux
16 associated with this dry deposition is usually expressed as the product of the
17 surface layer concentration of the species and a quantity called the deposition
18 velocity (Ganzeveld, L.N., and J. Lelieveld, 1995 and *other references*). The
19 deposition velocity is generally regarded as the inverse of serial resistances,
20 consisting of an aerodynamic resistance associated with atmospheric
21 turbulence, a quasi laminar sub-layer resistance accounting for molecular
22 diffusion near the surface and bulk surface resistance associated with the
23 uptake of gases and particles by the canopy, soils, water, snow and ice. The
24 first two resistances can be calculated as a function of the surface roughness,
25 windspeed and stability. The surface resistance, which generally controls the
26 dry deposition of many gases such as ozone, is controlled by surface cover
27 type and its biogeophysical properties such as temperature, wetness, stomatal
28 uptake, and amount of biomass. The dry deposition process of aerosols is
29 controlled by impaction, brownian diffusion and sedimentation, which are
30 related to the aerosol mass and size distributions.

31

2.5 Advances in computing technology

The development of global atmospheric and "earth" system models over the past decade would not have been possible without the remarkable advances in computational capacity. There have been algorithm improvements ranging from highly automated solvers such as SMVGear to improved sparse matrix techniques (Ref). New versions of scientific languages such as Fortran 90 and modern utilities such as source control software have improved the development process and at the end model reliability, though rounding errors and computer artifacts have been reported (Rosinski and Williamson, 1997; Lawrence *et al.*, 1999b). But it is the improvement in "raw" computer power from the gigaflop range a decade ago toward the teraflop mark today that has enabled our greatly improved simulations, together with large increases in storing capacities. Not only can we regularly perform higher resolution studies on a global basis but many complex elements such as clouds and subgrid processes can be simulated with enhanced fidelity at the global scale due to improved process detailed studies.

Today, with computer systems capable of sustaining hundreds of gigaflops, global simulations with regional spatial resolutions are practical. And models coupling realistic oceans, sea ice, biogeochemistry, and a chemically active atmosphere are on the horizon.

3 Applications of the models

3.1 Model validation and intercomparisons

The accuracy and consistency of models used to simulate tropospheric chemistry and perform future predictions has been tested over the past five years through inter-comparison exercises.

Parameterization of convection in the models has been tested through simulations of the distribution of Radon-222, by comparing model results and observations. Twenty global 2-D and 3-D models participated in that exercise, which demonstrated that deep convection is not well represented by most models. Upper troposphere simulations appear to be very sensitive to the

1 treatment of moist convection and to the scale of deep convection (Jacob
2 *et al.*, 1997).

3 24 photochemical codes used in CTMs of various scales have been
4 isolated from the transport parameterizations, and have been compared within
5 the IPCC'94 "Photocomp" intercomparison exercise (Olson *et al.*, 1997;
6 WMO, 1995). Their results show that model to model differences of 30% or
7 more exist in the calculation of ozone and OH concentrations. These
8 differences result from differences in the calculated photolysis rates, kinetic
9 data, numerical methods used to solve the equations, and the set of
10 photochemical reactions adopted to represent tropospheric photochemistry. In
11 particular, the ozone photo-dissociation rates differ by $\pm 20\%$, whereas the best
12 agreement of $\pm 5\%$ was obtained for the NO_2 photolysis rates, the other rates
13 agreeing within $\pm 15\%$. The largest deviations between models were calculated
14 when non-methane hydrocarbons chemistry was included.

15 The large dispersion of the results from calculations by several 2-D and 3-
16 D models of ozone changes resulting from a 20% increase in CH_4
17 concentrations showed that the ability of the models to predict tropospheric
18 ozone changes induced by methane perturbations was not satisfactory (WMO,
19 1994).

20 A more recent intercomparison by Kuhn *et al.* (1998) of tropospheric
21 chemical models for atmospheric conditions over Europe showed differences
22 in oxidants levels up to 40% due to gas phase chemistry.

23 Following the recent fast development of global 3-D CTMs, an
24 intercomparison exercise of these new generation of models has been
25 performed in 1997-1998, under the initiative of GIM/IGAC. The objective of
26 the Tropospheric Ozone Global Model Intercomparison Exercise was to
27 systematically evaluate the capabilities of the current generation of 3-D global
28 models to simulate tropospheric ozone and their precursor gases, and to
29 identify key areas of uncertainty in our understanding of the tropospheric
30 ozone budget (Kanakidou *et al.*, 1999a; 1999b). Thirteen global CTMs
31 participated in this exercise. Significant differences have been detected
32 between the models although all of them capture the general patterns in the

1 global distribution of carbon monoxide, nitrogen oxides and ozone. The
2 comparison between model results, which used different surface emissions,
3 and observations at selected stations indicates the models deviate from the
4 observed annual mean CO concentrations by about $\pm 50\%$. The main features
5 of the ozone distribution were captured by all models although differences at
6 some locations up to a factor of 3 have been detected between models.
7 Maximum deviations of models from surface ozone observations are of the
8 order of 50% whereas models deviate much more from observations in the
9 free troposphere and particularly close to the tropopause level where the ozone
10 concentrations are sensitive to the parameterization of cross-tropopause
11 transport. Interestingly, the photochemical lifetime of methane in the
12 troposphere up to 300 hPa (or to the closest model level) was calculated to be
13 7.5 years globally and 8.6 years in the southern hemisphere against 6.8 years
14 in the northern hemisphere (as the medians of model results). Model results
15 vary within 30% of these values. This north-south asymmetry in the computed
16 OH distribution requires further investigation.

17 **Figures of CO and ozone intercomparison will be added**

18

19 **3.2 Use of photochemical models for supporting field campaigns**

20 Photochemical models can play an important role in field campaigns, both
21 in helping to evaluate the observations, as well as in the planning and
22 execution stages. Constrained box models have been particularly useful in
23 helping to point out possible problems with the measurement techniques
24 (Crawford *et al.*, 1996), as well as to point towards possible missing
25 knowledge of photochemical processes, e.g. a missing sink for OH in the
26 marine boundary layer (Eisele *et al.*, 1996). Recently, more complex
27 chemistry-transport models have also come into the picture. For instance,
28 MOZART (table xx.1) was used to examine the O₃ photochemical budget of
29 the Pacific Ocean based on data from MLOPEX (Brasseur *et al.*, 1996). The
30 O₃ budget was further analyzed by Lawrence (1996) using a box model
31 constrained by the MLOPEX observations (Ridley *et al.*, 1992) and

1 concentrations calculated using the MATCH model. The differences were
2 found to be largely due to the NO_x levels, which points out the importance of
3 high quality NO_x measurements (Crawford *et al.*, 1996). Other examples of the
4 use of 3-D CTMs for interpreting campaign data are the study of Singh *et al.*
5 (1996), which concluded that transport of Asian NO_y into the PEM-West A
6 region served as a major source of NO_y during the campaign, and Lawrence
7 *et al.* (1999), who concluded that while convective pumping of low-ozone
8 marine boundary layer air is the main process responsible for producing O₃
9 minima in the upper troposphere, their severity may be influenced by a
10 missing O₃ sink, e.g. halogens. Finally, models have been employed to
11 evaluate the sampling done during a campaign: Ehhalt *et al.* (1997) used a
12 CTM with surrogate tracers to demonstrate that the sampling during PEM-
13 West A and B was likely sufficient to capture the mean in the region sampled,
14 while Lawrence *et al.* (1999a) used O₃ simulations to conclude that the single
15 cruise through the CEPEX region was likely insufficient to capture the mean,
16 although it did point out that extremely low levels of ozone occur which had
17 not been previously observed.

18 Models are often used in planning campaigns by providing estimates of
19 what one might expect in terms of concentrations and gradients of various
20 species. CTMs can also provide estimates of the amount of sampling which is
21 needed to obtain a certain desired degree of representativeness in a future
22 campaign (Lawrence, 2000), similar to the analysis which can be done with
23 previous observations (Logan, 1999). Finally, during the last few years,
24 photochemical models have seen increasing use in forecasting during the
25 intensive field phases of campaigns. One of the first examples were described
26 by Lee *et al.* (1997), who forecasted stratospheric constituents in the polar
27 vortex for the ASHOE/MESA and SESAME campaigns, and by Flatoy *et al.*
28 (1999) who provided tropospheric chemistry forecasts for the POLINAT
29 campaign. Both of these studies used regional models. Global tropospheric
30 chemistry forecasts were done by Lawrence *et al.* (2000), Rasch *et al.* (2000),
31 and Collins *et al.* (2000) for the INDOEX campaign. In all cases, the forecasts
32 were received by the field investigators. Despite inaccuracies in the model

1 predictions, on several occasions, the forecasts were able to help point towards
2 events which were of interest to observe.

3

4 **3.3 CTM results and climate forcing**

5 Calculations of the radiative forcing due to changes in the distribution of
6 well-mixed gases such as CO₂, CH₄, N₂O and the CFCs have been performed
7 over the last decades using radiative models. As seen in the previous chapters,
8 ozone is more and more recognized as a greenhouse gas with an estimated
9 contribution to the enhanced greenhouse effect since the preindustrial period
10 of about 20%. Accurate calculations of the radiative forcing of ozone requires
11 the knowledge of the spatial and temporal changes of the ozone distribution in
12 the troposphere. The development of the CTMs has allowed the calculation of
13 the three-dimensional evolution of ozone over the last century (Berntsen *et al.*,
14 1997; Roelofs *et al.*, 1997; Brasseur *et al.*, 1998b and other references).
15 However, previous studies have shown that changes in ozone in the vicinity of
16 the tropopause might be the most important in terms of radiative forcing
17 (Refs). No data are currently available concerning the long-term evolution of
18 ozone in this altitude region, which is also a region where most models have a
19 rather low vertical resolution, and calculated concentrations are affected by
20 errors in the parameterization of exchanges between the stratosphere and the
21 troposphere.

22

23 **4 New developments**

24 **4.1 Nesting/variable resolution**

25 With the current computer power available global chemistry-transport
26 models (CTMs) with extensive chemistry can have horizontal grids of ~ 250
27 km or even ~100 km. It can be important to increase the resolution of a model
28 over a region of interest, since transport and chemistry (including sources and
29 sinks) are expected to be simulated more accurately with increasing resolution.
30 Furthermore, comparisons of measurements and model results are more
31 straightforward and significant in a high-resolution model. Two different

1 approaches can achieve the increase in resolution, (1) place a high-resolution
2 grid inside a coarse resolution grid where greater resolution or accuracy is
3 desired (over a fixed region or following the path of a particular phenomenon)
4 and (2) create a model with variable resolution.

5 Both approaches have pros and cons and have been used extensively in
6 meteorological forecasting and to a lesser extent in studies involving
7 chemistry. This section will briefly describe both techniques. It is important to
8 remember that CTMs require the knowledge of meteorological fields
9 (including cloud properties) to calculate the transport and transformation of
10 chemical species. A meteorological model simulation over the area of interest
11 provides this information (Brasseur *et al.*, 1999 and references therein) which
12 is then used offline.

13

14 **4.1.1 Nesting approach**

15 The nesting approach consists of inserting a finer resolution model inside a
16 coarse resolution model. There are basically two approaches to limited-area
17 modeling, which can be characterized as one- and two-way interacting
18 (Phillips and Shukla, 1973). In the one-way approach, time-dependent
19 conditions are specified at the boundaries of a limited area, and the model is
20 then integrated at high resolution over this area. In this setup, the larger scales
21 of the flow that cannot be simulated on the fine grid are allowed to affect the
22 fine grid solution. Discontinuities and distortions can develop at the interface
23 in absence of feedbacks from the fine to the coarse grid. Also, because of the
24 variation in resolution, reflection and refraction of waves occur (Courtier and
25 Geleyn, 1988), particularly if the resolution varies abruptly (Gravel and
26 Staniforth, 1992). Finally, one-way nesting implicitly assumes that small-scale
27 phenomena have no major influence on the larger scale treated on the coarse
28 grid (Skamarock *et al.*, 1989). This is usually not the case for the physical and
29 chemical processes in the atmosphere or the ocean. The two-way interactive
30 nested grid approach addresses this problem. The procedure consists of
31 integrating the fine grid along with the coarse grid. The lateral boundary

1 conditions for the fine grid are taken from the coarse grid solution. The
2 solution on the coarse grid is then updated with the fine grid solution at any
3 coarse grid location where the two grids overlap (Skamarock *et al.*, 1989).
4 Nevertheless, numerical dispersion problems may still occur at resolution
5 interfaces, particularly if the resolution varies too rapidly.

6 In a meteorological forecast model, the boundary conditions are set on all
7 the prognostic variables (wind, temperature, humidity, cloud properties). In a
8 CTM, the boundary conditions pertain to the chemical species distribution.
9 Lateral boundary conditions (values or fluxes) are calculated by interpolating
10 the necessary fields from the coarse grid solution. This interpolation
11 introduces errors and noise. Because short-lived species adjust quickly to the
12 ambient levels of long-lived species, only the latter need to be calculated at the
13 boundary. Also, long-lived species usually exhibit a smoother distribution that
14 tends to decrease the interpolation errors. The short-lived species are then
15 calculated explicitly for the conditions defined by the long-lived ones. This
16 ensures that the chemical system is balanced with the set of equations defining
17 the chemical mechanism, both on the coarse and the fine grids. As far as we
18 know only the one-way nesting approach has been used in CTMs (Chang
19 *et al.*, 1987; Ebel *et al.*, 1991; Hess *et al.*, 1999). Nevertheless, in going from
20 fine to coarse grid only the long-lived need to be considered for the reason
21 described above.

22

23 **4.1.2 Variable resolution approach**

24 Even in an ideal situation where all the problems related to the
25 specification of boundary conditions are solved, there is still the practical
26 difficulty of having two systems (global and nested) to maintain (Côté *et al.*,
27 1993). It would therefore be interesting to have a single model in which the
28 resolution could be varied such that high resolution is focused over an area of
29 interest, and therefore provides both global and regional simulations.

30 Courtier and Geleyn (1988) have described the first application of a
31 conformal transformation that creates a region of high resolution with a

1 continuous transition from coarse to high. This variable resolution model, with
2 the pole rotated over the area of interest, leaves the governing equations
3 almost unchanged (except for the multiplication of a few terms by a local map
4 factor). Because there is a variation in model resolution, problems similar to
5 loss of information and wave reflection at the boundaries in the nesting
6 approach will have counterparts in this method but with a less damaging
7 intensity (Courtier and Geleyn, 1988). There are nevertheless severe
8 limitations, mostly associated with the use of a spectral model (Côté *et al.*,
9 1993). Côté *et al.* have therefore applied the same map transformation but with
10 a finite-element discretisation (and other numerical specificities), with
11 considerable success (Côté *et al.*, 1993).

12 In the case of CTMs, this approach might not be as feasible since there is
13 no model available at this point that could provide the necessary
14 meteorological fields on a variable resolution grid. It is therefore required to
15 create such data sets by interpolating results from regular grid meteorological
16 models. This can be first a cumbersome task and second, introduce noise in
17 the dynamical fields, which might translate into spurious vertical velocities.
18 Such approach has nevertheless been applied to the case study of the
19 MLOPEX data (Ginoux, 1998). In that case, a triangular grid was used, with
20 the equations of transport solved by the finite element method. Although the
21 variable resolution approach is conceptually appealing, the limited number of
22 models that could create the necessary fields for driving the CTM has
23 hampered its use. The future might reside in the online simulation of
24 chemistry within a variable resolution model.

25

26 **4.2 Data assimilation and inverse modeling**

27 A large amount of observation of meteorological parameters, distributions
28 of atmospheric chemical species, ecosystems etc. has been collected over the
29 last 2 decades, and the new generation of earth satellite observations will
30 provide even much larger datasets. However, it is not possible to measure all
31 the atmospheric quantities simultaneously in time and space, and the retrieval

1 of satellite data will generally give access to sparse, heterogeneous and
2 irregular distributions of atmospheric quantities. Objective approaches to
3 combine our a priori knowledge about the physical system under consideration
4 with these usually sparse and irregular observations are often referred to as
5 data assimilation. Up to now, data assimilation techniques have mostly been
6 used in numerical weather prediction, data retrievals from remote sensing
7 experiments, and inverse modeling. Some interesting pioneering work on
8 assimilating observations of chemical species in the atmosphere using
9 photochemical models has been done recently and results of these recent
10 research efforts demonstrated the feasibility of the approach and promised
11 important benefits.

12 The mathematical basis of data assimilation is estimation theory or inverse
13 problem theory. In a conventional "forward" problem, one uses a set of a priori
14 parameters to predict the state of the physical system. In the "inverse" or
15 estimation problem, one attempts to use available observations of the state of
16 the system to estimate poorly known model parameters and/or the state itself.
17 Very broadly, commonly used data assimilation methods can be divided into
18 variational and sequential techniques.

19 In variational data assimilation, one attempts to find optimal parameters
20 (e.g. optimal initial conditions) that minimize a discrepancy between model
21 results and measurements for a chosen analysis period. The variational data
22 assimilation technique can be thought of as a constrained least-squares fit to a
23 set of observations distributed over some period of time. The constraints are
24 given by the model equations. In the sequential method, observations are
25 "blended" with model simulations with certain weights as they become
26 available to form new initial conditions for the model for the next time step.
27 The optimal weights are obtained from estimates of the model errors, errors of
28 the current observations and errors of observations incorporated into the model
29 previously.

30 Lyster *et al.* (1997) for the first time have used a two-dimensional
31 transport model on isentropic surfaces and the Kalman filter technique to
32 assimilate CLAES- and HALOE-measured methane from the UARS satellite.

1 Although very computationally expensive, their pioneering approach allows
2 production of synoptic maps from irregularly distributed satellite
3 measurements. Fisher and Lary (1996) have used variational data assimilation
4 for assimilating and mapping the UARS/CLAES observations of O₃, NO₂, and
5 HNO₃ using a fairly simple 6 species/19 reactions photochemical box model in
6 conjunction with a trajectory model. This was the first application of data
7 assimilation techniques for analysis of photochemically active species in the
8 stratosphere. Elbern *et al.* (1997) extended this variational to assimilation of
9 various tropospheric gases. Khattatov *et al.* (1999) have applied the variational
10 approach as well as the extended Kalman filter for assimilation of satellite
11 stratospheric measured species using a relatively sophisticated box model and
12 a trajectory model. It was also shown that concentrations of a number of non-
13 observed species can be successfully derived from available data. Lamarque
14 *et al.* (1999) have applied a similar method to assimilate with a 3-D CTM CO
15 observed from space.

16 The emissions of chemical trace gases specified at the surface are
17 generally poorly quantified, as they depend on complex processes related to
18 meteorological conditions and human factors. As more and more observations
19 of chemical species become available, it is in principle possible, using inverse
20 modeling techniques, to optimize surface emissions, which also improves the
21 agreement between observed and calculated distributions. Different methods
22 have been developed over the past few years, and they have been first used to
23 optimize surface emissions of CO₂ (Enting and Mansbridge, 1991; Bousquet
24 *et al.*, 1999), CH₄ (Hein *et al.*, 1997; Houweling *et al.*, 1999) and CFCs
25 (Hartley and Prinn, 1993; Mahowald *et al.*, 1997), and more recently of CO
26 (Bergamaschi *et al.*, 2000). The use of such methods is currently limited, as
27 the number of observations sites is relatively small. Furthermore, optimization
28 of surface emissions using inverse modeling requires an accurate treatment of
29 the mixing between the boundary layer and the free troposphere. In the near
30 future, more and more observations of tropospheric species will become
31 available from satellite observations, which may considerably improve the

1 results possibly leading to new insights into the distribution of surface
2 emissions of chemical species and on their spatial and temporal variability.

3

4 **4.3 Aerosols and climate**

5 The representation of the climatic effect of aerosols in global models has
6 first used static simplified distributions derived from observations and Mie-
7 calculations to assign optical parameters. Most of the model studies
8 investigating the direct and indirect effect of aerosols and climate used these
9 static climatologies. Since the pioneering study by Langner and Rodhe (1991),
10 who used a coarse resolution chemical-transport model based on
11 climatological meteorology, the complexity of the aerosol precursor
12 chemistry, of particles dry deposition and wet removal included in the models
13 has increased dramatically. Several models treat the aerosol precursor
14 chemistry and the evolution of the particle mass interactively with the
15 meteorology, taking into account the complex interactions between cloud
16 processes, heterogeneous chemistry and wet removal (Benkovitz *et al.*, 1997;
17 Feichter *et al.*, 1997, Roelofs *et al.*, 1998; Rasch *et al.*, 1999; Koch *et al.*,
18 1999). However, the physical and optical properties of the aerosol components
19 are prescribed. Such an approach allows the representation of the high
20 variability of the mass distributions of the particles and is used more
21 particularly when aerosol-cloud interactions are studied.

22 Recent attempts have been undertaken in order to calculate also the
23 particle number concentration using parameterizations of aerosol formation
24 and dynamical processes. Two kinds of such models were developed, using
25 spectral or bin schemes. In the spectral scheme, one or more aerosol modes of
26 the particle distribution are described by lognormal distributions (Schultz
27 *et al.*, 1998; Wilson *et al.*, 1999). In bin schemes, the particle mass is
28 distributed over different size classes, each bin being characterized by its
29 geometric mean diameter. Such schemes, which allow to reproduce changes in
30 size distribution when a large number of size classes are taken into account,

1 have been applied for example for sulfuric acid in the stratosphere (Timreck,
2 1999) and sea-salt aerosols (Gong *et al.*, 1997).

3 Most of global climate and chemistry –transport models have so far only
4 considered the bulk aerosol mass of some specific components rather than the
5 size spectra of externally and internally mixed aerosols and their size-
6 dependent chemical composition. However, the size distribution and the
7 chemical composition of the particles control the optical and deliquescence
8 properties, the activation of particles to cloud condensation nuclei and their
9 subsequent formation to cloud droplets. Currently, work is under way to
10 improve the understanding of the presence of nitrate and organic aerosols,
11 using thermodynamic equilibrium models. In particular, the description of the
12 state of mixture is a challenging task for future research.

13

14 **4.4 Coupled earth system models**

15 As processes occurring in the oceans, atmosphere and continental areas
16 determine the distribution of chemical species in the atmosphere are linked,
17 coupled models are required to study the feedbacks between these different
18 components of the Earth system. A few groups have started to work on
19 integrated models, or Earth-system models, in which global dynamics,
20 chemistry, biology and oceans are interactively coupled. Such models should
21 help to understand how changes in climatic conditions affect the distribution
22 of species such as greenhouse gases, as well as how changes in greenhouse
23 gases affect climatic conditions. It should be noted however that the validation
24 of such coupled models will represent a great challenge in the future.

25 Even with all our present computational power, the development of highly
26 coupled models is a daunting task that requires compromises to achieve
27 century scale simulations. The spatial resolution of the experiments is often
28 coarse, and therefore even parameterizations of important processes have to be
29 greatly simplified. We can expect that future advances in computing will allow
30 us to build interactive more accurate coupled models capable of century scale
31 simulations.

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Table 1: Salient features of several recent global chemical transport models for oxidant chemistry

Model	Focus	Horizontal Resolution	Chemistry	References
MOGUNTIA	O ₃	4 x 5 (?)	O ₃ -CH ₄ -CO-NO _x -HO _x	Crutzen and Zimmermann (1991)
LLNL CTM	NO _x /NO _y	Lagrangian	NO _x /HNO ₃	Penner et al. (1991)
GFDL/GCTM	NO _x /NO _y	265 km	Prescribed OH; parameterized NO _y chemistry	Kasibhatla et al. (1991, 1993); Levy et al. (1999)
GFDL/GCTM	O ₃	265 km	Prescribed NO _x ; parameterized O ₃ chemistry	Levy et al. (1997)
ECHAM	O ₃	3.75 x 3.75	Online; O ₃ -CH ₄ -CO-NO _x -HO _x	Roelofs et al. (1995; 1997)
IMAGES	O ₃ + related species	5 x 5	O ₃ -CH ₄ -CO-NMHC-NO _x -HO _x	Muller and Brasseur (1995)
U. Oslo CTM	O ₃	8 x 10	O ₃ -CH ₄ -CO-NMHC-NO _x -HO _x	Berntsen et al. (1997a)
TM3	O ₃ + related species	5 x 3.8	O ₃ -CH ₄ -CO-NMHC-NO _x -HO _x	Houweling et al. (1998)
Harvard/GISS CTM	O ₃ + related species	4 x 5	O ₃ -CH ₄ -CO-NMHC-NO _x -HO _x	Wang et al. (1998a; b; c); Wang and Jacob (1998)
MOZART	O ₃ + related species	2.8 x 2.8	O ₃ -CH ₄ -CO-NMHC-NO _x -HO _x	Brasseur et al. (1998a); Hauglustaine et al. (1998)
MATCH-MPIC	O ₃ + related species	1.9 x 1.9	O ₃ -CH ₄ -CO-NO _x -HO _x	Crutzen et al. (1999); Lawrence et al. (1999)

Table 2: Inventories available within the IGAC/GEIA activity

Species	Yearly (Y) or Seasonal (S)	Reference
NO _x from soils	S	Yienger and Levy, 1995
Anthropogenic NO _x	Y	Benkovitz <i>et al.</i> , 1996
Anthropogenic NO _x	S	Voldner <i>et al.</i>
Anthropogenic SO ₂	Y	Benkovitz <i>et al.</i> , 1996
Anthropogenic SO ₂	S	Voldner <i>et al.</i>
Volcanic sulfur	Y	Andres and Kasgnoc, 1998
Nitrous oxide	Y	Bouwman <i>et al.</i> , 1995
Volatile organic compounds	S	Guenther <i>et al.</i> , 1995
Reactive chlorine	Y	8 papers → ??
Black carbon from fossil fuel	Y	Dignon <i>et al.</i>
Black carbon from biomass burning	Y	Cooke and Wilson

Table 3

Species	Global amount emitted (Tg)
CH₄	
Fossil fuel : combustion	4.8
Fossil fuel : production	89.3
Biofuel	14.1
Industrial processes	0.8
Land use/waste treatment	211.4
CO	
Fossil fuel	262.6
Biofuel	181.0
Industrial processes	34.8
Land use/waste treatment	495.9
NO_x	
Fossil fuel	21.9
Biofuel	1.3
Industrial processes	1.5
Land use/waste treatment	6.2
NM-VOC	
Fossil fuel:combustion	41.6
Fossil fuel: non combustion	27.3
Biofuel	30.7
Industrial processes	33.5
Land use/waste treatment	44.4

Units: CH₄ emissions in Tg CH₄/year, CO emissions in Tg CO/year,
 NO_x emissions in Tg N/year, NM-VOC emissions in Tg NM-VOC/year.