ARPALAZIO

Corso di formazione
Attività di monitoraggio della qualità dell’aria: i modelli di dispersione degli inquinanti in atmosfera e le misure in atmosfera

Chimica dell’atmosfera e modellizzazione delle reazioni chimiche

Camillo Silibello

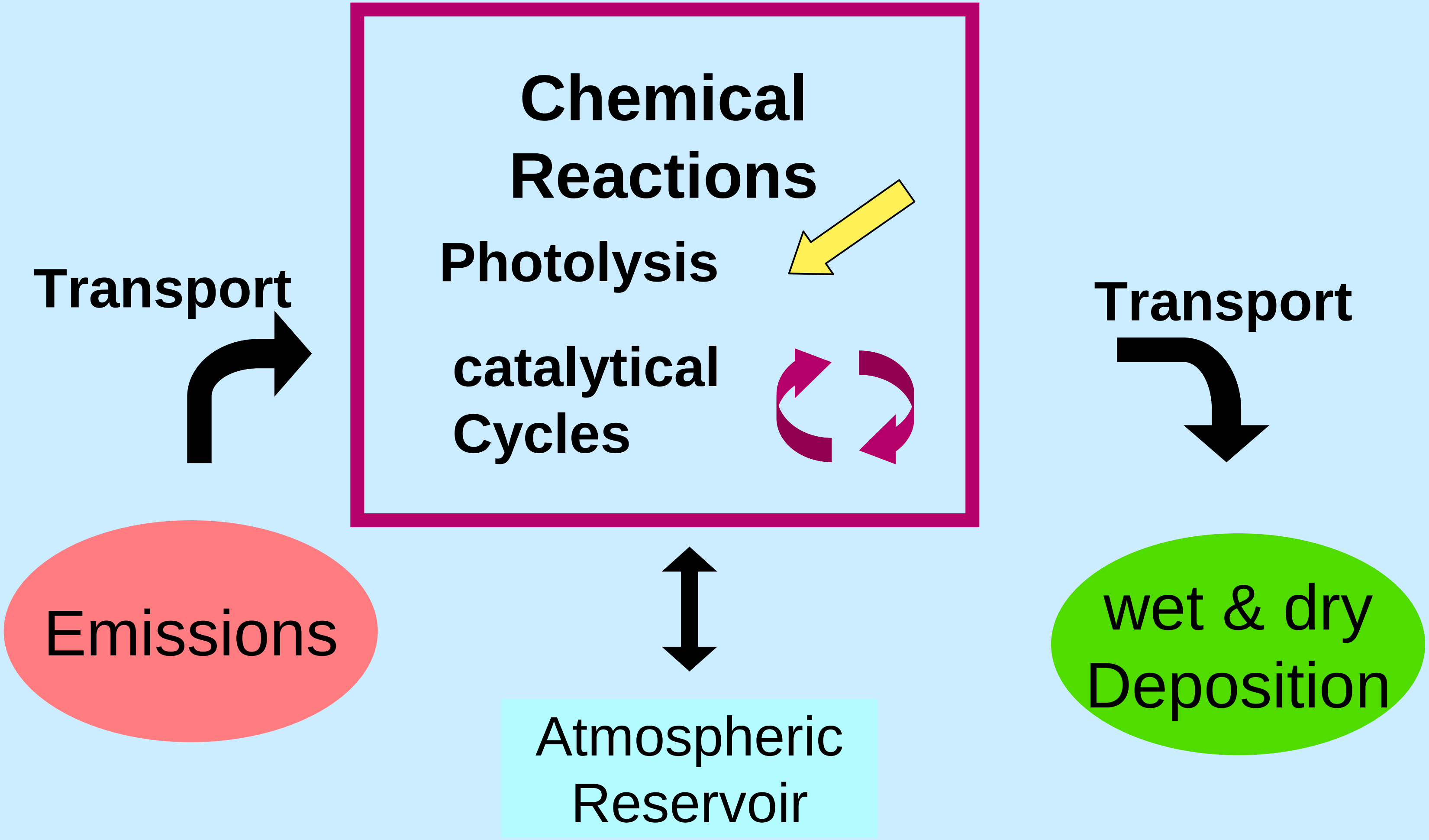
ARIANET

25 novembre 2011
Roma

… fatalmente siete transitati da un mondo ad un altro, da un contesto cristallino di fisici e matematici ad un ambiente <u>fumoso</u> ed <u>interdisciplinare</u>. In questa necessità di contaminazione risiede la sfida per la ricerca ambientale …

Francesco Tampieri e Domenico Anfossi

$$\frac{\partial c_i}{\partial t} + \boxed{\mathbf{V}_h.\nabla_h c_i + \frac{\partial}{\partial z} w_c c_i - \frac{\partial}{\partial z} K_Z \frac{\partial c_i}{\partial z}} = \boxed{E} + \boxed{R} - \boxed{D}$$



Chemical Reactions

Photolysis

catalytical Cycles

Transport

Transport

Emissions

wet & dry Deposition

Atmospheric Reservoir

Chemical reactions

Unimolecular reactions	$A \rightarrow B + C$	$d[A] / dt = - k [A]$
Bimolecular reactions	$A + B \rightarrow C + D$	$d[A] / dt = - k [B] [A]$
Trimolecular reactions	$A + B + M \rightarrow C + D + M$	$d[A] / dt = - k [B] [M] [A]$
Photolysis reactions (if $\nu < \nu_{limit}$)	$A + h\nu \rightarrow B + C$	$d[A] / dt = - J [A]$

Chemical reactions

The gas-phase chemistry operator involves solution of a system of ordinary differential equations (ODE) of the form:

$$\frac{d[\mathrm{A}]}{dt} = P - L = P - l[\mathrm{A}]$$

$$[\mathrm{A}](t) = \quad [\mathrm{A}](0)\exp\left(-\frac{t}{l}\right)$$

$$\tau = \frac{1}{l}\ldots \quad \text{chemical lifetime}$$

- **Chemistry is budget of loss (*L*) and production (*P*) rate;**
- **Usually *L* $\approx$ *P;***
- **A's loss rate (*d[A]/dt*) $\propto$ [A];**
- **Loss rate coefficient "*l*" is often $\propto$ to [OH] (hydroxyl radical) in troposphere.**

Solving the system of (ODE)

***The big difficulty**: the set of ODE is ‘**stiff**’*
chemical lifetimes cover a very large range of time scales!

CH_4 + OH → CH_3 + H_2O

$$\frac{d[CH_4]}{dt} = -k[OH][CH_4]$$

***k* = 6.2 10^{-15} cm^3 $molec^{-1}$ s^{-1} (at 298 °K)**

[OH] = 5 10^5 molec cm^{-3}

Typical lifetime of CH_4:

τ_{CH4} = 1 / (k [OH]) = 10.2 years

$O(^1D)$ + M → O + M

$$\frac{d[O(1D)]}{dt} = -k[M][O(1D)]$$

***k* = 2.6 10^{-11} cm^3 $molec^{-1}$ s^{-1} (at 298 °K)**

[M] = [N_2] = 1.9 10^{19} molec cm^{-3}

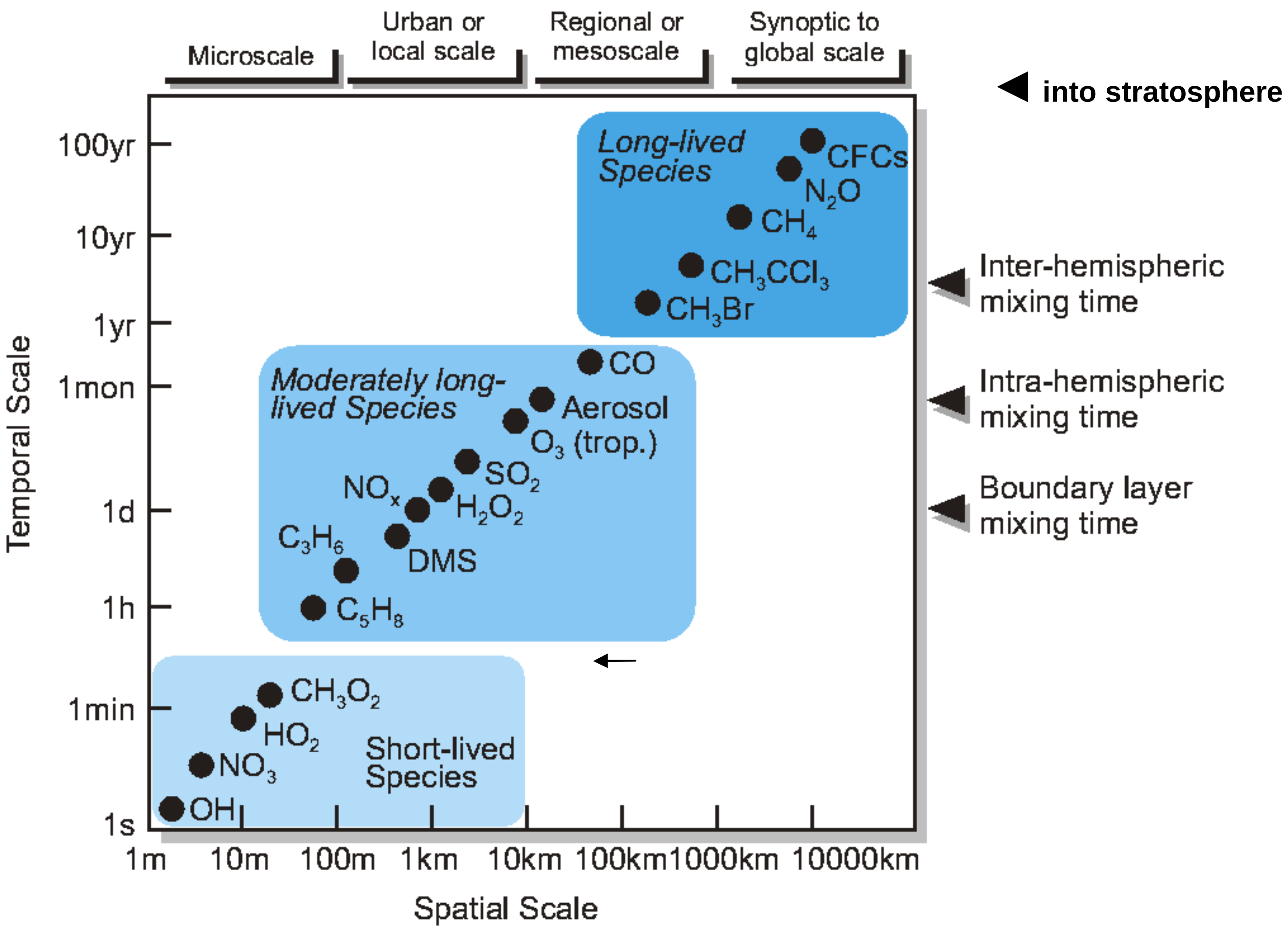
Typical lifetime of $O(^1D)$:

$\tau_{O(1D)}$ = 1 / (k [M]) = 2 · 10^{-9} s

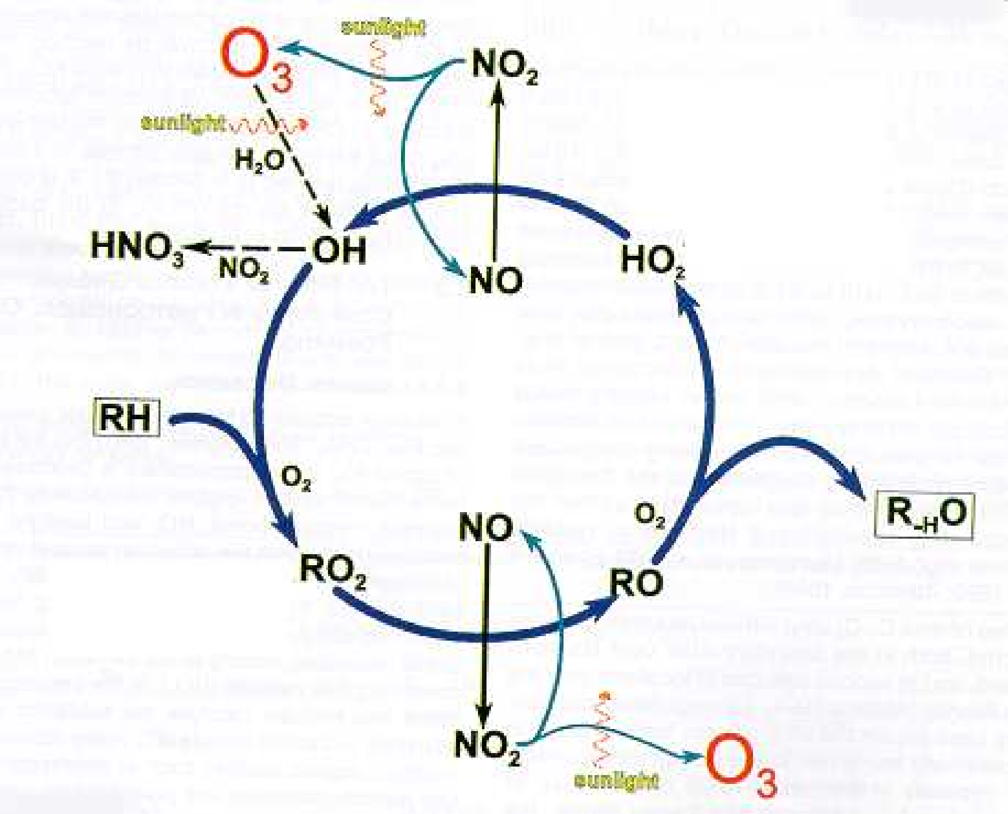
Time step necessary to resolve all the chemical reactions ?

Chemical Lifetime / transport scale

Species with τ > 10 min are transported



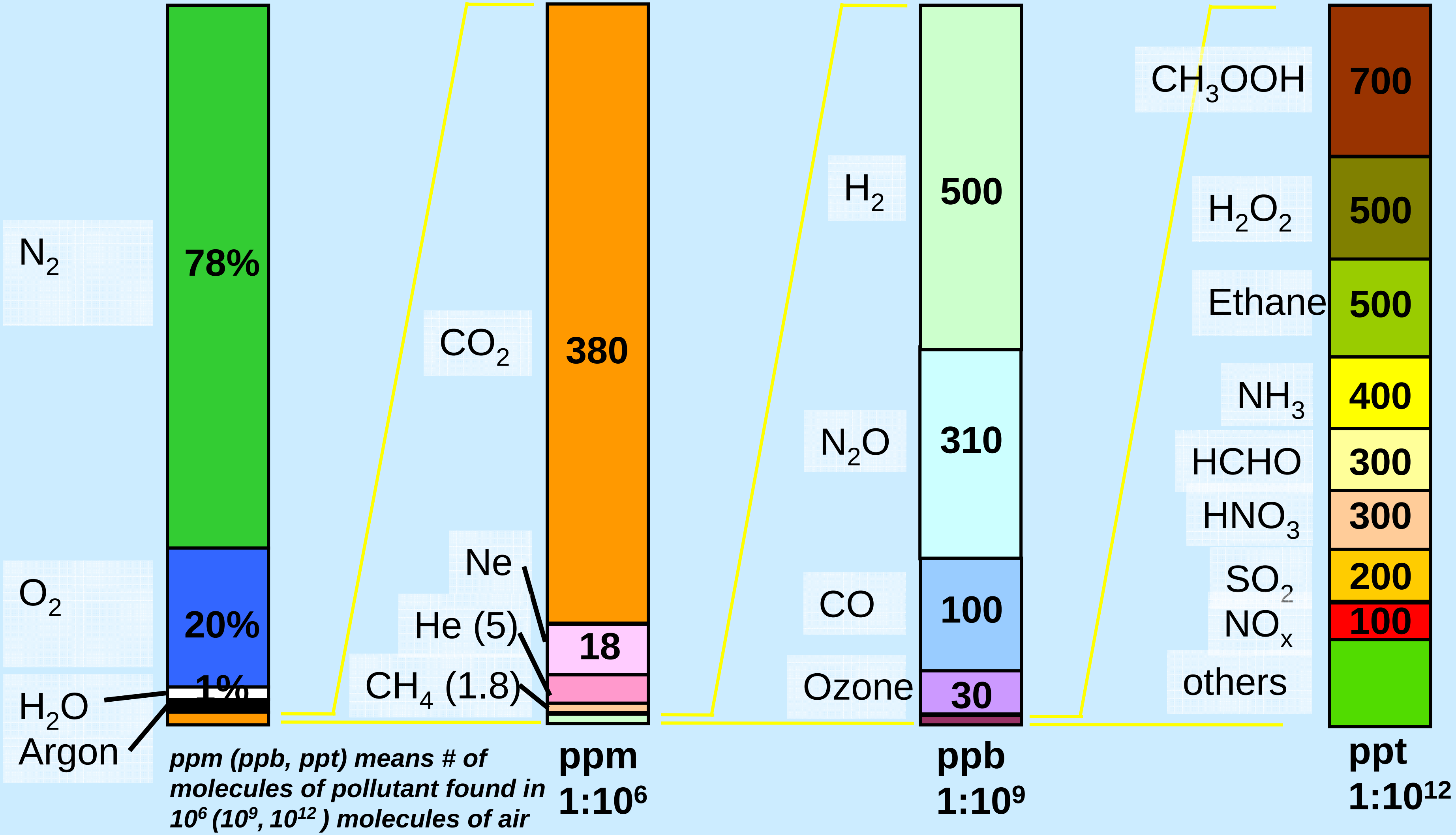
After Seinfeld and Pandis [1998]


O3
sunlight
NO2
sunlight
H2O
HNO3
NO2
OH
NO
HO2
RH
O2
RO2
NO
O2
RO
R-HO
NO2
sunlight
O3

Smog derives from a combination of the words *smoke* and *fog*.

London smog	Los Angeles smog
Characterized by high SO_2 and particle concentration in the presence of fog. Also referred as *sulfurous smog.*	Characterized by high oxidants (mainly O_3) and solar radiation. It was first recognized in the Los Angeles area. The term smog is misleading in this case, as smoke and fog are not key components. The appropriate term is *photochemical air pollution*.

Atmospheric Composition



ppm (ppb, ppt) means # of molecules of pollutant found in 10^6 (10^9, 10^{12}) molecules of air

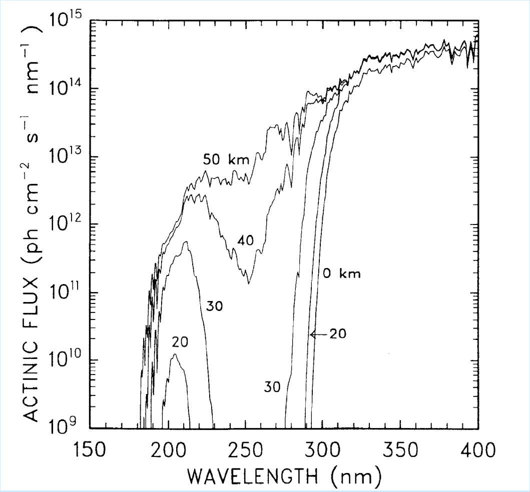
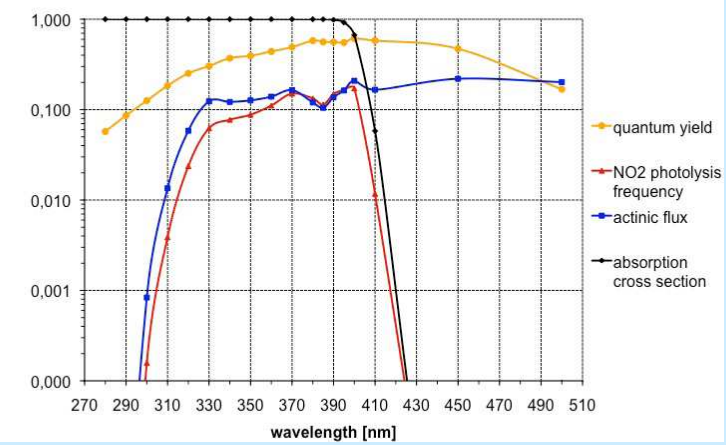
Small concentrations of pollutant do matter because:

- chemical conversion is non-linear;
- small concentrations could mean high turn-over, i.e. high reactivity.

Solar radiation and chemistry

The reaction that produces ozone in the atmosphere:

$$O + O_2 + M \rightarrow O_3 + M$$

Stratospheric	Tropospheric
For solar radiation with a wavelength of less than 242 nm: $O_2 + h\nu \rightarrow O + O$	For wavelengths less than 424 nm: $NO_2 + hv \rightarrow NO + O$ $\frac{d[NO_2]}{dt} = -J[NO_2]$
	
little radiation with wavelengths less than ~290 nm makes it down to the troposphere	Photolysis rate $J=\int q_\lambda \sigma_\lambda I_\lambda \, d\lambda$ where q_λ is quantum yield, σ_λ is cross section and I_λ is the actinic flux

The Hydroxyl Radical

Tropospheric gas-phase chemistry is driven by the hydroxyl radical OH:

$O_3 + h\upsilon \rightarrow O(^1D)$

$O(^1D) + M \rightarrow O(^3P) + M \; (+O_2 \rightarrow O_3) \quad (\sim 90\%)$

$O(^1D) + H_2O \rightarrow 2\,OH\cdot \quad (\sim 10\%)$

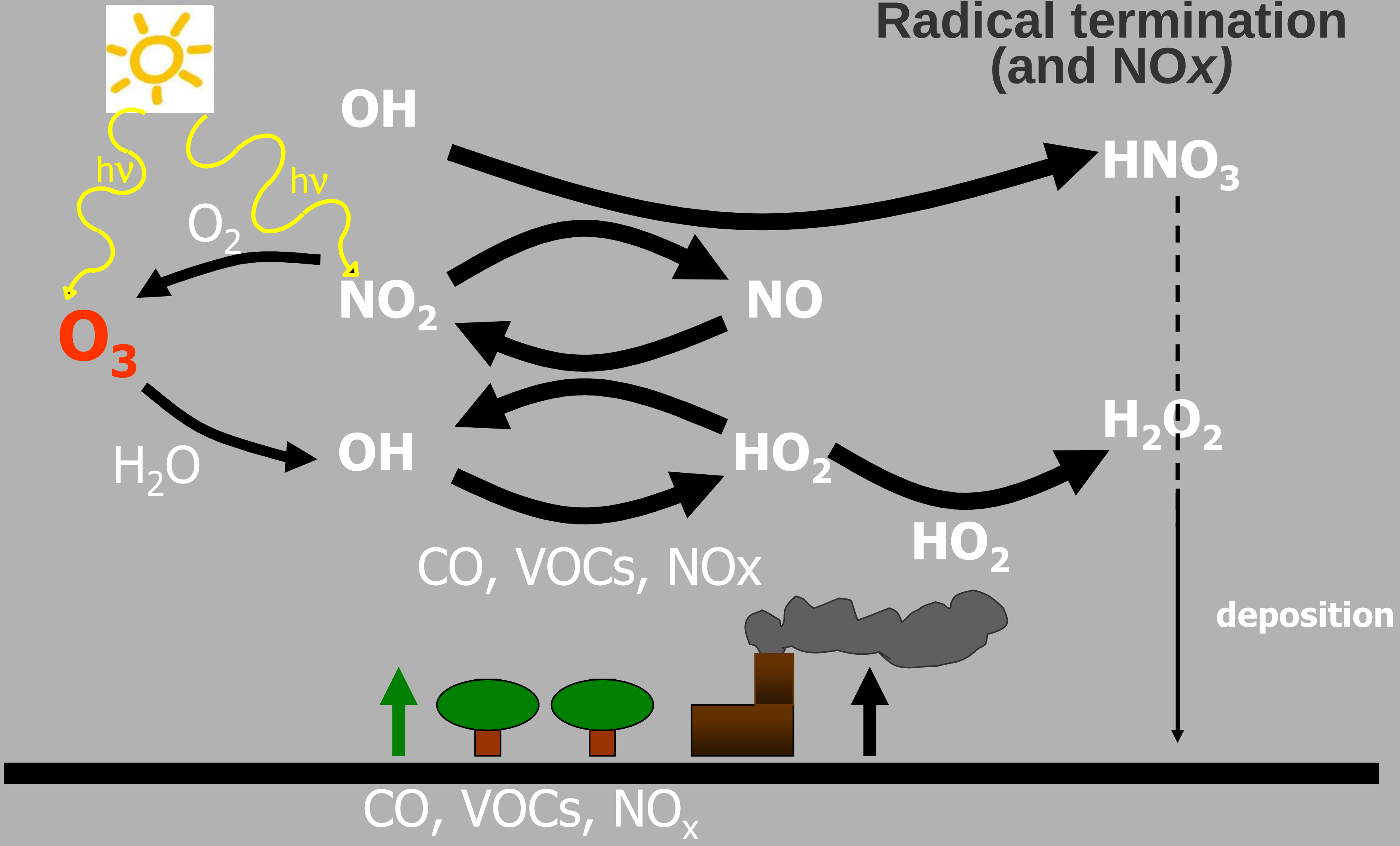
OH initiates the atmospheric oxidation of a wide range of compounds in the atmosphere:

- **referred to as 'detergent of the atmosphere' or *'the scavenger'*;**
- **typical concentrations near the surface ~10^6 - 10^7cm^{-3};**
- **very reactive, effectively recycled.**

Radical Initiation

Radical Propagation

Radical termination (and NO*x*)



hν

hν

O_2

O_3

H_2O

OH

NO_2

NO

OH

HO_2

HNO_3

H_2O_2

HO_2

CO, VOCs, NOx

deposition

CO, VOCs, NO_x

HO_2: hydroperoxyl radical

Radical Initiation
OH formation

Primary source of OH·

$O_3 + h\nu \rightarrow O(^1)D$

$O(^1)D + H_2O \rightarrow 2\ OH\cdot$

Secondary sources of OH·

$HONO + h\nu \rightarrow OH\cdot + NO$

$H_2O_2 + h\nu \rightarrow 2\ OH\cdot + NO$

$HO_2\cdot + NO \rightarrow OH\cdot + NO_2$

$HO_2\cdot + O_3 \rightarrow OH\cdot + O_2$ (low-NOx)

Radical Propagation
HO_2 and RO_2 formation

HO_2 production

$CO + OH\cdot \rightarrow H + CO_2$

$H + O_2 + M \rightarrow HO_2\cdot + M$

$OH\cdot + O_3 \rightarrow HO_2\cdot + O_2$ (low-NOx)

RO_2 production

$CH_4 + OH\cdot \rightarrow CH_3\cdot + H_2O$

$CH_3\cdot + O_2 + M \rightarrow CH_3O_2\cdot + M$

RO_2: organic peroxy radicals

Radical Propagation
CO oxidation / O_3 production

$CO + OH\cdot \rightarrow CO_2 + H\cdot$

$H\cdot + O_2 + M \rightarrow HO_2\cdot + M$

$NO + HO_2\cdot \rightarrow NO_2 + OH\cdot$

$NO_2 + h\nu \rightarrow NO + O$

$O + O_2 + M \rightarrow O_3$

$CO + 2\,O_2 + h\nu \rightarrow CO_2 + O_3$

Per ogni mole di CO ossidata viene formata 1 mole di O_3 (e di CO_2).

Radical Propagation
CH_4 oxidation / O_3 production

$CH_4 + OH\cdot + O_2 \rightarrow CH_3O_2\cdot + H_2O$

$CH_3O_2\cdot + NO \rightarrow CH_3O\cdot + NO_2$

$CH_3O\cdot + O_2 \rightarrow HCHO + HO_2\cdot$

$HO_2\cdot + NO \rightarrow OH\cdot + NO_2$

$NO_2 + h\nu \rightarrow NO + O$ (2x)

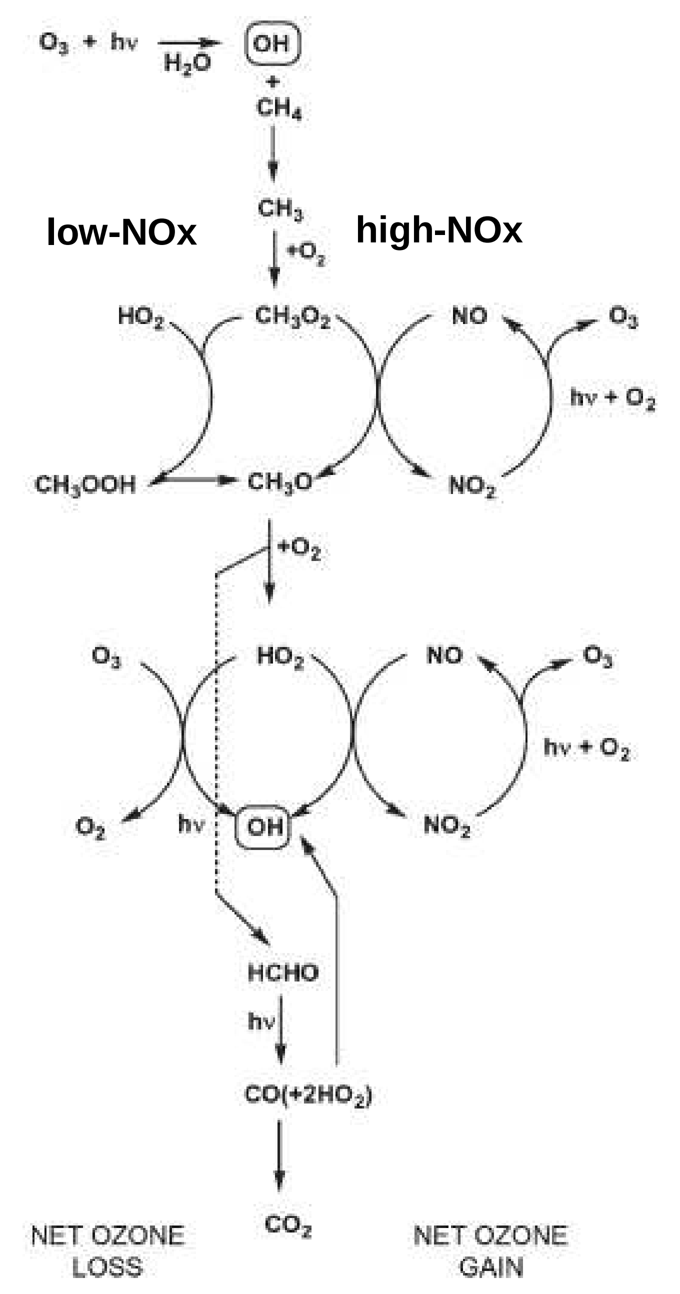
$O + O_2 + M \rightarrow O_3 + M$ (2x)

$CH_4 + 4\,O_2 \rightarrow HCHO + H_2O + 2\,O_3$

Per ogni mole di metano ossidata vengono formate 2 moli di O_3. L'ulteriore fotodissociazione/ossidazione di HCHO produce ulteriori radicali HO_2:

$HCHO + h\upsilon \rightarrow CO + 2\,HO_2\cdot$

$HCHO + OH\cdot \rightarrow HO_2\cdot + CO + H_2O$



Solar radiation and chemistry

O_3-NO-NO_2 photochemical steady state

$NO_2 + h\upsilon \rightarrow NO + O$ J_1 (1)

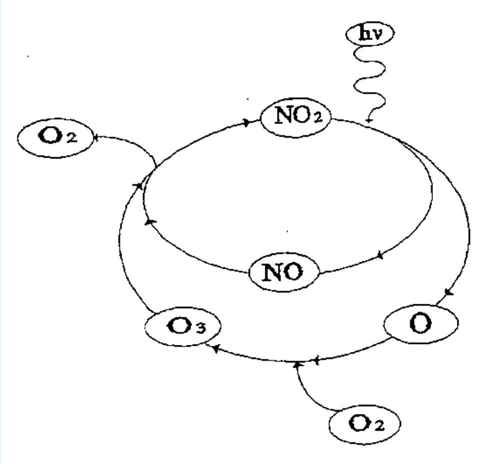
$O + O_2 + M \rightarrow O_3 + M$ (2)

$O_3 + NO \rightarrow O_2 + NO_2$ K_1 (3)

$$d[NO_2]/dt = \text{Prod} - \text{Loss} = 0$$

$$K_1[NO][O_3] = J_1[NO_2]$$

$$[NO]/[NO_2] = J_1/K_1[O_3]$$



Cycling has no net effect on ozone

Presence of peroxy radicals: $HO_2\cdot$,$RO_2\cdot$

$NO_2 + h\upsilon \rightarrow NO + O$ **(2x)** (1)

$O + O_2 + M \rightarrow O_3 + M$ **(2x)** (2)

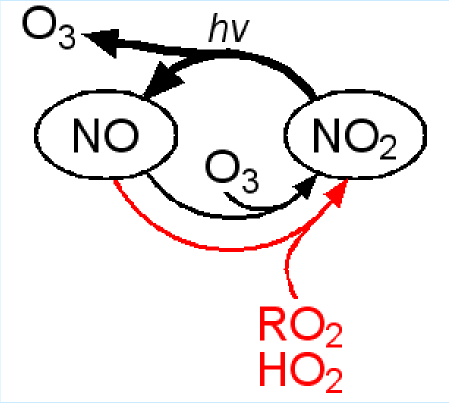
$HO_2\cdot + NO \rightarrow NO_2 + OH\cdot$ (4)

$RO_2\cdot + NO \rightarrow NO_2 + RO\cdot$ (5)

$RO_2\cdot + O_2 \rightarrow O_3 + RO\cdot$ (6)

$HO_2\cdot + O_2 \rightarrow O_3 + OH\cdot$ (7)

$2\ HO_2\cdot + 2\ RO_2\cdot + 4\ O_2 \rightarrow 4\ O_3 + 2\ OH\cdot + 2\ RO\cdot$



Production of ozone and radicals

What breaks the cycle? Radical and NOx Termination

HNO_3 and H_2O_2 formation

$OH\cdot + NO_2 \rightarrow HNO_3$ (high-NOx)

$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2$ (low-NOx)

Both HNO_3 and H_2O_2 will photolyse or react with OH to, in effect, reverse these pathways:

- **but reactions are slow (lifetime of several days);**
- **both are very soluble:**
  - **washout by precipitation;**
  - **dry deposition;**
- **in PBL they are effectively a loss;**
- **situation is more complicated in the upper troposphere (no dry deposition, limited wet removal).**

What breaks the cycle?
Radical and NOx Termination
ROOH formation

$$HO_2\cdot + CH_3O_2\cdot \rightarrow CH_3OOH + O_2 \text{ (low-NOx)}$$

Methyl-hydroperoxide (CH_3OOH):

- **can photolyse or react with OH with a lifetime of ~ 2 days:**
  - **return radicals to system;**
  - **important source of radicals in upper tropical troposphere;**
- **moderately soluble and can be removed from atmosphere by wet or dry deposition (loss of radicals)**

What breaks the cycle? Radical and NOx Termination

Peroxyacyl nitrates (PANs) formation

Formed from oxidation of acetaldehyde:

$$CH_3CHO + OH\cdot\ (+\ O_2) \rightarrow CH_3C(O)O_2\cdot + H_2O$$

$$CH_3C(O)O_2\cdot + NO_2 + M \rightarrow CH_3C(O)O_2NO_2 + M$$

Decomposition is strongly temperature dependent:

- **from 30 minutes at 298K near the surface to several months under upper tropospheric conditions;**
- **NO_x exported from boundary layer to remote troposphere in the form of PAN;**

Observations show PAN is dominant NOy compound in northern hemisphere spring troposphere (insoluble).

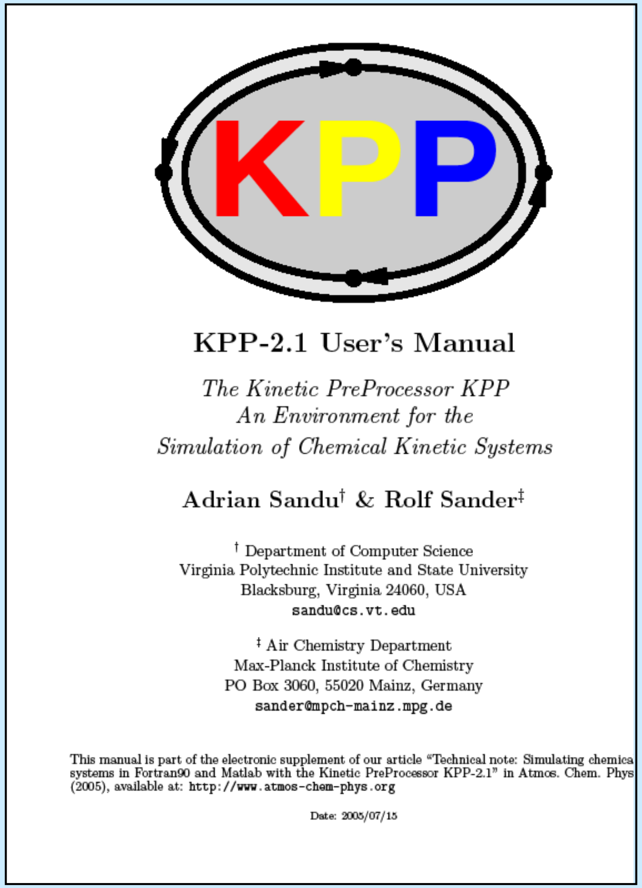
Automatic generation of gas-phase chemical mechanism files (subroutines) using KPP (Kinetic Pre-Processor)

KPP is a pre-processor that allows to:

- incorporate different ***chemical mechanisms*** into the airshed models (SAPRC99, POPS-Hg);
- prepare files containing the mechanism-specific ***data*** and ***subroutines*** required by the airshed model;
- use of robust, accurate and efficient solvers (Lsode, Rosenbrock, …) to integrate the stiff system of ordinary differential equations (ODEs)
- update mechanism with additional species and equations
- develop adjoint code.

The use of KPP avoid the problematic hand-coding phase:

- ✓ **extensive**;
- ✓ **inflexible** and **outdated**;
- ✓ **difficult** for users interested in running the model with alternate mechanism;
- ✓ prone to **errors** and difficult to **debug.**



KPP

KPP-2.1 User's Manual

The Kinetic PreProcessor KPP
An Environment for the
Simulation of Chemical Kinetic Systems

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This manual is part of the electronic supplement of our article "Technical note: Simulating chemica systems in Fortran90 and Matlab with the Kinetic PreProcessor KPP-2.1" in Atmos. Chem. Phys (2005), available at: `http://www.atmos-chem-phys.org`

Date: 2005/07/15

KPP requires the UNIX tool programs ***flex***, ***yacc***, and ***sed*** to be installed on the system.

KPP
Input files

.spc file:** ***Definition of chemical species as variable or fixed value.

.eqn file:** ***Writing chemical reactions in KPP format

***.kpp file: Model description, computer language, precision, integrator (e.g. Rosenbrock solver) etc.**

***.def file: User defined functions**

KPP species (.spc)

```
#include atoms
#DEFVAR
{-------------- Inorganics -------------}
NO        = N + O;
NO2       = N + 2O;
NO3       = N + 3O;
HNO3      = H + N + 3O;
N2O5      = 2N + 5O;
PAN       = 2C + 3H + 5O + N;
SO2       = S + 2O;
H2SO4     = 2H + S + 4O;
…
```

#	Reaction	Rate
1	$NO_2 + hv = NO + O_3$	radiation dependent
2	$NO + O_3 = NO_2 + O_2$	ARR (2.2 E-12,-1430)
3	$NO_2 + O_3 = NO_3 + O_2$	ARR (1.2 E-13,-2450)
4	$NO + NO_3 = 2NO_2$	ARR (8.0 E-12,250)
5	$NO_2 + NO_3 = N_2O_5$	PT dependent
6	$N_2O_5 = NO_2 + NO_3$	special function
7	$NO_2 + NO_3 = NO + NO_2 + O_2$	ARR (2.5 E-14,-1230)
8	$NO_3 + hv = 0.15NO + 0.85NO_2 + 0.85O_3 + O_2$	3.29*KR (1)
9	$NO_3 + HO_2 = HNO_3 + O_2$	2.50 E-12
10	$O_3 + hv = 2OH$	radiation dependent
11	$NO + OH = HONO$	PT dependent
12	$HONO + hv = NO + OH$	0.205*KR(1)
13	$NO_2 + OH = HNO_3$	PT dependent
14	$HNO_3 + hv = NO_2 + OH$	4.4 E-5*KR(1)
15	$HNO_3 + OH = NO_3 + H2O$	ARR (9.4 E-15,778)
16	$N_2O_5 + H_2O = 2HNO_3$	1.30 E-21
17	$CO + OH = HO_2 + CO_2$	special function (Atkinson e Lloyd, 1984)
18	$O_3 + OH = HO_2 + O_2$	ARR (1.9 E-12,-1000)
19	$NO + HO_2 = NO_2 + OH$	ARR (3.7 E-12,240)
20	$NO_2 + HO_2 = HNO_4$	special function (Atkinson e Lloyd, 1984)
21	$HNO_4 = NO_2 + HO_2$	special function (Atkinson e Lloyd, 1984)
22	$O_3 + HO_2 = OH + 2O_2$	ARR (1.4 E-14,-600)
23	$HO_2 + HO_2 = H_2O_2 + O_2$	special function (Atkinson e Lloyd, 1984)
24	$H_2O_2 + hv = 2OH$	radiation dependent
25	$H_2O_2 + OH = HO_2 + H2O$	ARR (2.9 E-12,160)
26	$NO_2 + H_2O = HONO + HNO_3\text{-}NO_2$	4.00 E-24
27	$HNO_4 + hv = NO_2 + HO_2$	1 E-4*KR(1)
28	$HNO_4 + OH = NO_2 + H_2O + O_2$	ARR (4E-12,380)
29	$SO_2 + OH = SO_4 + HO_2$	PT dependent

$$ARR(A,B)=Ae^{B/T} \quad .$$

KPP reactions(.eqn)

```
#Equations
{Inorganic Reactions}
{1} NO2 + hv = NO :              phk(1); {fcm_saprc99_phk('NO2_______',1e0,zenith);}
{2} O3 + NO = NO2 :              ARR(1.80e-12,1370.0e0,0.0e0);
{3} O3 + NO2 = NO3 :             ARR(1.40e-13,2470.0e0,0.0e0);
{4} OH + NO2 = HNO3 :            FALL(2.43e-30, 0.0e0,-3.10e0,1.67e-11,0.0e0,-2.10e0,0.60e0);
{5} CCO_O2 + NO2 = PAN :         FALL(2.70e-28,0.0e0,-7.10e0,1.20e-11,0.0e0,-0.90e0,0.30e0);
{6} PAN = NO2 :                  FALL(4.90e-3,12100.0e0,0.0e0,4.0e+16,13600.0e0,0.e0,0.3e0);
{7} OH + SO2 = H2SO4 :           FALL(4.00e-31,0.0e0,-3.30e0,2.00e-12,0.0e0,0.0e0,0.45e0);
{8} NO3 + hv = NO :              phk(2); {fcm_saprc99_phk('NO3NO____',1e0,zenith);}
{9} NO3 + hv = NO2 :             phk(3); {fcm_saprc99_phk('NO3NO2___',1e0,zenith);}
{10} NO2 + NO3 = N2O5 :          FALL(2.80e-30,0.0e0,-3.50e0,2.00e-12,0.0e0,0.20e0,0.45e0);
{11} N2O5 = NO2 + NO3 :          FALL(1.e-3,11000.0e0,-3.5e0,9.7e+14,11080.0e0,0.1e0,0.45e0);
{12} N2O5 + H2O = 2HNO3 :        (2.60e-22);
{13} NO + NO3 = 2NO2 :           ARR(1.80e-11,-110.0e0,0.0e0);
…
```

KPP Main Input file

(.kpp)

```
#MODEL      KPP_gas
#INTEGRATOR kpp_lsode
#LANGUAGE   Fortran90
#DRIVER     none
#HESSIAN    on
#STOICMAT   on
```

KPP User defined functions (.def)

```
#INLINE F90_RATES
  subroutine update_phk(zenith)
    real(kind=sp), intent(in) :: zenith
    integer :: phr_index ! photolitic reaction index
    do phr_index=1,nphr
      phk(phr_index) = qy(phr_index) * phk_lookup(zenith, pf_index( phr_index ) ) / 60e0
    end do
  contains
real(kind=sp) function phk_lookup( zenith, pf_index )
      real(kind=sp), intent(in) :: zenith
      integer, intent(in) :: pf_index
      integer :: i
      if( zenith > zenith_max )then
……..
```

SAPRC99 chemical mechanism

(Statewide Air Pollution Research Center)

- It is a lumped molecule mechanism, where either generalized (lumped) or surrogate species are used to represent organic compounds.
- It contains more than 3 times the number of organic species as the CB-IV. Organic reaction products are treated in more detailed than in CB-IV.
- The kinetics and mechanism parameters can be specified by the user.

BOX model tests (KPP) using SAPRC99 chemical mechanism

```
1987 7 1 12             ! SIMULATION DATE: YEAR, MONTH, DAY, HR
120                     ! NR OF HOURS
45. 0. 0                ! BOX LATITUDE, LONGITUDE, TIME ZONE
300.                    ! duration to be integrated in seconds
288.15 101325. 50.      ! Temperature [K],  Pressure [Pa],  RH [%]
```

Concentrations in [ppm]

'AIR‘	1.0000E+06
'O2‘	2.0900E+05
'H2O‘	1.0000E+04
'H2‘	5.0000E-01
'CH4‘	1.7000E+00
'O3‘	0.0300
'NO‘	0.0001
'NO2‘	0.0001
'HNO3‘	0.0001
'CO‘	0.1000
'H2O2‘	0.0020
'HCHO‘	0.0010

‘LAND’

'ISOPRENE‘	0.0000

‘BIO’

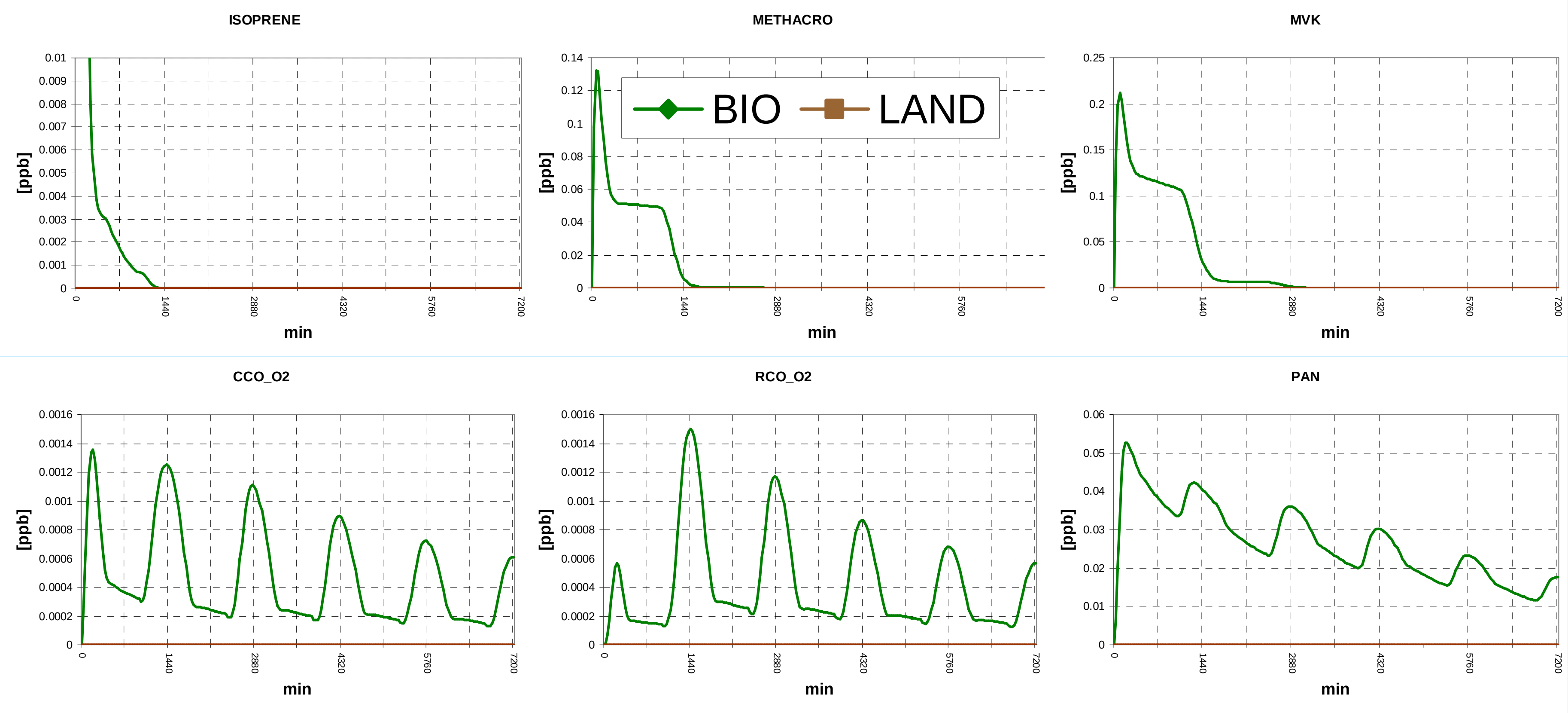
'ISOPRENE‘	0.0010

BOX model tests using SAPRC99 chem. mech.

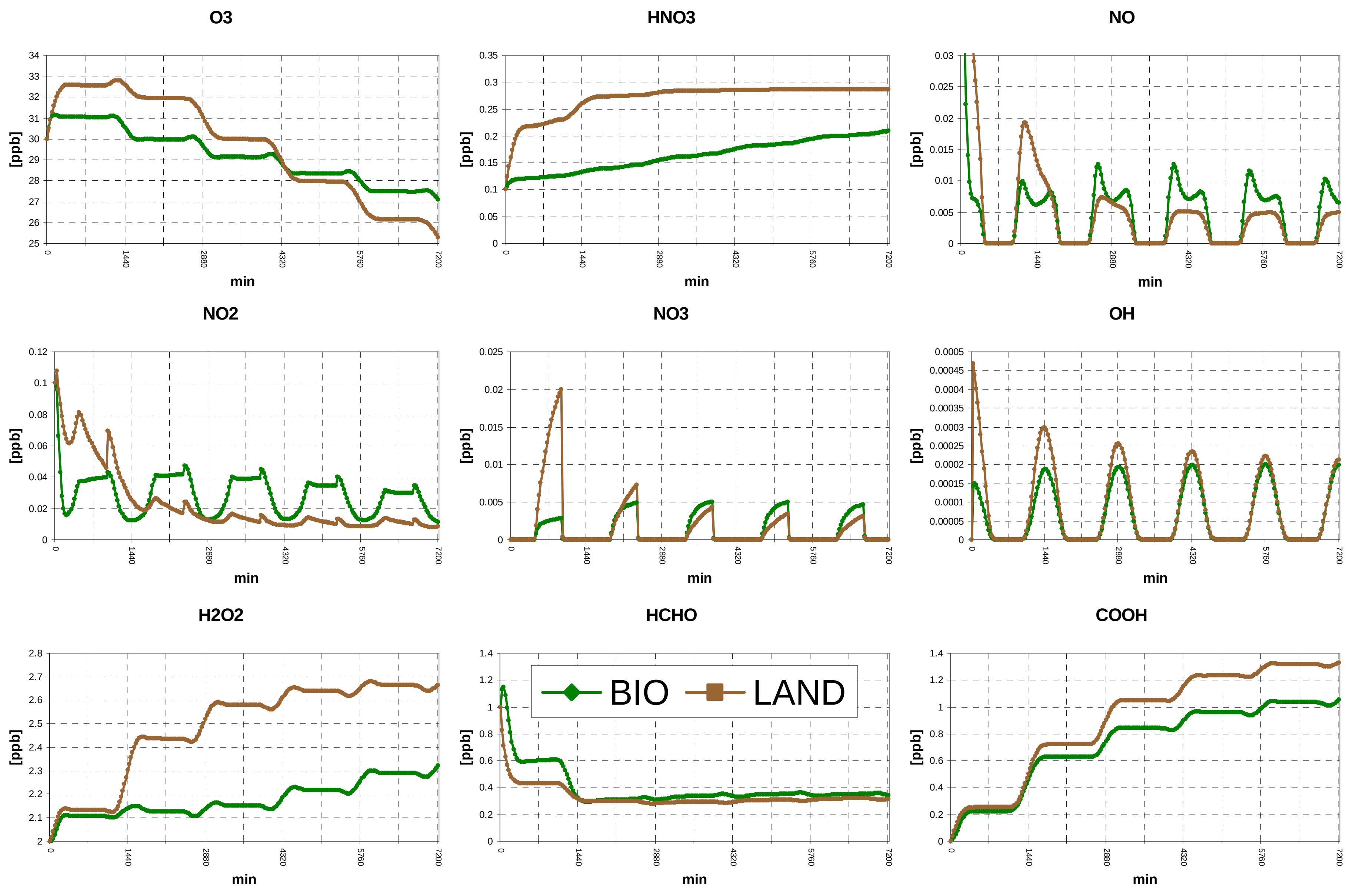
Gas-phase isoprene chemistry:

$$\mathrm{ISOP} + (\mathrm{OH}\cdot, O_3) \rightarrow \mathrm{MACR, MVK} + (\mathrm{OH}\cdot, O_3, h\nu) \rightarrow \text{radicals } (CH_3C(O)O_2\cdot, \ldots)$$

$$CH_3C(O)O_2\cdot + NO_2 \rightarrow \mathrm{PAN}$$



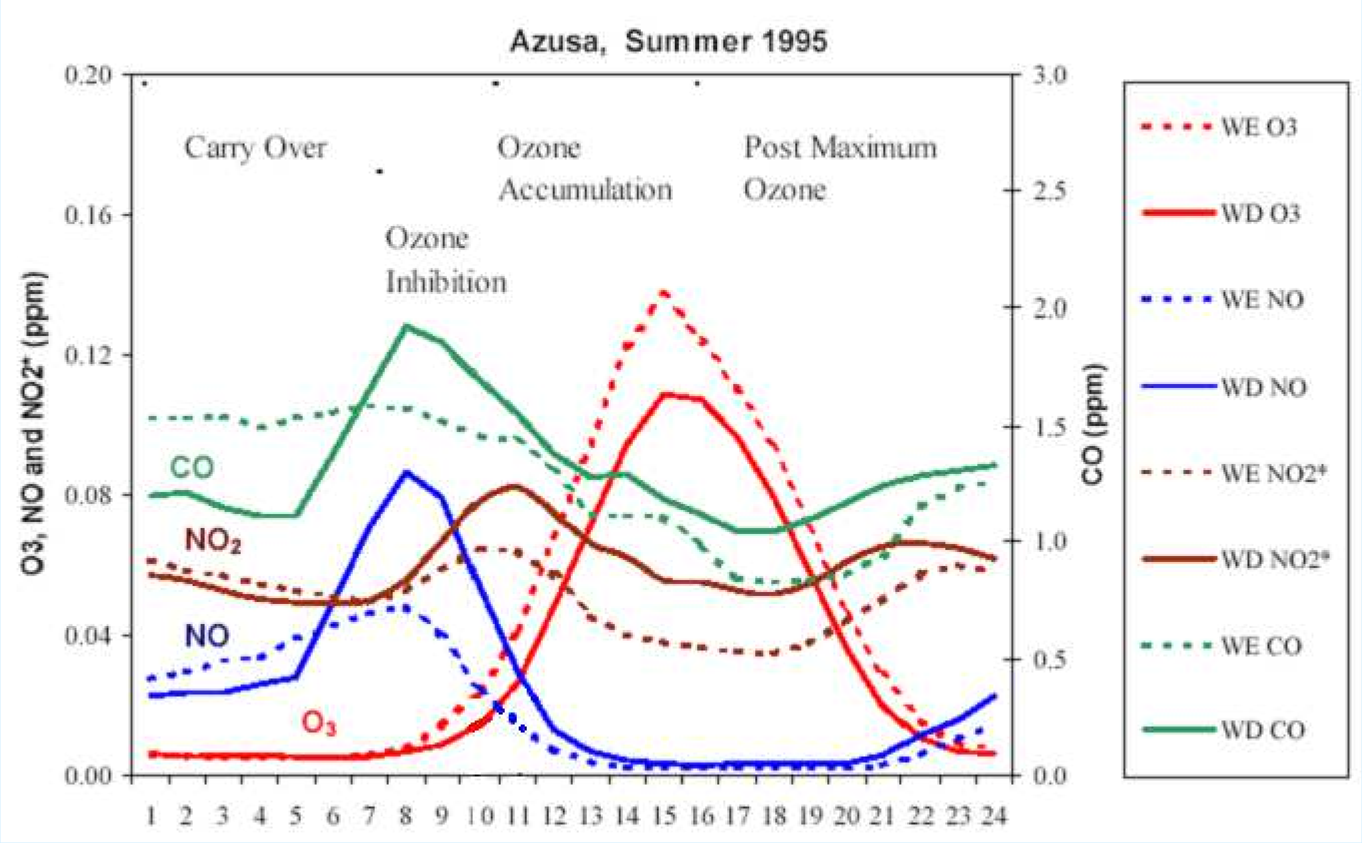
BOX model tests using SAPRC99 chem. mech.



NOX/VOC vs P(O_3)

High NOx/VOC	Low NOx/VOC
• Typical for urban areas;	• Typical for rural/remote areas;
• Peroxy radical oxidation of NO to form NO_2 (O_3 production): $HO_2\cdot + NO \rightarrow OH\cdot + NO_2$ $RO_2\cdot + NO \rightarrow RO\cdot + NO_2$	• O_3 destruction in a chain sequence involving OH formation: $HO_2\cdot + O_3 \rightarrow OH\cdot + 2\,O_2$ $OH\cdot + O_3 \rightarrow HO_2\cdot + O_2$
• NOX loss through OH and RO_2reaction with NO_2 (NOX termination): $OH\cdot + NO_2 + M \rightarrow HNO_3 + M$ $RO_2\cdot + NO_2 + M \rightarrow PAN$	• peroxy radical self-reactions become important sink for radicals (radical termination): $HO_2\cdot + HO_2\cdot \rightarrow H_2O_2$ $HO_2\cdot + RO_2\cdot \rightarrow ROOH + O_2$
• ozone production is [VOC] limited $P(O_3) \propto [VOC]/[NOX]$	• ozone production is [NOX] limited $P(O_3) \propto [NOX]$

O_3 *“Weekend effect”*



$O_3 + NO \rightarrow NO_2$ $\quad$ $NO + HO_2(RO_2) \rightarrow NO_2$

$O_3 + NO_2 \rightarrow NO_3$ $\quad$ $NO_2 + h\nu\ (+O_2) \rightarrow O_3$

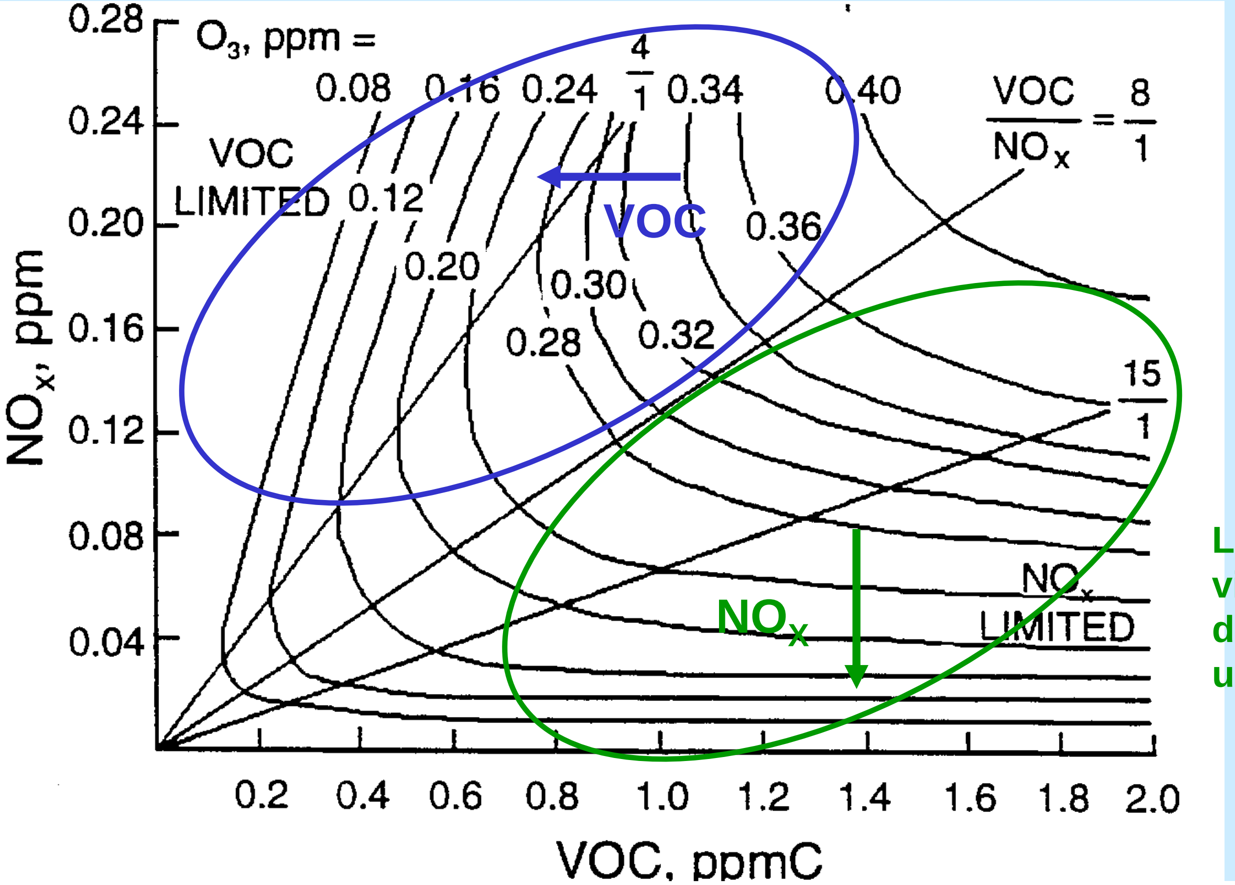
$NO_2 + OH \rightarrow HNO_3$ (WD)

“O3 isopleth diagram”

Area of effective VOC control
(most often highly populated areas)

Abundant NO_2 removes OH, inhibiting oxidation of VOCs and HO_2/RO_2 formation (low utilization of NO_x emissions)

$$P(O_3) \propto \frac{[VOC]}{[NO_X]}$$



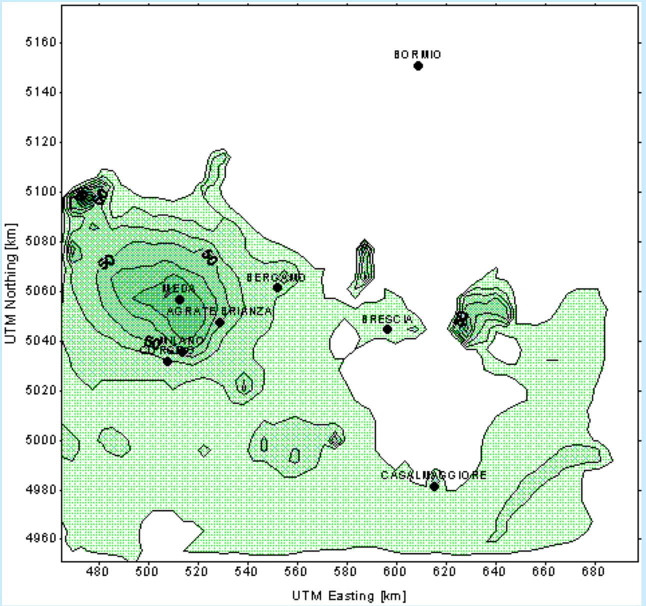
NOx control effective
(areas with high biogenics)

Lack of NO_x limits ozone formation via photolysis, increased destruction of HO_2/RO_2 (high utilization of NO_x emissions)

$$P(O_3) \propto [NO_X]$$

Strategie di controllo dell’ozono

*Secondo alcuni studi modellistici (Milford et al., 1994; Silmann, 1995) è possibile valutare il regime fotochimico di una zona in funzione del valore assunto da alcuni **indicatori**.*
Tali studi suggeriscono che, ai fini della riduzione dei livelli di ozono, il controllo delle emissioni di VOC sia maggiormente efficace nelle aree 'VOC sensitive' caratterizzate da valori pomeridiani di NO_y (= NO_x + NO_z; ove NO_z = prodotti di ossidazione degli NO_x) superiori a 10-15 ppb e da rapporti O_3/NO_z inferiore a 6-11.

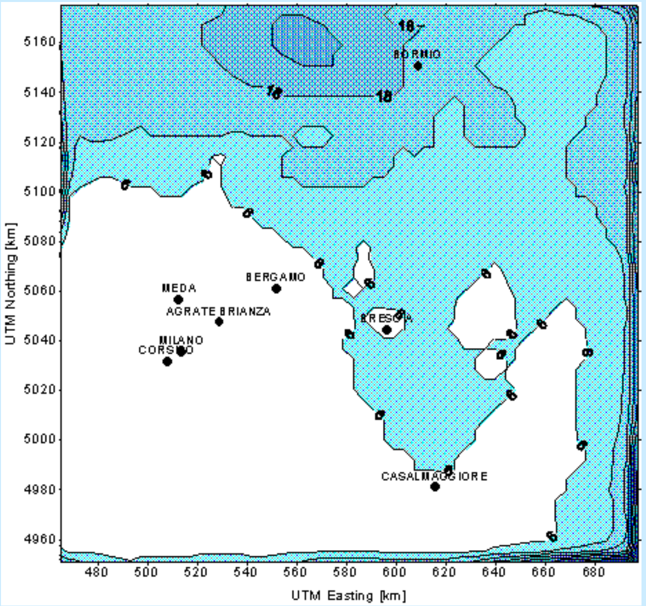


VOC limited

NO_y

O_3/NO_z

NOx limited

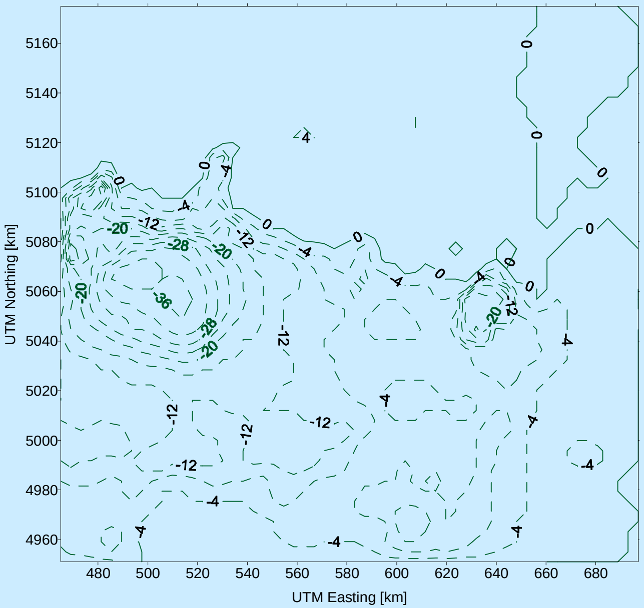


Strategie di controllo dell’ozono

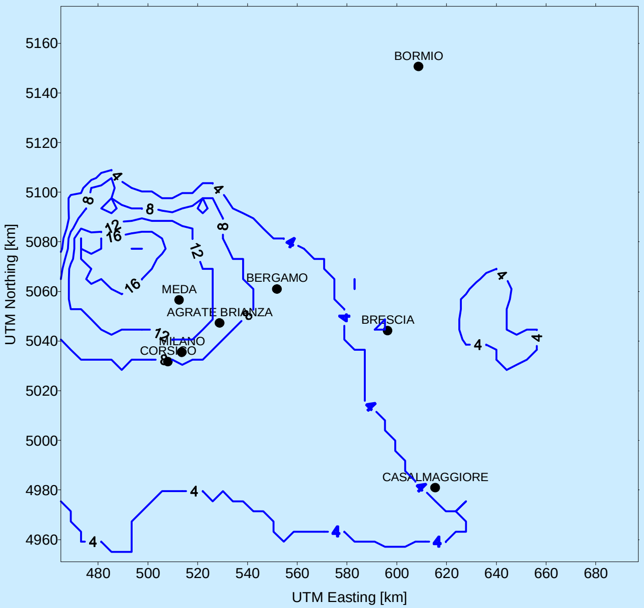
*Nella regione ‘**VOC limited**’ (NOy > 10-15 ppb):*

- *la riduzione del 35% delle emissioni antropogeniche di VOC determina una riduzione dei livelli di O_3 fino a 16 ppb;*
- *viceversa la riduzione del 35% delle emissioni di NOx determina un aumento delle concentrazioni di O_3 fino a 36 ppb;*

riduzione del 35% delle emissioni di NOx

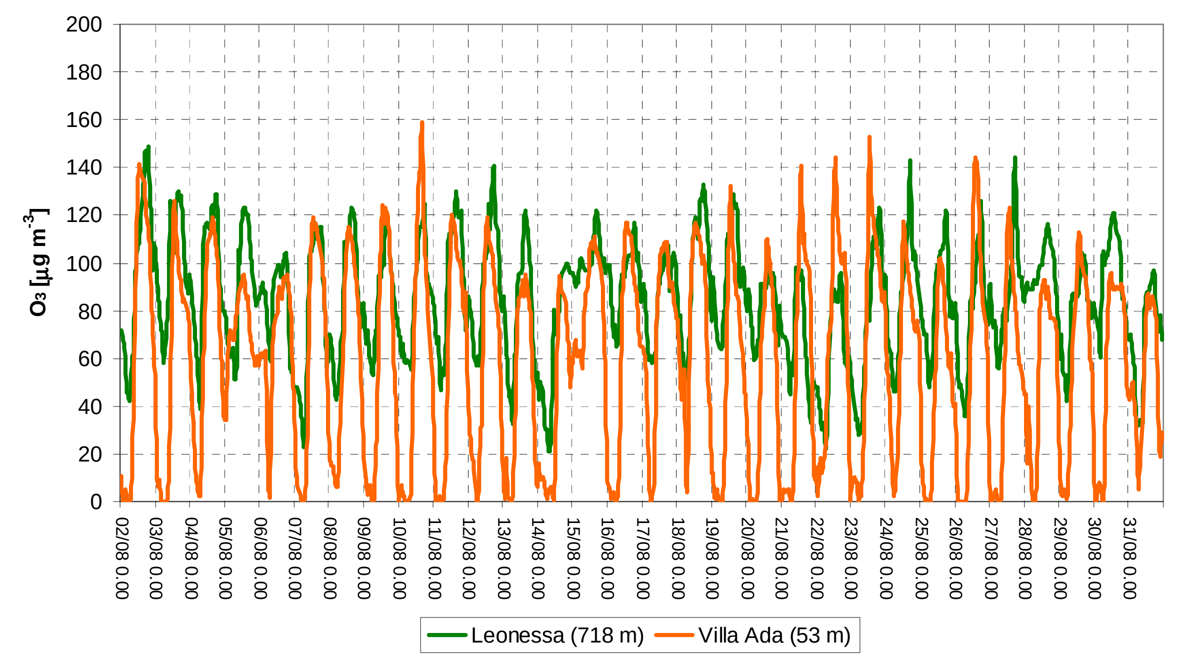


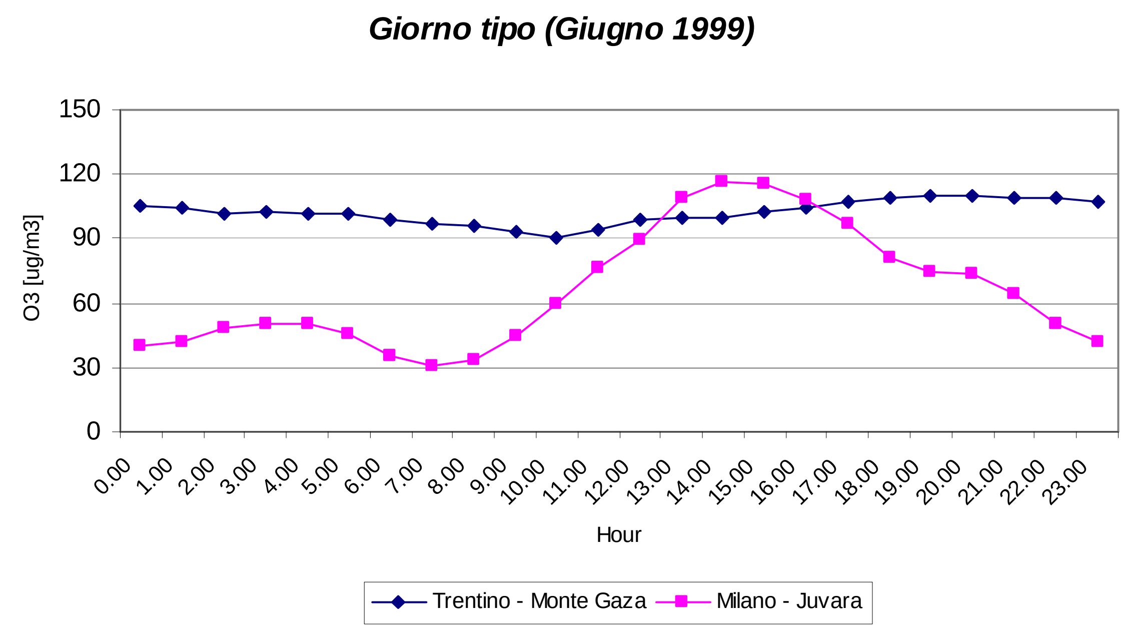
riduzione del 35% delle emissioni di VOC



*Nella regione **$\mathrm{NO_x}$ limited’** entrambe le politiche di riduzione delle emissioni producono effetti trascurabili sui livelli di O_3.*

O_3 "urban vs rural"





Summary

- Under atmospheric conditions (p and T) but no sunlight atmospheric chemistry of the gas phase would be slow;
- Sun radiation (UV) splits (**photolysis**) even very stable molecules such as O_2 (but also O_3 or NO_2) in to very reactive molecules;
- These fast reacting molecules are called **radicals** and the most relevant is **OH** (Hydroxyl radical);
- photolysis of ozone is the most significant source of **OH**;
- Reaction with **OH** is the most important loss mechanism in the troposphere for very common species such as CO, NO_2, O_3 and hydrocarbons;
- atmospheric oxidation of hydrocarbons initiated by **OH** radical leads to:
  - production of peroxy radicals (**HO_2**, **RO_2**) which interact with O_3-NO-NO_2 cycle to photo-chemically produce ozone;
  - production carbonyl compounds (aldehydes and ketones) which undergo further oxidation;
  - recycling of **OH**;
- Radical (and NOx) termination by formation of nitric acid (HNO_3) or peroxides (H_2O_2, ROOH);
- NOx concentrations control whether local chemistry creates or destroys ozone;