EMEP MSC-W model: Chemistry, status + changes

David Simpson

Norwegian Meteorological Institute

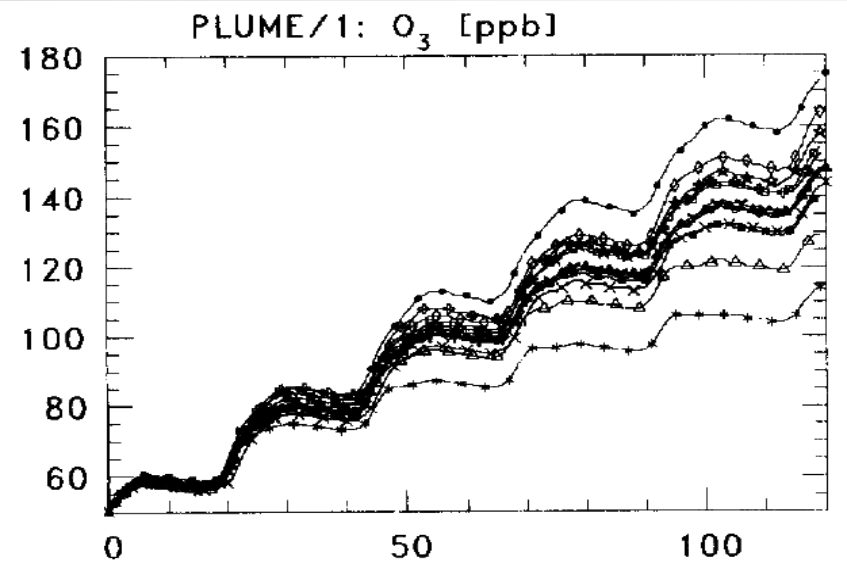
Outline:

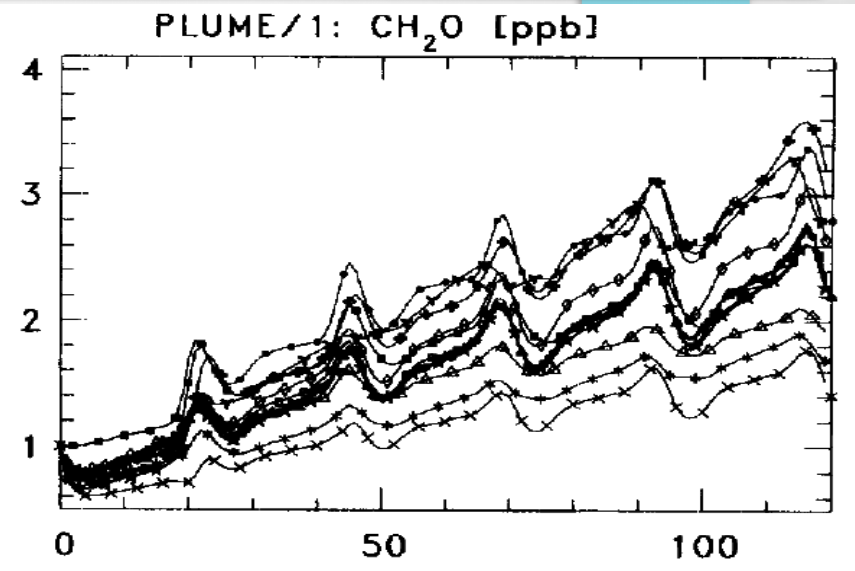
- Gas-phase chemistry
- SOA module
- Code structure
- Recent updates
- Miscellaneous (GenChem, other schemes)

Gas-phase chemistry:

- EmChem09
  - 72 species
  - 137 reactions
  - 10 VOC (1 BVOC = isoprene)
- Update of previous EMEP chemical schemes, which date back to Eliassen, Hov, et al 1982
- 'Surrogate species' method, with relatively more RO2 chemistry than e.g. CB schemes

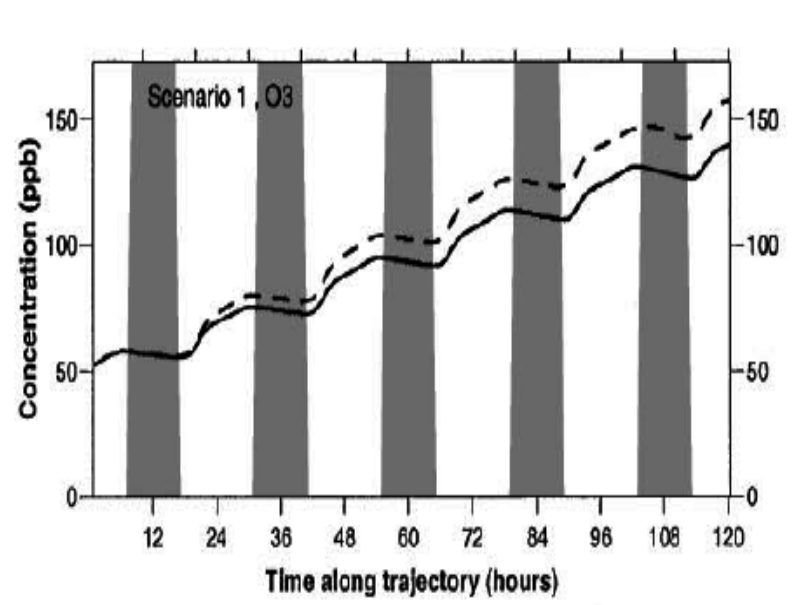
Early comparisons.....

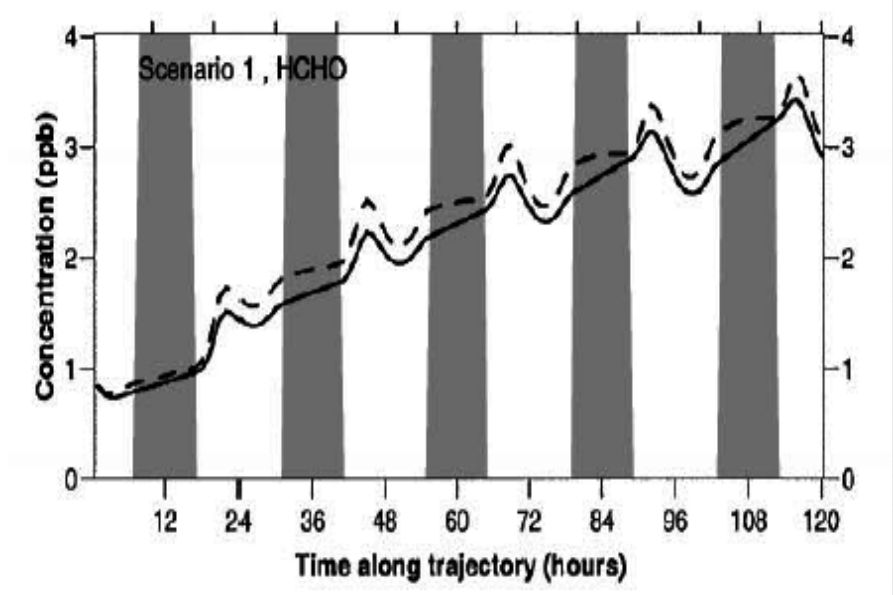




Kuhn et al., Atm.Env., 1998, with EMEP, IVL, 4 x RADM, 3 x CB4, ...

Follow-up: EMEP vs most complex (IVL): comparisons.....

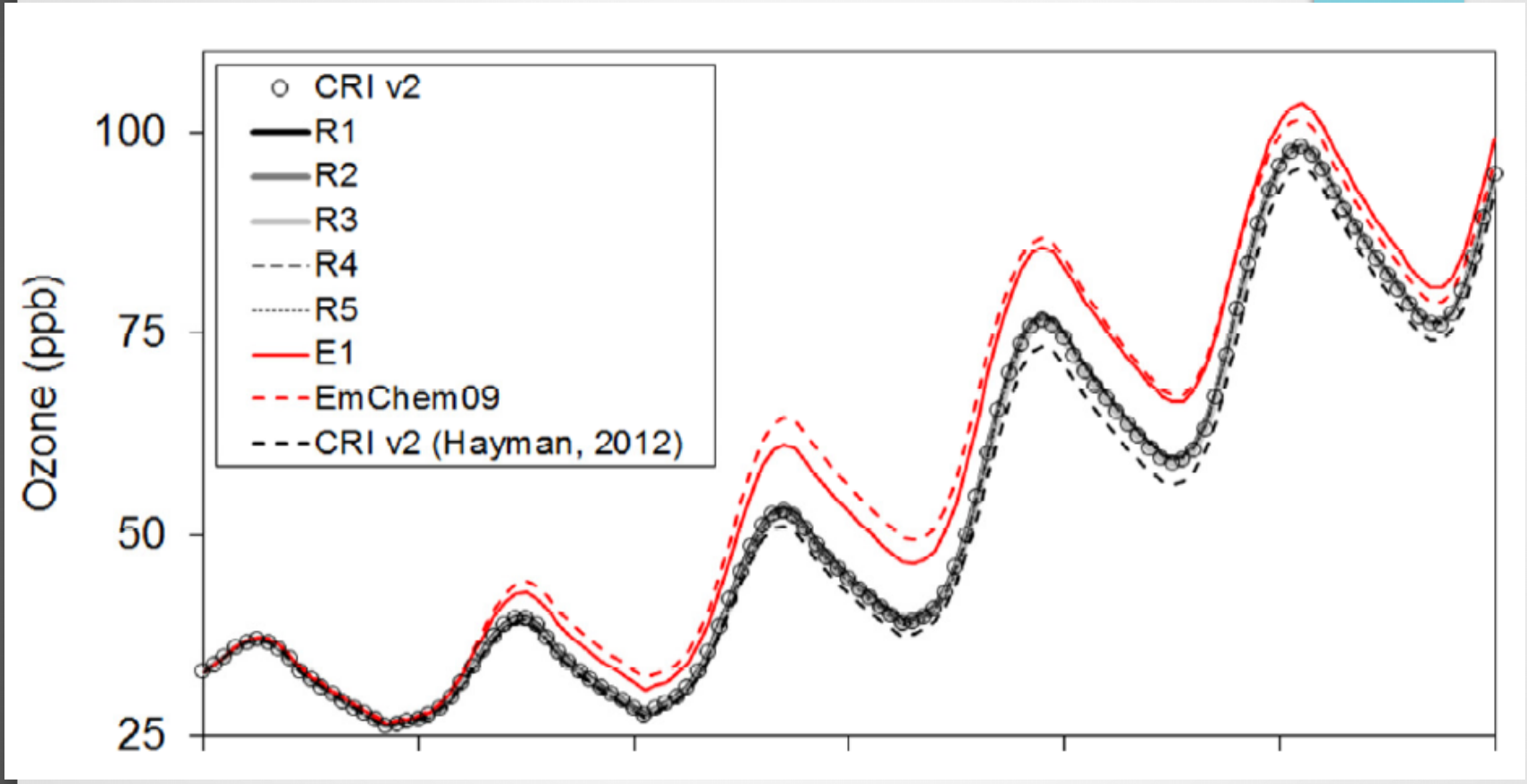




Andersson-Sköld & Simpson, Atm.Env., 1999, same setup as Kuhn et al. (+other cases)

- EMEP model compared well :-)

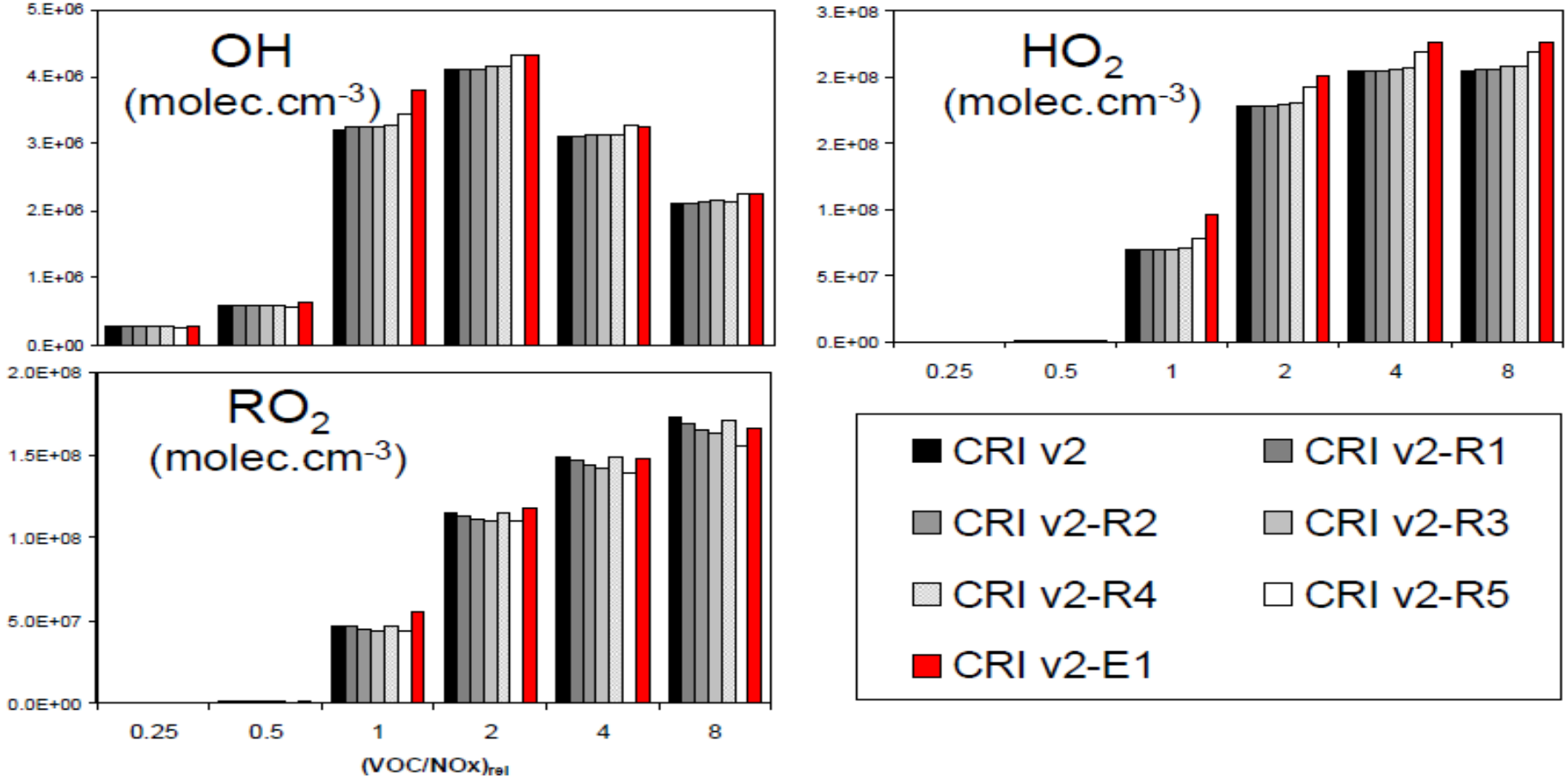
2009: Comparison with CRI model.



Ozone changes (c/o Mike Jenkin), simple plume

- CRI v2 ~ 1000 reactions, 112 AVOC

Comparison with CRI model.



Radicals (c/o Mike Jenkin)

- How do we handle chemistry in the model?

- CM_ files:

```
ChemFunctions_ml.f90
Chem_ml.f90
CM_BoundaryConditions.inc
CM_BoundaryConditions.inc.txt
CM_ChemGroups_ml.f90
CM_chempackages.txt
CM_ChemRates_ml.f90
CM_ChemSpecs_ml.f90
CM_DryDep.inc
CM_EmisBioNat.inc
CM_EmisFiles.inc
CM_emislist.csv
CM_EmisSpecs.inc
CM_Reactions1.inc
CM_Reactions2.inc
CM_WetDep.inc
CoDep_ml.f90
```

- CM_ChemSpecs_ml
-
- Species -
  - Number
  - Indices
  -

```
!>-------------------------------------------------------------
  module  ChemSpecs_adv_ml
!-------------------------------------------------------------

...
   integer, public, parameter ::  NSPEC_ADV = 126

   integer, public, parameter ::    &
     IXADV_O3           =   1    &
   ,  IXADV_NO          =   2    &
..
 !-------------------------------------------------------------
  end module ChemSpecs_adv_ml
!>-------------------------------------------------------------

  module  ChemSpecs_shl_ml
!-------------------------------------------------------------

...
     IXSHL_OD           =   1    &
   ,  IXSHL_OP          =   2    &

....
!-------------------------------------------------------------
  module  ChemSpecs_tot_ml
!-------------------------------------------------------------
   integer, public, parameter ::  NSPEC_TOT = 142

   integer, public, parameter ::    &
     OD           =   1    &
   ,  OP          =   2    &
~
```

- CM_ChemSpecs_ml
- + characteristics
  -

```
...
  contains
  subroutine define_chemicals()

...
  !                                                MW  NM   C    N   S  ExtC    C*  dH
    species(OD    ) = Chemical("OD    ",  16.0,  0,  0,   0,  0,  0.0,  0.0, 0.0 )
    species(OP    ) = Chemical("OP    ",  16.0,  0,  0,   0,  0,  0.0,  0.0, 0.0 )
    species(OH    ) = Chemical("OH    ",  17.0,  0,  0,   0,  0,  0.0,  0.0, 0.0 )
    species(HO2   ) = Chemical("HO2   ",  33.0,  0,  0,   0,  0,  0.0,  0.0, 0.0 )
.
    species(O3    ) = Chemical("O3    ",  48.0,  0,  0,   0,  0,  0.0,  0.0, 0.0 )
    species(NO    ) = Chemical("NO    ",  30.0,  0,  0,   1,  0,  0.0,  0.0, 0.0 )
    species(NO2   ) = Chemical("NO2   ",  46.0,  0,  0,   1,  0,  0.0,  0.0, 0.0 )
    species(PAN   ) = Chemical("PAN   ", 121.0,  0,  2,   1,  0,  0.0,  0.0, 0.0 )
    species(NO3   ) = Chemical("NO3  ",  62.0,  0,  0,   1,  0,  0.0,  0.0, 0.0 )
```

- CM_Reactions1.inc

```
!-> O3

      P =   &
          rct(1,k) * xnew(OP )  &
        + 0.15*rct(37,k) * xnew(CH3CO2 ) * xnew(HO2 )  &
        + 0.29*rct(60,k) * xnew(MACO3 ) * xnew(HO2 )

      L =  &
          rct(5,k)* xnew(NO )  &
        + rct(6,k)* xnew(NO2 )  &
        + rct(7,k)* xnew(OH )  &
        + rct(8,k)* xnew(HO2 )  &
        + AQRCK(ICLRC2,K)* xnew(SO2 )  &
        + rct(43,k)* xnew(C2H4 )  &
        + rct(44,k)* xnew(C3H6 )  &
        + rct(50,k)* xnew(C5H8 )  &
        + rct(53,k)* xnew(MACR )  &
        + rct(58,k)* xnew(MVK )  &
        + rcphot(IDAO3,K)  &
        + rcphot(IDBO3,K)

      xnew(O3)=  ( xold(O3) + dt2 * P) /(1.0 + dt2*L )
```

- CM_ChemGroups_ml

```
!>------------------------------------------------------------<

  module  ChemGroups_ml
!-------------------------------------------------------------

  use ChemSpecs_tot_ml  ! => species indices
  use OwnDataTypes_ml   ! => typ_sp
  implicit none
  private
! Assignment of groups from GenIn.species:
 public :: Init_ChemGroups

! ------- Gas/particle species ------------------
..

  integer, public, parameter ::  INDEX_WDEP_OXN_GROUP = 2
  integer, public, target, save, dimension(4) :: &
                  WDEP_OXN_GROUP     = (/ HNO3,HONO,NO3_F,NO3_C /)

  integer, public, parameter ::  INDEX_WDEP_PPM10_GROUP = 3
  integer, public, target, save, dimension(11) :: &
                  WDEP_PPM10_GROUP     = (/ POM_F_WOOD,POM_F_FFUEL,
UEL_NEW,EC_F_FFUEL_AGE,EC_C_FFUEL,REMPPM25,REMPPM_C /)
```

OA, POA, SOA ;-)

OA: Subject=Horrendous!

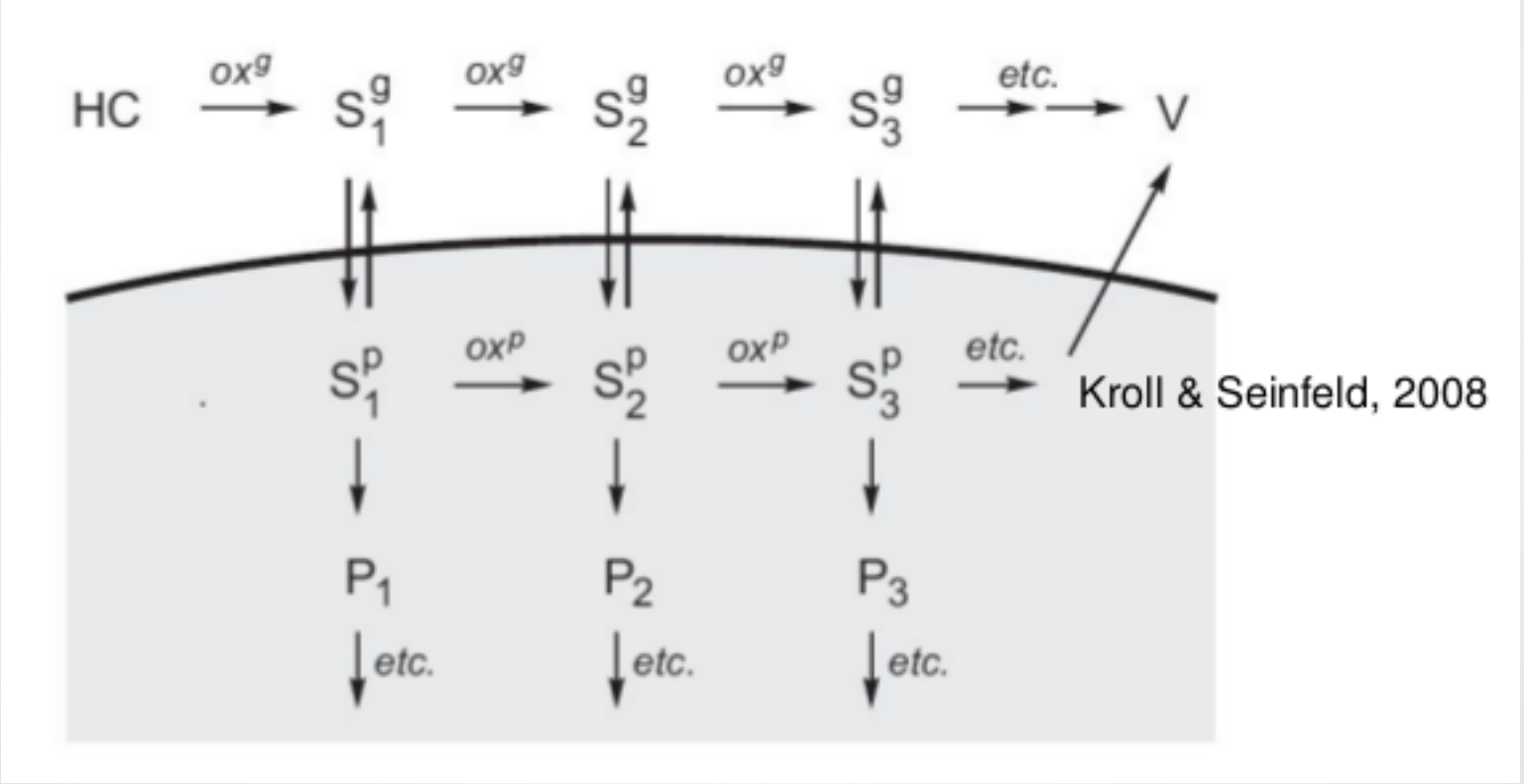
Some issues:

- Which precursors? (Isoprene, terpenes, aromatics ..)
- 1000s of compounds, mainly unknown.
- Gas-phase? Aqueous-phase? Particle-phase?
- Thermodynamics/Volatility
- Aging
- Artifact-rich observations!

See e.g. Donahue et al., Atmos. Environ., 2009, Hallquist et al., ACP, 2009

OA cont,

- Need to deal with equilibria, e.g.



OA cont., “VBS”:

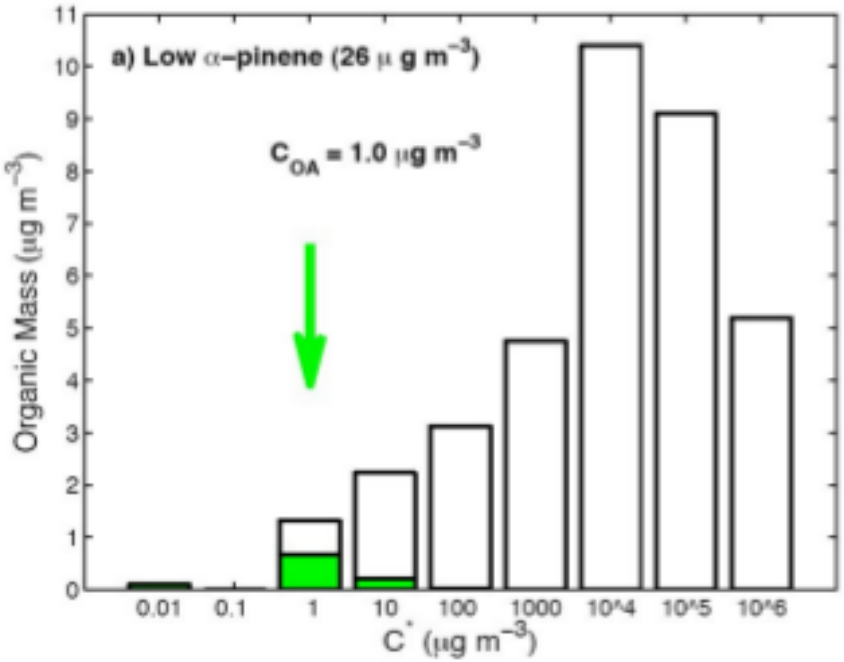
- Volatility Basis Set (Donahue and colleages)

- Gas-Particle partitioning:

$$\frac{A_i}{G_i} = \frac{C_{OA}}{C_i^*}$$

where

- C_i^* is saturation concentration, $= f$(Vapour pressure)



OA in model code:

- Code tracks species, not phase, for advection
- Gas/aerosol fractions calculated using partitioning theory in My_SOA_ml
- Affects deposition, aging reactions etc.
-

OA in model code:

- Origin (GenChem) of reactions looks like:

```
1.2e-11*exp(444.0*TINV)    [OH] + apinene = TERPPeroxy

KRO2NO TERPPeroxy + NO  = NO2 + 0.08 BSOC_ug1 + 0.672 NON_C_BSOA_ug1
                        + 0.813333 BSOC_ug10 + 6.832 NON_C_BSOA_ug10
                        + 1.34 BSOC_ug1e2 + 11.256 NON_C_BSOA_ug1e2
                        + 3.333333 BSOC_ug1e3 + 28. NON_C_BSOA_ug1e3
~
```

- - ie produces range of products of different volatility

OA in CM_Reactions2:

- Gas-phase chemistry

```
!-> BSOC_UG1

      P =   &
          0.002833*rct(40,k)*xnew(ISRO2)*xnew(NO)  &
        + 0.0255*rct(47,k)*xnew(ISRO2)*xnew(HO2)  &
        + 0.08*rct(40,k) * xnew(TERPPEROXY ) * xnew(NO )  &
        + 0.715333*rct(75,k) * xnew(TERPPEROXY ) * xnew(HO2 )  &
        + rct(85,k)*xnew(OH) * xnew(BSOC_UG10 )
]
      L =  &
          rct(84,k)*xnew(OH)

      xnew(BSOC_UG1)=  ( xold(BSOC_UG1) + dt2 * P) /(1.0 + dt2*L )
```

OA final words:

- OA schemes can give many very different answers.

The basic rule:

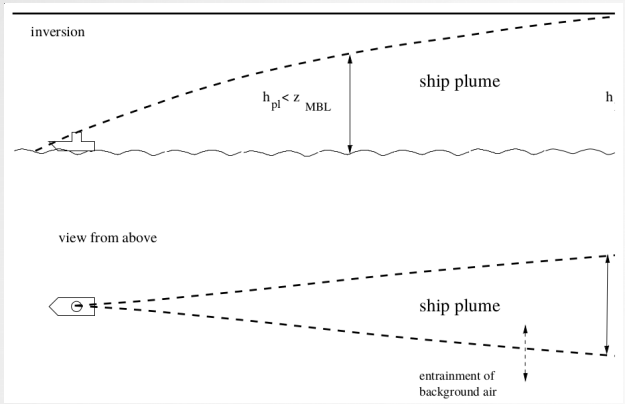
Garbage in ⇒ 

⇒ Garbage out:

SOA twist:

Garbage in the middle! 

2015 Changes 1: ShipNOx

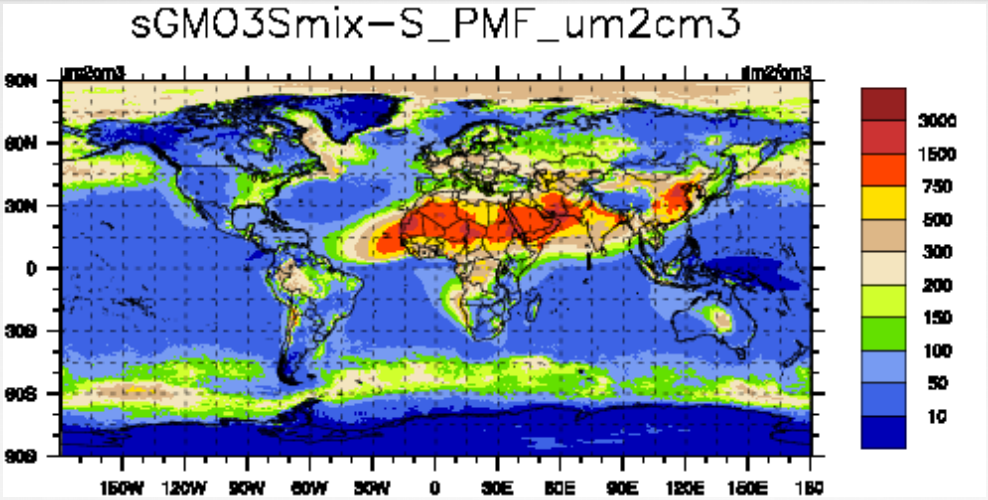


- Non-linearity of ozone chemistry can cause ship plumes to
  - Generate too much O3
  - Give too long lifetime for NOx

- ShipNOx:
- Pragmatic solution to provide faster conversion to HNO3 and reduce O3 production over oceans.
- Loosely (very!) based on GEOS-Chem PARANOX (Vinken et al, 2011)
- 50% of ship NO emitted as 'ShipNOx'

$$\text{ShipNOx} + \text{OH} \Rightarrow \text{HNO}_3 \quad \text{R1}$$
$$\text{ShipNOx} \Rightarrow \text{HNO}_3 \quad \text{R2}$$

2015 Changes 2: Aerosol surface area



- Aerosol surface area (S) now calculated using 'Gerber' functions
  - Empirical, we like ;-)
  - Avoids too much reliance on e.g. MARS/ISORROPIA
  - Unclear if high S due to fine-dust, sea-salt is correct
  - Large implications for e.g. modelling in Asia!

2015 Changes 3: gas-aerosol interactions

- Gas-aerosol rates now depend on surface area
- Replaces older & cruder system
- Links inorganic chemistry to dust & sea-salt

$$k_X = \frac{1}{4} c_X S \gamma_X$$

Table 1.1: Main aerosol-uptake reactions in rv4.7 EMEP model

Reaction		γ
$N_2O_{5\ (g)}$	$\longrightarrow 2\ HNO_{3\ (aq)}$	Options: Smix, SmixTen, or fixed values. See Sect.1.2.1
$HNO_{3\ (g)} + \text{sea-salt}_c$	$\longrightarrow NO_{3,c}$	0.01
$HNO_{3\ (g)} + \text{dust}_c$	$\longrightarrow NO_{3,c}$	0.02
$HO_{2\ (g)} + PM_c$	$\longrightarrow \frac{1}{2} H_2O$	0.2
$O_{3\ (g)} + \text{dust}_c$	$\longrightarrow HO_2$	1.0×10^{-6}

Notes: $NO_{3,c}$ represents coarse mode nitrate. These uptake reactions are applied whenever RH exceeds 40 %.

Options for N2O5 hyrolysis

- N2O5 + H2O -> 2 HNO3
- Important loss of Nx in troposphere!

- In config_emep.nml
  - USES %n2O5hydrolysis = **'SmixTen'**

- Options:
  - Smix

$$\gamma = f_{SIA}\gamma_{SIA} + f_{OM}\gamma_{OM} + f_{ss}\gamma_{ss} + f_{du}\gamma_{du}$$

  - **SmixTen = Smix/1**0
  - Gamma:0.002

- These rates are **very** uncertain and will likely be revised in future. Feel free to test

Miscellaneous 1: Mass balance

- Please check : fracmass in RunLog

```
++++++++++++++++++++++++++++++++++++++++++++++++++
Mass balance   1    Sulphur
++++++++++++++++++++++++++++++++++++++++++++++++++
                sumint      summas     fluxout      fluxin    fracmass
 Sulphur   3.4648E+07  4.2275E+07  5.2910E+09  3.6425E+09  1.0117E+00
     ifam       totddep       totwdep          totem
        1     1.795E+09     4.573E+09     7.888E+09
++++++++++++++++++++++++++++++++++++++++++++++++++
Mass balance   2    Nitrogen
++++++++++++++++++++++++++++++++++++++++++++++++++
                sumint      summas     fluxout      fluxin    fracmass
 Nitrogen  7.3405E+07  1.3389E+08  1.1912E+10  8.8174E+09  1.0078E+00
     ifam       totddep       totwdep          totem
        2     5.729E+09     1.245E+10     2.110E+10
++++++++++++++++++++++++++++++++++++++++++++++++++
Mass balance   3    Carbon
++++++++++++++++++++++++++++++++++++++++++++++++++
                sumint      summas     fluxout      fluxin    fracmass
 Carbon    3.7819E+11  3.7403E+11  4.5251E+13  4.5136E+13  1.0004E+00
     ifam       totddep       totwdep          totem
        3     4.346E+09     1.018E+10     1.080E+11
++++++++++++++++++++++++++++++++++++++++++++++++++
```

Miscellaneous 2: GenChem

- A note on GenChem
- Pre-processor
  - Reads ascii chemical equations and description files
  - Produced all CM_ files
- 2013 statement: Needs code-clean and documentation before release. Will try to do in 2013…
- 2015 status: Code was 'cleaned' – converted to python for ESX model. Needs to be re-implemented in EMEP and documented (still!)

- GenChem input

```
1.40e-12*exp(-1310*tinv)      NO + O3 = NO2 ;
KMT07                         OH + NO = HONO ;
3.60e-12*exp(270*tinv)        HO2 + NO = OH + NO2 ;
1.80e-11*exp(110*tinv)        NO + NO3 = 2.000 NO2 ;
1.40e-13*exp(-2470*tinv)      NO2 + O3 = NO3 ;
KMT08                         OH + NO2 = HNO3 ;
KMT09                         HO2 + NO2 = HO2NO2 ;
KMT10                         HO2NO2 = HO2 + NO2 ;
3.20e-13*exp(690*tinv)        OH + HO2NO2 = NO2 ;
4.50e-14*exp(-1260*tinv)      NO2 + NO3 = NO + NO2 ;
KMT03                         NO2 + NO3 = N2O5 ;
KMT04                         N2O5 = NO2 + NO3 ;
2.00e-11                      NO3 + OH = HO2 + NO2 ;
........
```

Miscellaneous 3: Chemical schemes

- Have several mechanisms ready processed (almost):

Mechanism	Species	Reactions	Photochemical Reactions	Emitted VOCs (No. Biogenic)	Ref.
CRI v2	465	1202	185	116 (3)	Jenkin et al. (2008)
CRI v2 R5	195	569	96	3 (3)	Watson et al. (2008)
CBM-IV	38	95	13	10 (1)	Gery et al. (1989)
CB-05	70	189	27	16 (2)	Yarwood et al. (2005)
OSRM	70	197	25	15 (1)	Hayman et al. (2010)
EMEP-EmChem03[a]	69	135		10 (1)	Simpson et al. (2003a), Andersson-Sköld and Simpson (1999)
EMEP-EmChem09[a]	72	137	26	10 (1)	This work
EMEP-EmChem09soa	[b]	[b]	26	11 (2)	Bergström et al. (2012)[c]

Miscellaneous 4: odds n' ends

- The model has some 'untried' components
- ISORROPIA instead of MARS/EQSAM
- PointSource_ml
  - Allows stacks, plume rise, gaussian spread (in vertical)
  - (cooperation with NILU/M. Karl)
  - 'probably works' but not 100% integrated in mass budget
- Use at own risk! Please ask!

Papers: chemistry in EMEP model....

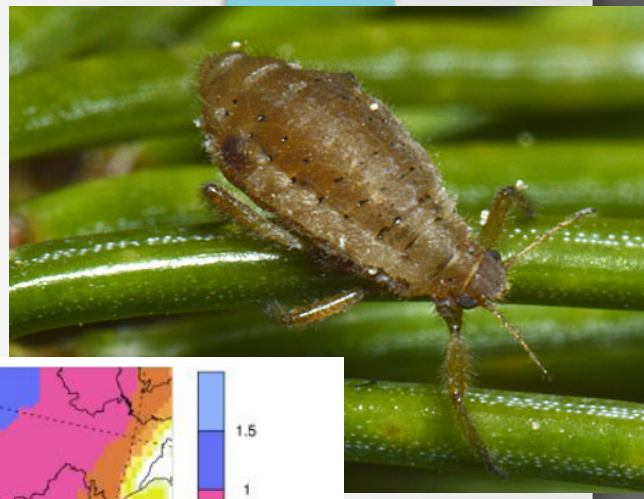
- **Eliassen, A.; Hov, Ø., et al. A Lagrangian long-range transport model with atmospheric boundary layer chemistry J. Appl. Met., 1982, 21, 1645-1661**
- Hov,Ø. Models of the chemical turnover in the atmospheric boundary layer, PhD, University of Oslo, 1981
- Isaksen, I. & Hov,Ø. Calculation of trends in the tropospheric concentration of O3, OH, CO, CH4 and NOx Tellus, 1987, 39B, 271-285
- Simpson, D. Long period modelling of photochemical oxidants in Europe. Calculations for July 1985 Atmos. Environ., 1992, 26A, 1609-1634
- Simpson, D.; Andersson-Sköld, Y. & Jenkin, M. E. Updating the chemical scheme for the EMEP MSC-W oxidant model : current status The Norwegian Meteorological Institute, Oslo, Norway, 1993
- Simpson, D. Biogenic emissions in Europe 2: Implications for ozone control strategies J. Geophys. Res., 1995, 100, 22891-22906
- Kuhn, M.; et al., Intercomparison of the gas-phase chemistry in several chemistry and transport models Atm. Env., 1998, 32, 693-709
- Jonson, J.; et al., Chemical effects of UV fluctuations inferred from total ozone and tropospheric aerosol variations J. Geophys. Res., 2000, 105, 14561-14574B
- Andersson-Sköld, Y. & Simpson, D. Comparison of the chemical schemes of the EMEP MSC-W and the IVL photochemical trajectory models Atm. Env., 1999, 33, 1111-1129
- Simpson, D.; et al., The EMEP MSC-W chemical transport model -- technical description Atmos. Chem. Physics, 2012, 12, 7825-7865

And SOA:

- Andersson-Sköld, Y. & Simpson, D. Secondary organic aerosol formation in Northern Europe: a model study J. Geophys. Res., 2001, 106, 7357-7374
- Simpson, D.; Yttri, K.; Klimont, Z.; Kupiainen, K.; Caseiro, A.; Gelencsér, A.; Pio, C. & Legrand, M. Modeling Carbonaceous Aerosol over Europe. Analysis of the CARBOSOL and EMEP EC/OC campaigns J. Geophys. Res., 2007, 112, D23S14
- Simpson, D.; et al., Modelling SOA in EMEP: Experiments with the VBS Approach Transboundary Particulate Matter in Europe, Status Report 4/2004, The Norwegian Institute for Air Research (NILU), Kjeller, Norway, 2009
- Bergström, R.; et al., Modelling of organic aerosols over Europe (2002--2007) using a volatility basis set (VBS) framework: application of different assumptions regarding the formation of secondary organic aerosol Atmos. Chem. Physics, 2012, 12, 8499-8527
- Bergström, R.; Hallquist, M.; Simpson, D.; Wildt, J. & Mentel, T. F. Biotic stress: a significant contributor to organic aerosol in Europe? Atmospheric Chemistry and Physics, 2014, 14, 13643-13660

We 'bugged' the EMEP model ;-)

- Bergström et al, ACP, 2014.
- - unplanned' cooperation with Thomas Mentel, arising from a breakfast chat in earlier ECLAIRE meeting.
- - mixed models, smog-chambers and
- statistics on honey production



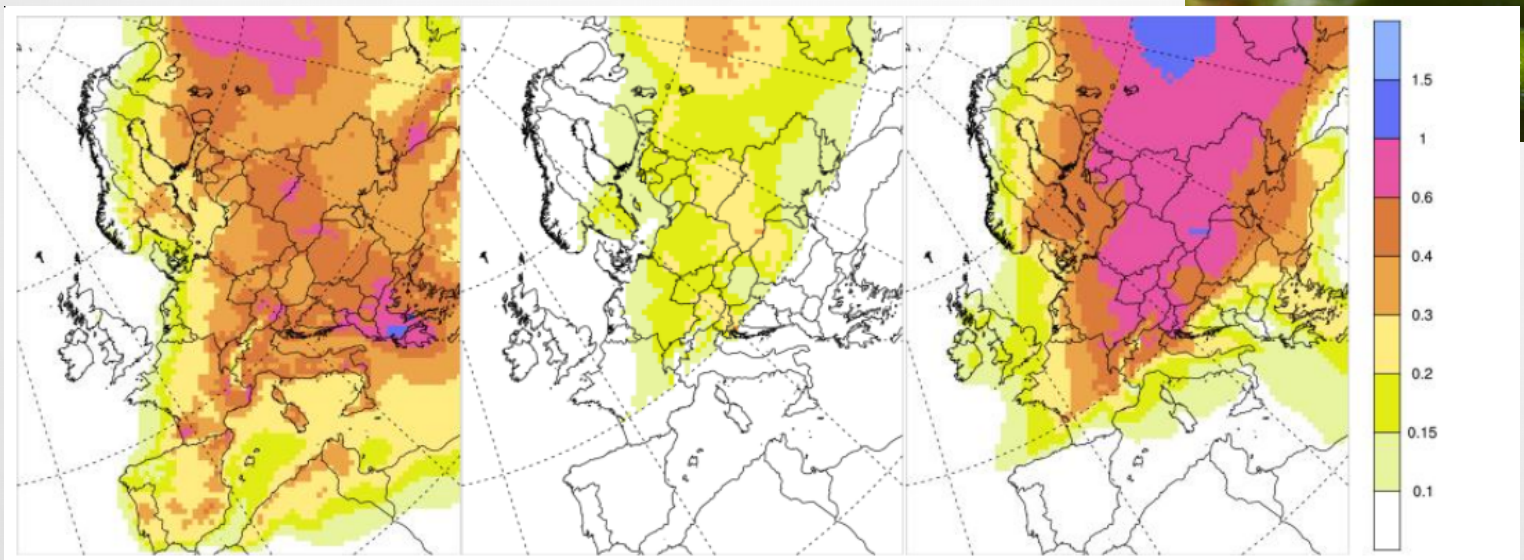


Figure SIE1. Model calculated 6-month mean (Apr-Sep) concentrations of biogenic SOA and biotic stress-induced OA (SIE-OA); **(a)** BSOA from constitutive emissions (reference simulation, Case 0), **(b)** SIE-OA in Case 1 (biotic stress with sesquiterpene (SQT) emissions), **(c)** SIE-OA in Case 2 (biotic stress with emissions of SQT and methyl salicylate). Unit: μg m^{-3}.

Almost final...

- The chemical schemes are getting more and more complex, e.g. SOA, aerosol schemes
- Difficult to summarise or address all issues related to EMEP model
- If interested in e.g. OA, or GenChem:
  - Please ask !


The end :-)