Heterogeneous chemistry - how to get from the literature to UKCA model treatment

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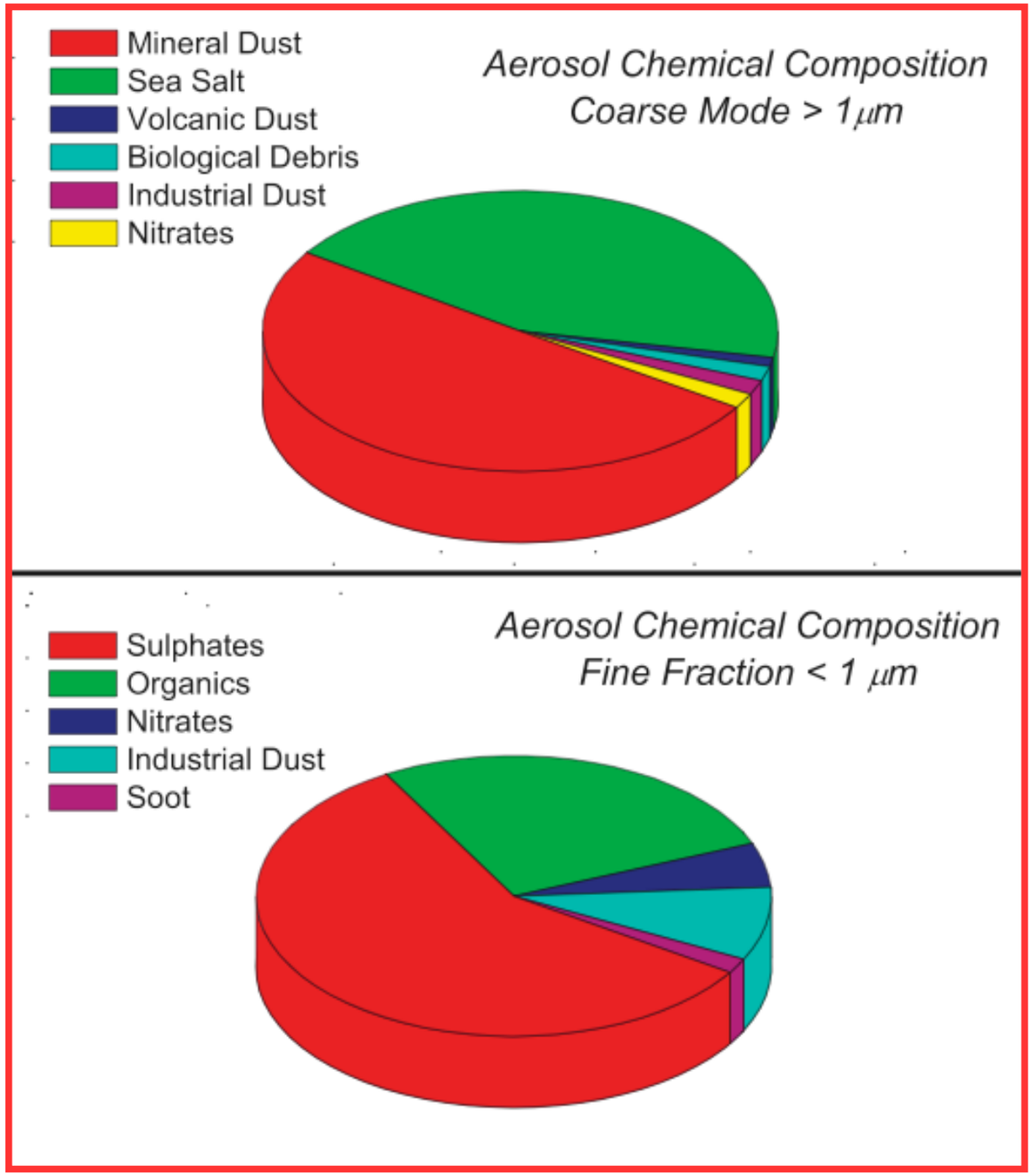
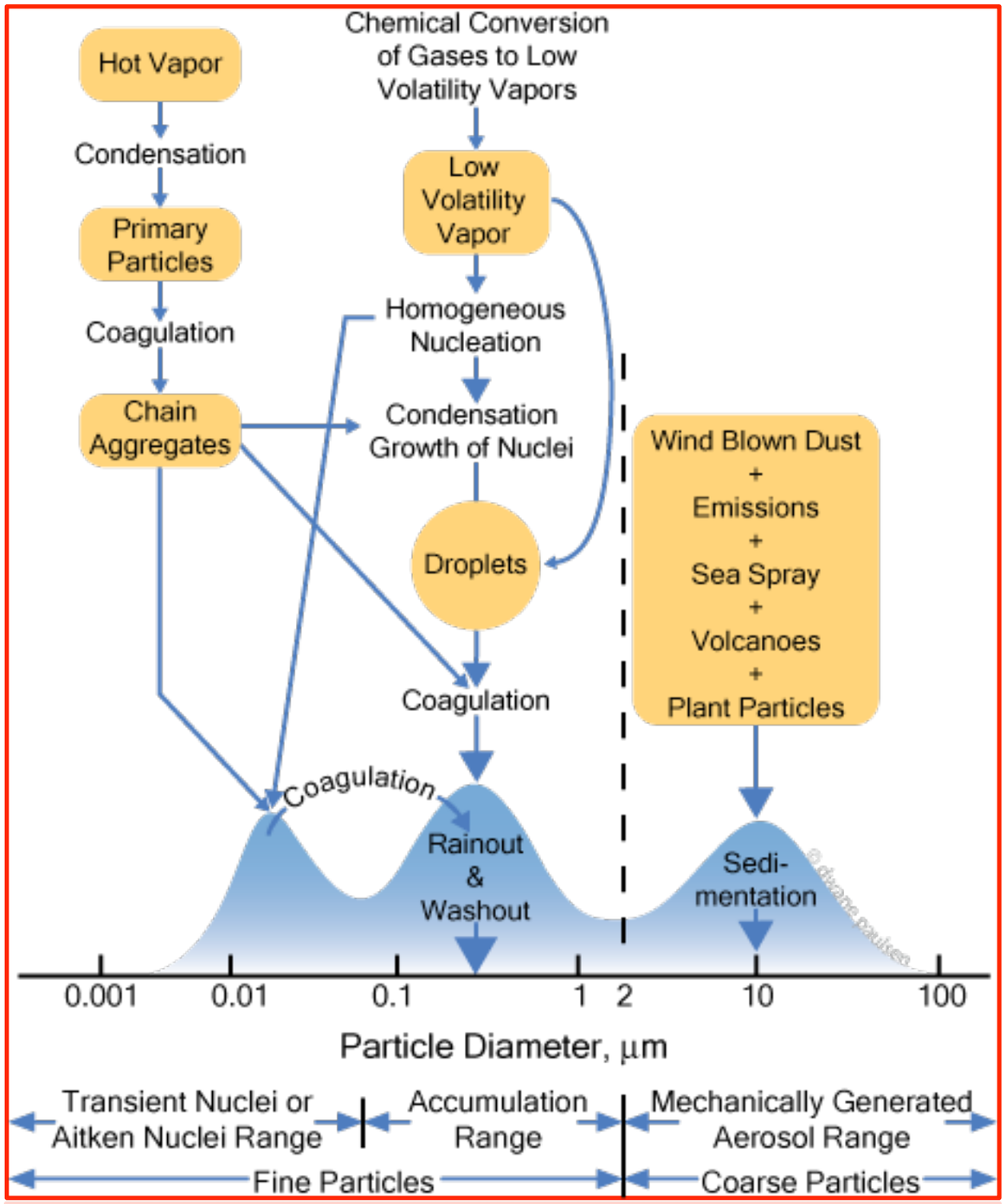
Chemical composition of tropospheric aerosol

- The particulate matter in the atmosphere is very diverse.
- Wide variety of primary sources - dust and sea salt are the strongest by mass.
- Chemical transformation of pollutants occurs within the atmosphere, and can lead to aerosol formation.
- $NO_x \rightarrow HNO_3 \rightarrow$ aerosol nitrate
- $SO_2 \rightarrow H_2SO_4 \rightarrow$ aerosol sulfate
- VOC → organics (carbon-rich)

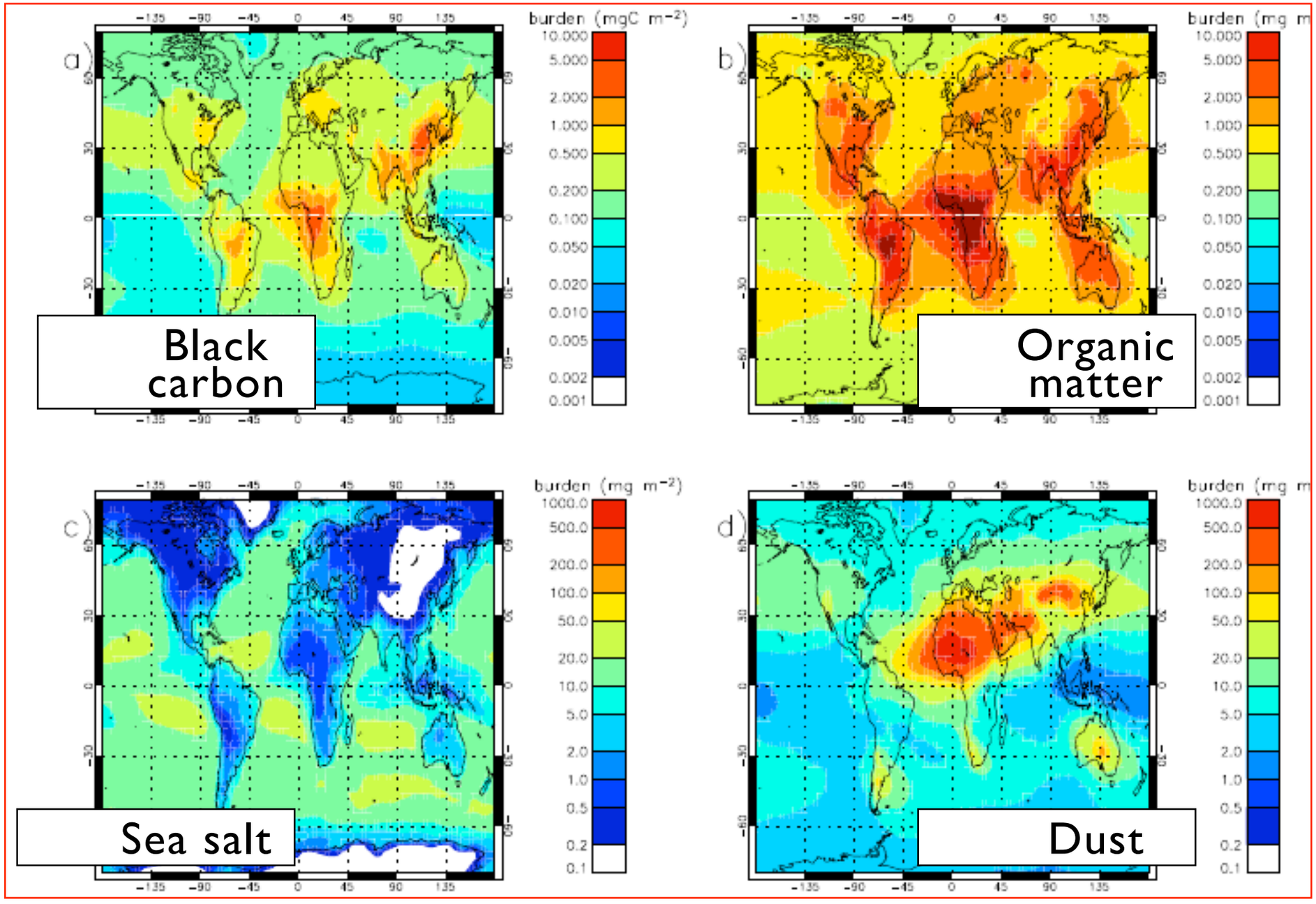


Size range spanned by atmospheric aerosol

- Sizes range from few nm up to hundreds of microns.
- The lifetime of small and large particles is short, but between 100nm and 2 μm, the lifetime can be up to a couple of weeks.
- Dust can be transported across oceans, volcanic aerosol can survive in the stratosphere for years.
- The integrated impact can be large.

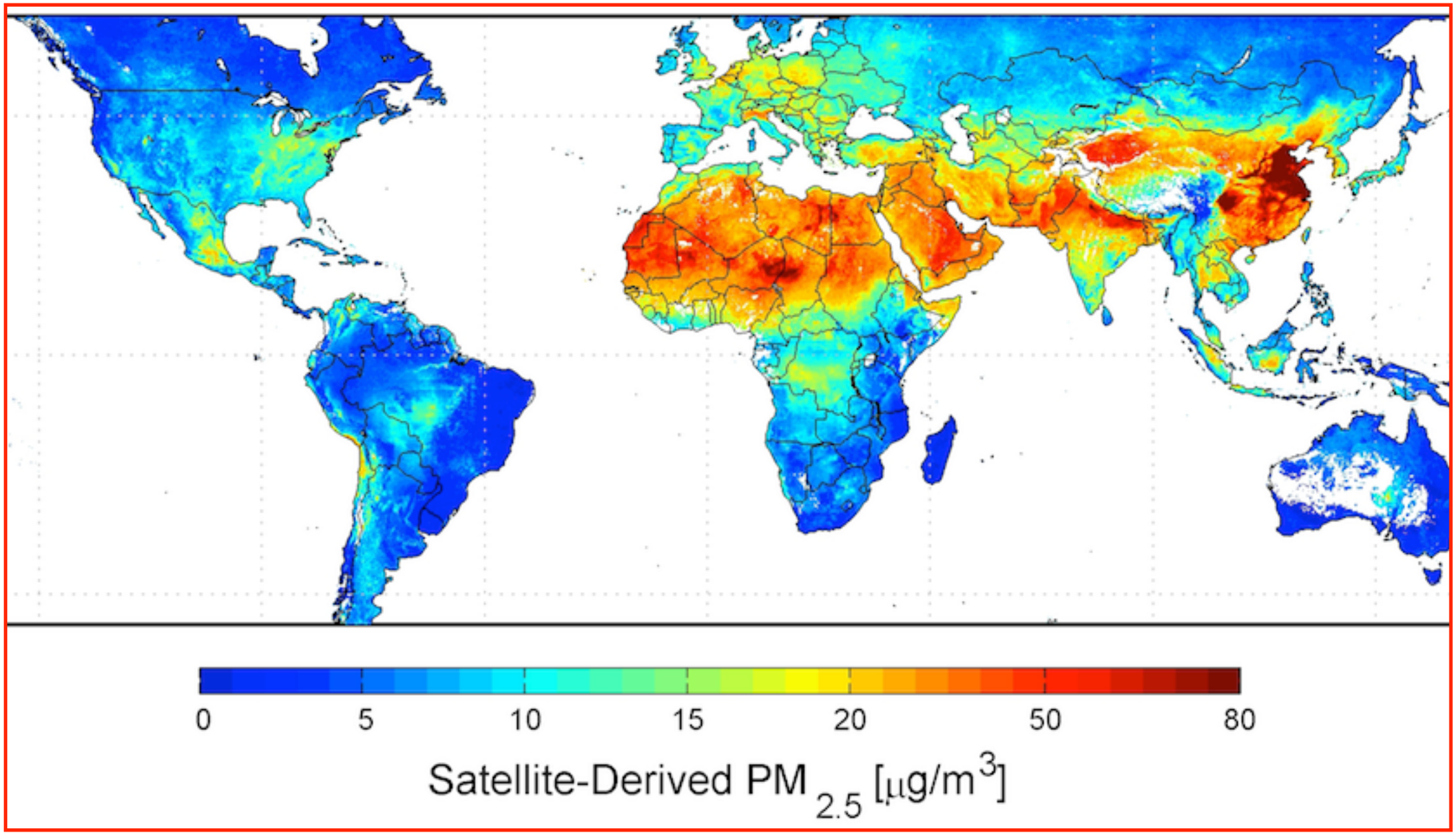


Current work - aerosol chemistry on a global scale



This aerosol model runs within the UK Met Office ‘Unified’ Climate Model.

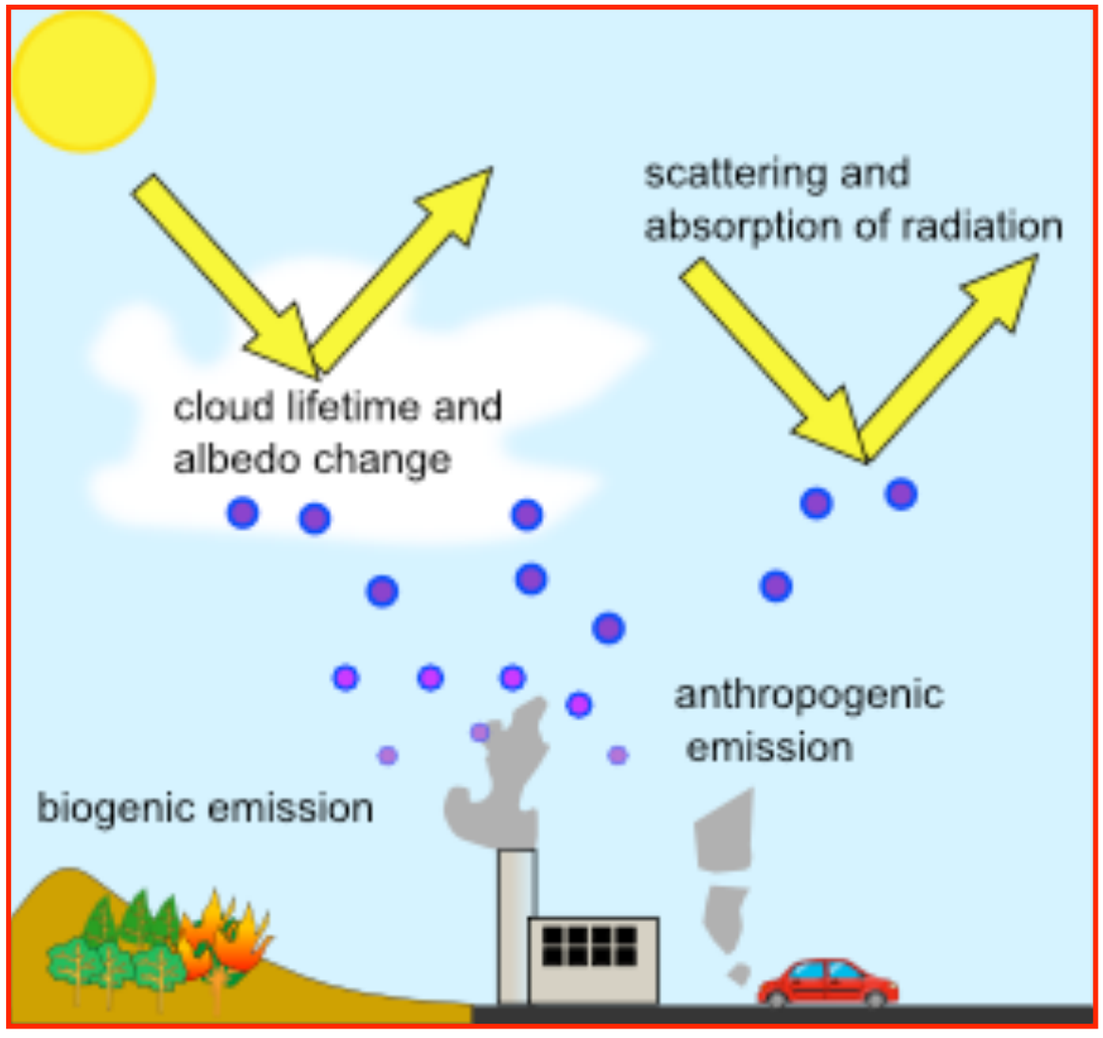
Global near-surface distribution of aerosol



Total (mass) particulate matter is shown (NB no measurements over oceans)

Aerosols and the chemistry of the troposphere

- Anthropogenic pollutants are degraded by the action of sunlight in the atmosphere to form aerosol.
- Absorption and scattering by the aerosol then change the amount of incident sunlight - local climate different in the neighbourhood of the emissions.
- Also changes the rate of degradation - a feedback loop is established.



Coupling between aerosol and oxidation

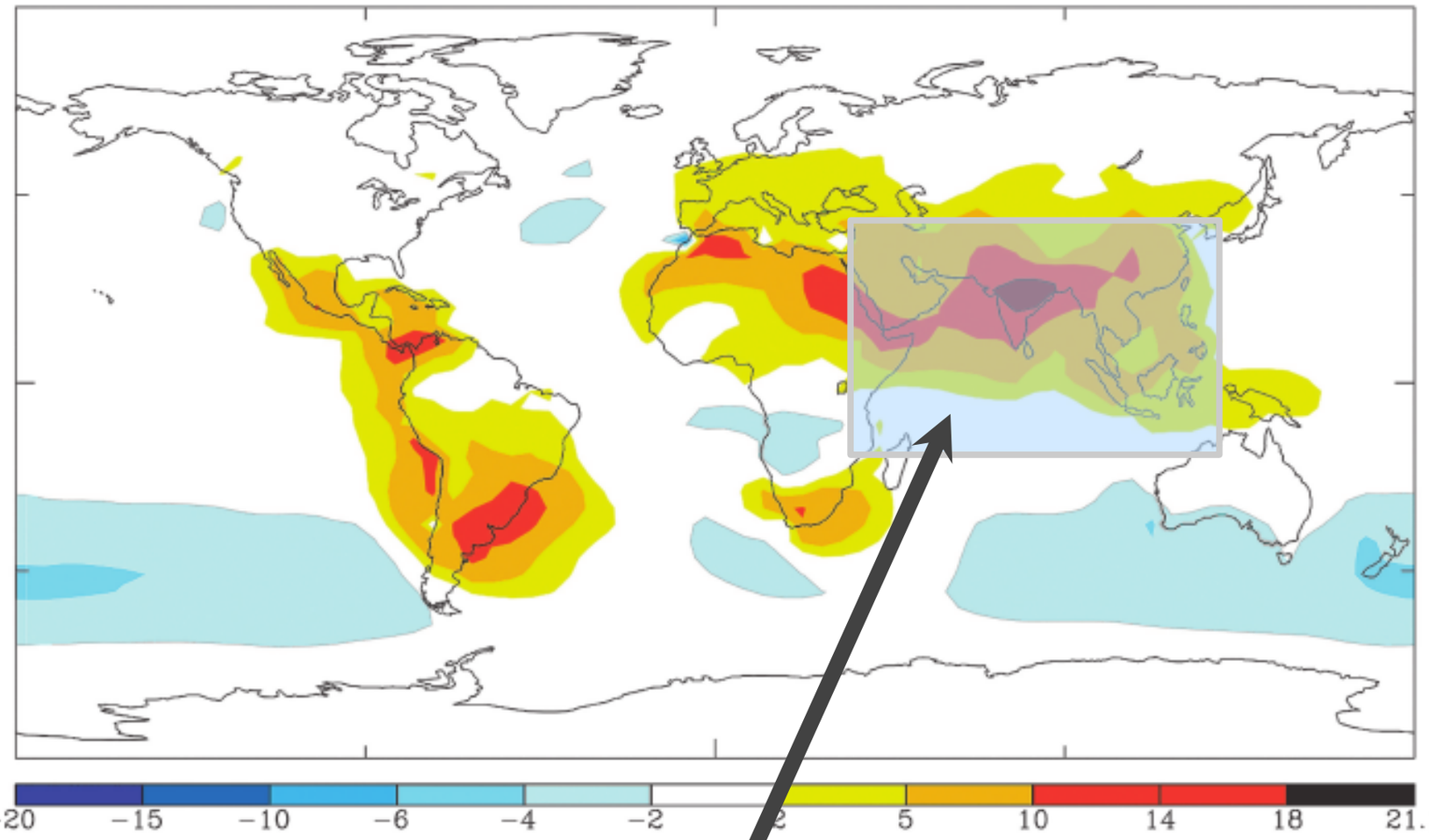


Fig. 1. Percentage difference in surface sulfate mixing ratio between future control simulation (2030C) and sensitivity simulation with future SO_2 emissions but present-day O_3 precursor emissions (2030SO_4) [i.e., 100 × (2030C − 2030SO_4)/2030C].

Regional variations in impact: higher future NOx emissions lead to large increase in [OH], more OH+SO_2, more sulfate. More aerosol means a decrease in solar radiation, moderating climate change.

Aerosols and their effect on ozone

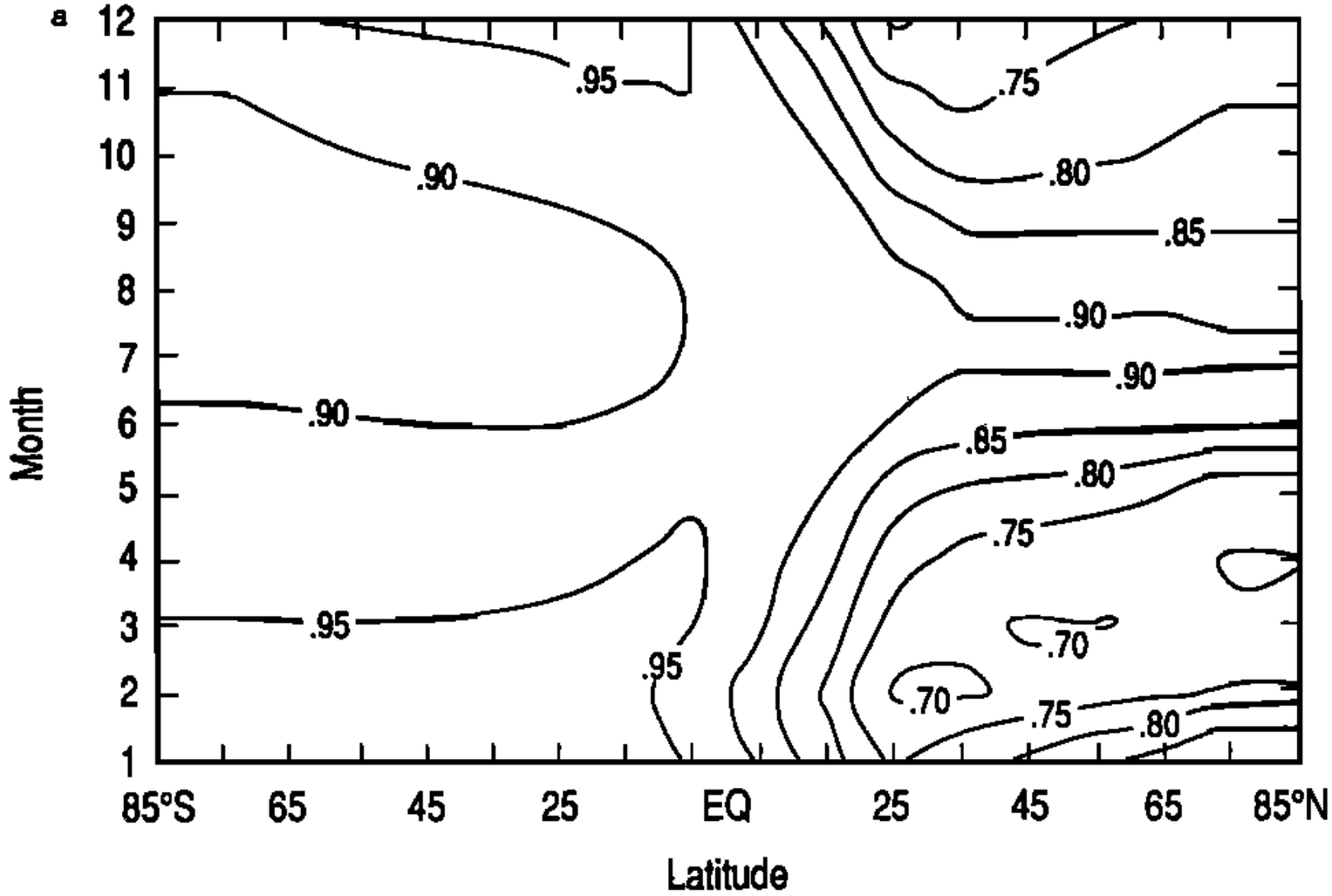


Fig. 9 from Dentener and Crutzen, 1993. The zonal mean monthly average ratio of O3 concentrations with aerosol reactions to those without for all months at 1000 hPa

Particulate matter in the atmosphere

- Serve as the germ or nucleus for cloud formation.
- Scatter incoming solar radiation (reduce heating at the surface).
- Absorb outgoing radiation (increase strength of greenhouse effect).
- Remove (and transform) trace gases and pollutants.
- Health effects

Chemical effects of particles in the atmosphere

- Partitioning to the aqueous phase - solubility controlled
- Adsorption onto solid surfaces
- Reactive uptake of trace gases
- Release of trace gases following reactive uptake

- Aerosols may enhance concentration and so open up new pathways of reactivity.

Prognostic equation for reaction of aerosol with gas X

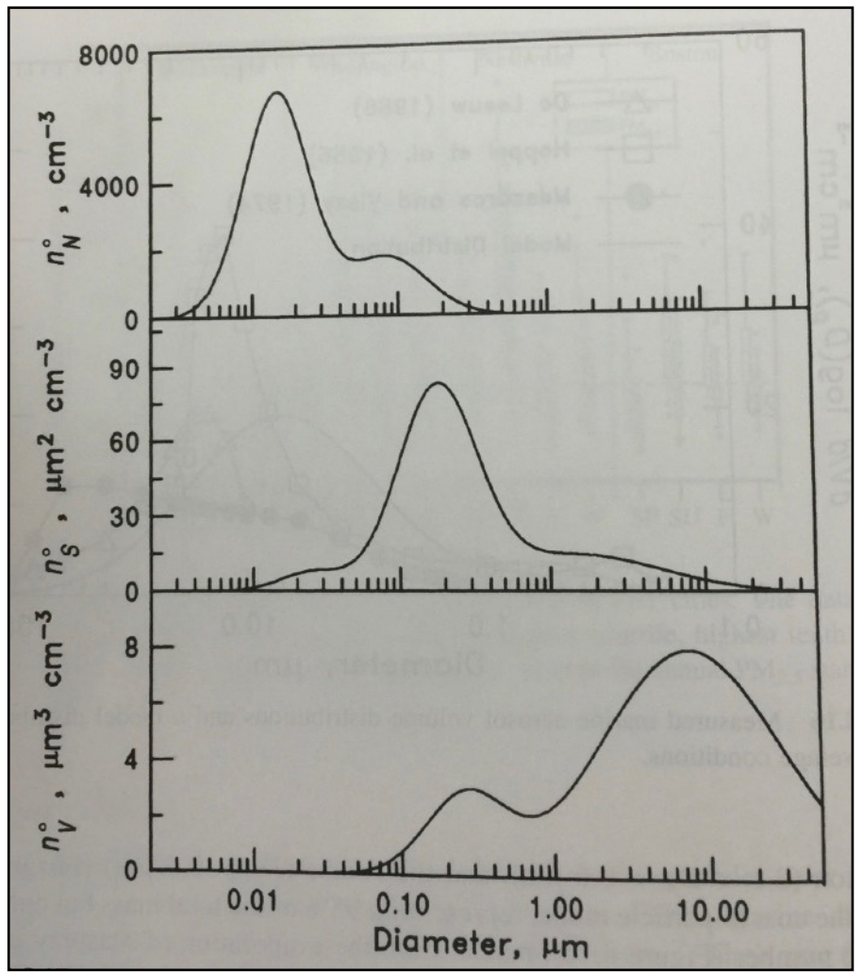
$$\frac{d[X]}{dt} = -k_{het}[X] \qquad c = \sqrt{\frac{8kT}{\pi m}}$$

$$k_{het} = \gamma S_a c/4$$

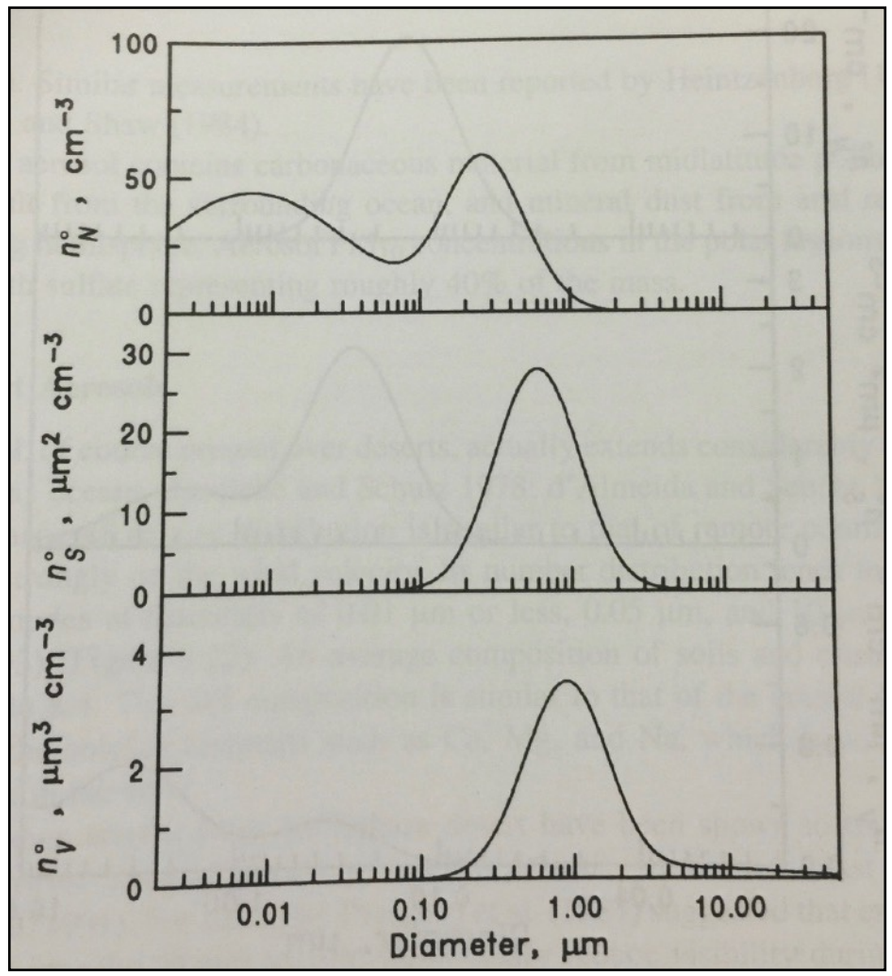
- Parameterise reaction/uptake via uptake coefficient, γ, $(0 < \gamma \leq 1)$
- Represents the probability that the gas phase species X is lost per collision with the aerosol surface.
- Make sure units of surface area density ($m^2\ m^{-3}$) and c (mean molecular speed of gas phase X, ms^{-1}) match.
- E.g. typical units of SA density - $\mu m^2\ m^{-3}$

Representative aerosol number, SA and mass distributions

Rural continental

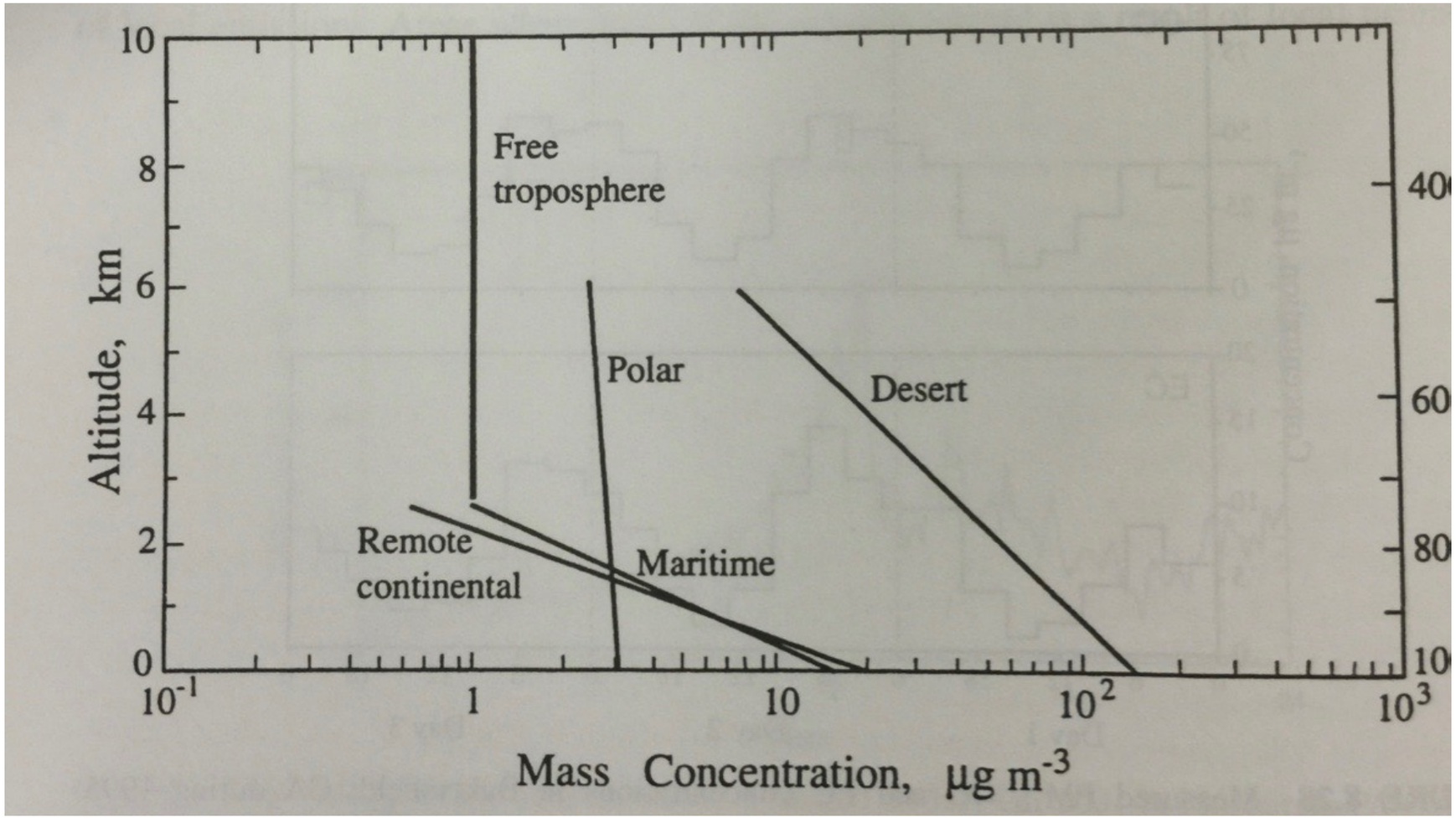


Free troposphere



Maximum of aerosol surface area density is in the accumulation mode

Tropospheric profile of aerosol mass



Figures taken from Seinfeld and Pandis, p. 375

Kinetics of removal of trace gases

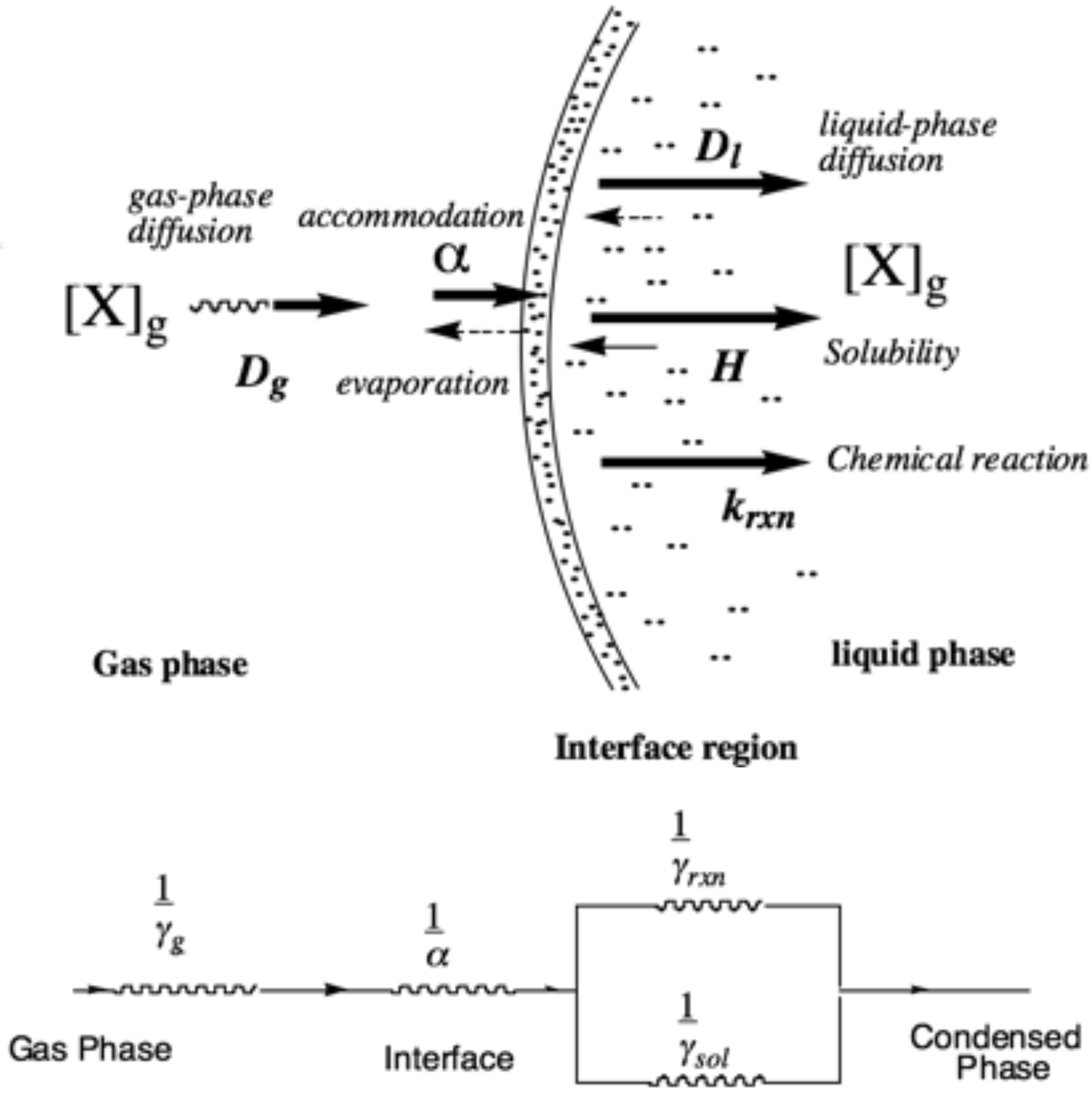
$$\frac{d[X]}{dt} = -k_{het}[X]$$

$$k_{het} = \gamma S_a c/4$$

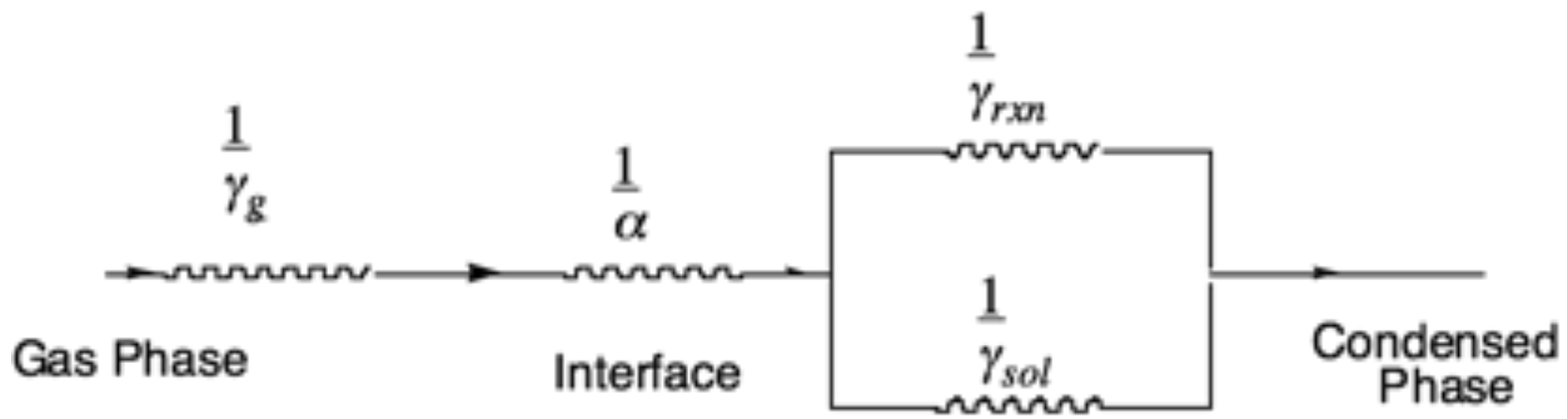
$$c = \sqrt{\frac{8kT}{\pi m}}$$

- The uptake coefficient, γ, contains the physical chemistry that you need to think about.
- This is generally what the experimentalists report.
- Tempting just to take the number from the paper and put it into the model, but there's usually scope to add a bit of value.
- The resistor framework provides the best way currently to do this, although there are other modelling frameworks available - e.g. Shiraiwa (PRA framework).

Trace gas uptake by liquids – a series of coupled steps



Trace gas uptake as a series of coupled steps



$$\frac{1}{\gamma} = \frac{1}{\gamma_g} + \frac{1}{\alpha} + \frac{1}{\gamma_{sol} + \gamma_{rxn}}$$

- The value of gamma can be set by any one of these processes.
- smallest $\gamma \Rightarrow 1/\gamma$ dominates sum - pays to identify the slowest step!
- If no reaction($\gamma_{rxn} = 0$) , then expect the aerosol to become saturated in the trace gas of interest. Over time, the net uptake will reduce to zero.

Trace gas uptake as a series of coupled steps

$$\frac{1}{\gamma} = \frac{1}{\gamma_g} + \frac{1}{\alpha} + \frac{1}{\gamma_{sol} + \gamma_{rxn}}$$

- γ_g represents the modification to the collision frequency (and uptake rate) if the particle is large or diffusion is slow to the particle surface. Depends of particle radius,r, and D_g, gas phase diffusion coefficient

$$\frac{1}{\gamma_g} = \frac{cr}{4D_g}$$

- α is the probability that having collided with the particle surface, the molecule X enters or sticks to the aerosol (NB one way). This can be the smallest probability for solid particles for which this probability is low and so this may control gamma.

- Conversely, when reaction is very fast (γ_{rxn} is large) the accommodation step may again be the slowest step and control γ (so-called 'accommodation-controlled uptake')

Trace gas uptake as a series of coupled steps

$$\frac{1}{\gamma} = \frac{1}{\gamma_g} + \frac{1}{\alpha} + \frac{1}{\gamma_{sol} + \gamma_{rxn}}$$

- γ_{sol} represents the uptake due to the equilibration of the condensed and gas phases
  - establishing a Henry's law equilibrium at which uptake and evaporation are equal
  - net uptake at this point is zero.

- Key points: that solubility is composition dependent - e.g. solubility of SO_2 increases in acidic aerosol; aerosol has probably equilibrated in a UKCA timestep.

$$\frac{1}{\gamma_{sol}} = \frac{\sqrt{\pi}c}{4HRT}\left(\frac{t}{D_l}\right)^{1/2}$$

- Fraction of gas X in aqueous phase can be calculated as

$$\frac{[X_{aq}]}{[X]} = 10^{-6}HRTL$$

Trace gas uptake as a series of coupled steps

$$\frac{1}{\gamma} = \frac{1}{\gamma_g} + \frac{1}{\alpha} + \frac{1}{\gamma_{sol} + \gamma_{rxn}}$$

- γ_{rxn} represents the uptake due to reaction within the aerosol volume.
- Key points: is composition dependent - N_2O_5 onto sulphate (fast) vs nitrate (slow); HO_2 onto organic aerosol; O_3 uptake by SOA. Most general form (rarely used)

$$\frac{1}{\gamma_{rxn}} = \frac{c}{4HRT\sqrt{D_l k_{rxn}}}\left(\coth q - \frac{1}{q}\right)$$

- krxn is the first-order (s^{-1}) rate constant for loss of X in solution; q is the ratio of particle radius to reacto-diffusive length, l.

$$q = \frac{r}{l} \qquad\qquad l = \sqrt{\frac{D_l}{k_{rxn}}}$$

Uptake onto solid surfaces

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{1}{\gamma_s}$$

- Here reaction is between a surface site or surface bound molecule
- Two limiting cases - Langmuir-Hinshelwood (most common by far) or Eley-Rideal
- For Langmuir-Hinshelwood, the reaction is between gas-phase X and a surface-bound molecule Y (here Y_s). Need info on concentration of Y and on partitioning at equilibrium between X and surface-bound X, given by K and N.

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{c(1 + K[X])}{4k_{rxn}[Y_s]KN}$$

- For more information see the IUPAC website, http://iupac.pole-ether.fr/htdocs/supp_info/NewHetIntroOct2009.pdf

Back of the envelope

- Need a representative surface area density (or range)
- And a gamma (or range of gammas)
- Then calculate k_{het} for the trace gas of interest
- Compare with other relevant rates e.g. reaction with O_3, dry deposition, wet removal, photolysis, ...
- Can also put into a box model and do an aerosol on/off experiment
  - E.g. KPP - http://people.cs.vt.edu/~asandu/Software/Kpp/
  - MECCA - http://www.rolf-sander.net/messy/mecca/mecca_box.html
  - DSMACC - https://github.com/barronh/DSMACC

Putting heterogeneous chemistry into UKCA

- Follow the tutorial for putting in a new chemical reaction.
- http://www.ukca.ac.uk/wiki/index.php/UKCA_Chemistry_and_Aerosol_vn10.9_Tutorial_6#Heterogeneous_Reactions

Heterogeneous Reactions

Heterogeneous reactions are those that occur on aerosol surfaces. There is no functional form defined for these reactions, with special code needed to be added for each case.

Heterogeneous Reaction Definition

The heterogeneous reactions are defined in the **`ukca_chem_master.F90`** module using the **`rath_t1`** Fortran type specification, usually in one array (**`rath_defs_master`**).

To format of this **`rath_t1`** type is

```
rath_t(N,'Reactant 1','Reactant 2','Product 1 ','Product 2 ','Product 3 ',&
'Product 4 ', Fraction of Product 1 produced, Fraction of Product 2 produced, Fraction of Product 3 produced,
Fraction of Product 4 produced,SCHEME,QUALIFIER,DISQUALIFIER,VN), &
```

i.e. there is no rate information provided. For reactions on PSCs special code has been added to the routines in **`ukca_hetero_mod.F90`**, and for other reactions there is code in **`asad_hetero.F90`**.

The settings for `N`, `SCHEME`, `QUALIFIER`, `DISQUALIFIER`, and `VN` are the same as in the adding new tracers tutorial, although here **`N`** should be incremented for each new **reaction**, where there might be the same reaction specified several times with changes to reaction rates or even species.

Examples of this type are

```
nrath_t1(2,'ClONO2    ','HCl       ','Cl        ','Cl        ','HONO2     ', &
'          ', 0.000, 0.000, 0.000, 0.000, S+ST,HP,0,107), &
!HSO3+H2O2(aq)
rath_t1(6,'SO2       ','H2O2      ','NULL0     ','          ','          ', &
'          ', 0.000, 0.000, 0.000, 0.000, TI+S+ST+OL+R,A,0,107),             &
```

To add new heterogeneous reactions you will need to append equivalent lines for the new reactions to the end of the array (increasing the array sizes accordingly), before adding code to either **`ukca_hetero_mod.F90`** (for stratospheric reactions) or **`asad_hetero.F90`** (for tropospheric reactions).

UKCA/ukca_chem_master.F90

```
64   ! Define chemistry types
65   INTEGER, PARAMETER :: ST  = 1   ! stratosphere-troposphere scheme
66   INTEGER, PARAMETER :: T   = 2   ! troposphere scheme
67   INTEGER, PARAMETER :: S   = 4   ! stratosphere scheme
68   INTEGER, PARAMETER :: R   = 8   ! RAQ scheme
69   INTEGER, PARAMETER :: OL  = 16  ! offline scheme
70   INTEGER, PARAMETER :: TI  = 32  ! troposphere-isoprene scheme
71
72   ! define qualifiers.
73   INTEGER, PARAMETER :: A  = 1          ! aerosol chemistry
74   INTEGER, PARAMETER :: TH = 2          ! tropospheric heterogeneous reactions
75   INTEGER, PARAMETER :: HP = 4          ! heterogeneous PSC chemistry
76   INTEGER, PARAMETER :: ES = 8          ! extended stratospheric reactions
```

```
381  ! Heterogeneous chemistry
382  ! Columns take the following meanings:
383  ! Item number, reactant1, reactant2, product1, product2, product3, product4,
384  ! unused x 3, chemistry scheme, qualifier, disqualifier, version
385  TYPE(rath_t1), PARAMETER :: rath_defs_master(1:n_het_master)=(/         &
386  rath_t1(1,'ClONO2    ','H2O       ','HOCl      ','HONO2     ','          ', &
387  '          ', 0.000, 0.000, 0.000, 0.000, S+ST,HP,0,107), &
388  rath_t1(2,'ClONO2    ','HCl       ','Cl        ','Cl        ','HONO2     ', &
389  '          ', 0.000, 0.000, 0.000, 0.000, S+ST,HP,0,107), &
390  rath_t1(3,'HOCl      ','HCl       ','Cl        ','Cl        ','H2O       ', &
391  '          ', 0.000, 0.000, 0.000, 0.0
392  rath_t1(4,'N2O5      ','H2O       ','H
393  '          ', 0.000, 0.000, 0.000, 0.0
394  rath_t1(5,'N2O5      ','HCl       ','C
395  '          ', 0.000, 0.000, 0.000, 0.0
```

```
410  ! Tropospheric heterogenous reactions
411  rath_t1(9,'N2O5      ','          ','HONO2     ','          ','          ', &
412  '          ', 2.000, 0.000, 0.000, 0.000, TI+R,TH,0,107),                &
413  ! Heterogenous
414  rath_t1(10,'HO2       ','          ','H2O2      ','          ','          ', &
415  '          ', 0.500, 0.000, 0.000, 0.000, TI,TH,0,107)  /)
```

Stratospheric aerosol chemistry – slightly different

UKCA/ukca_hetero_mod.F90

```
501   REAL, INTENT(IN)  :: sasa(kchmlev)
502   REAL, INTENT(IN)  :: thcl(kchmlev)
503   REAL, INTENT(IN)  :: th2o(kchmlev)
504   REAL, INTENT(IN)  :: tcnit(kchmlev)
505   REAL, INTENT(IN)  :: tn2o5(kchmlev)
506   REAL, INTENT(IN)  :: thocl(kchmlev)
507
```

```
125   REAL :: psc2(n_points)
126   REAL :: psc3(n_points)
127   REAL :: psc4(n_points)
128   REAL :: psc5(n_points)
129   REAL :: hk(n_points,5)
```

```
405   ! ##################################################################
406   SUBROUTINE ukca_calckpsc(sasa,t,th2o,thcl,tcnit,tn2o5,thocl,      &
407                            akpsc1,akpsc2,akpsc3,akpsc4,akpsc5,       &
408                            lpsa,lphocl,lppsc,lpsimp,                 &
409                            kchmlev,kstart,kend,dt)
410   !
411   !     CALCKPSC - CALCULATION OF HETEROGENEOUS REACTION RATES
412   !
```

```
405  ! ##################################################################
406  SUBROUTINE ukca_calckpsc(sasa,t,th2o,thcl,tcnit,tn2o5,thocl,      &
407                           akpsc1,akpsc2,akpsc3,akpsc4,akpsc5,      &
408                           lpsa,lphocl,lppsc,lpsimp,                &
409                           kchmlev,kstart,kend,dt)
410  !
411  !     CALCKPSC - CALCULATION OF HETEROGENEOUS REACTION RATES
412  !
```

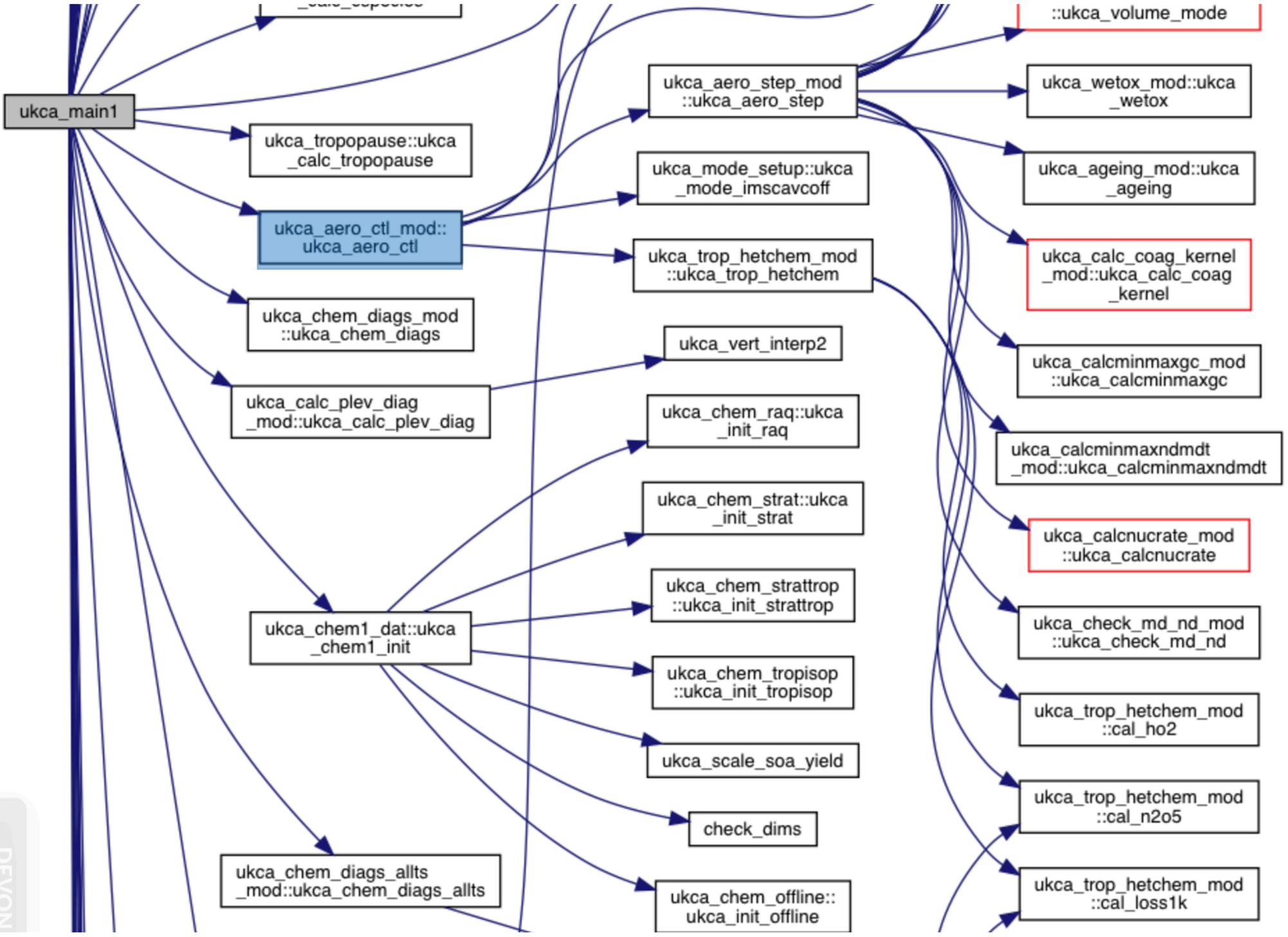
```
651       !
652       akpsc2(kstart:kend) = akpsc2(kstart:kend) +                &
653      ccnit(kstart:kend)*100.0*sasa(kstart:kend)*gam3b(kstart:kend)
654       akpsc3(kstart:kend) = akpsc3(kstart:kend) +                &
655       cn2o5(kstart:kend)*100.0*sasa(kstart:kend)*gam3c
```

```
256  WHERE ( zhcl > peps )
257    hk(:,2) = psc1 / zhcl
258    hk(:,3) = psc5 / zhcl
259    hk(:,5) = psc4 / zhcl
```

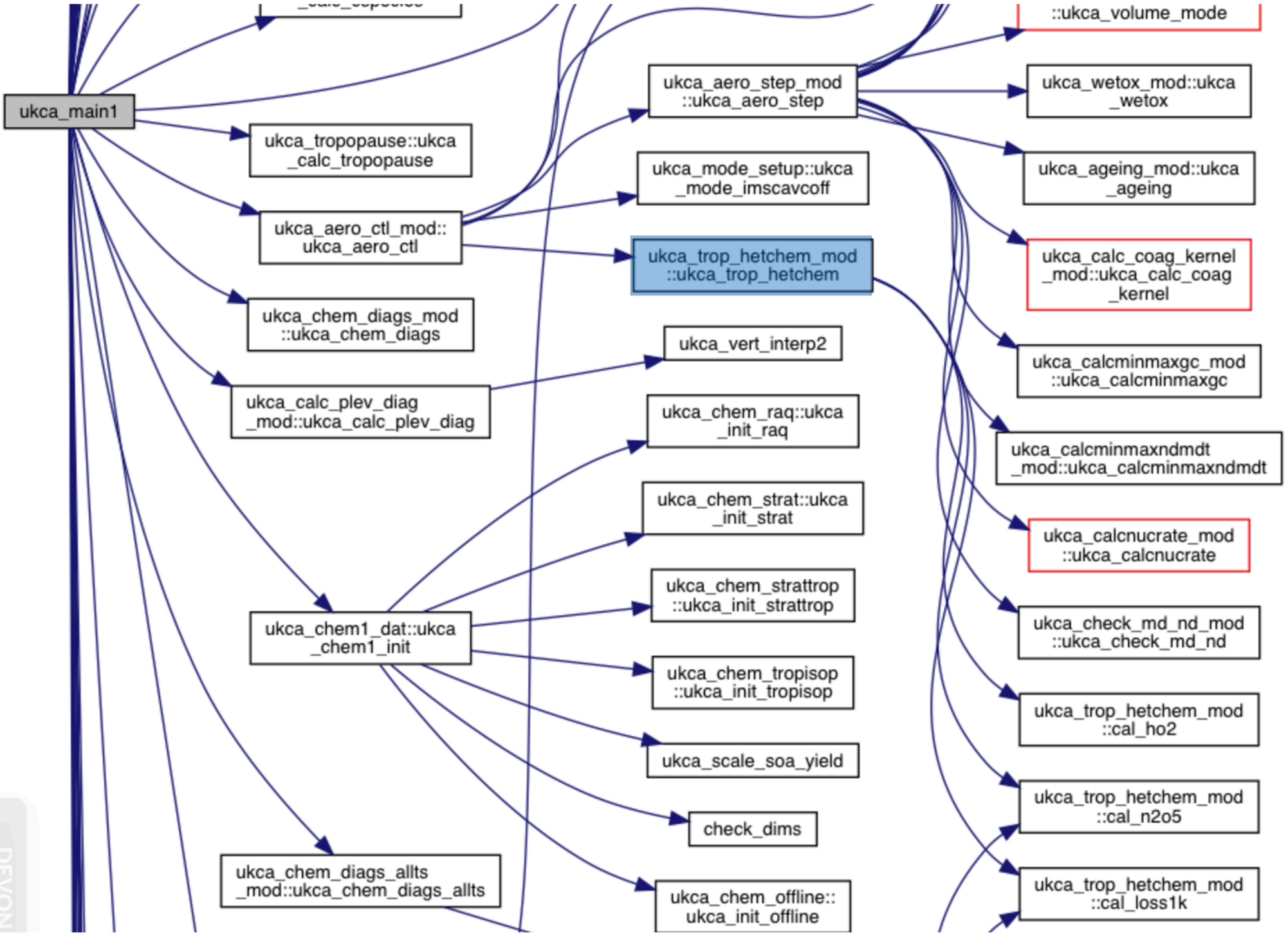
```
292  IF (n_hocl_hcl > 0) THEN
293    ! 3. HOCl + HCl --> Cl2 + H2O
294    rk(:,n_hocl_hcl) = hk(:,3)
295  END IF
```

The MODE aerosol chemistry – also slightly different

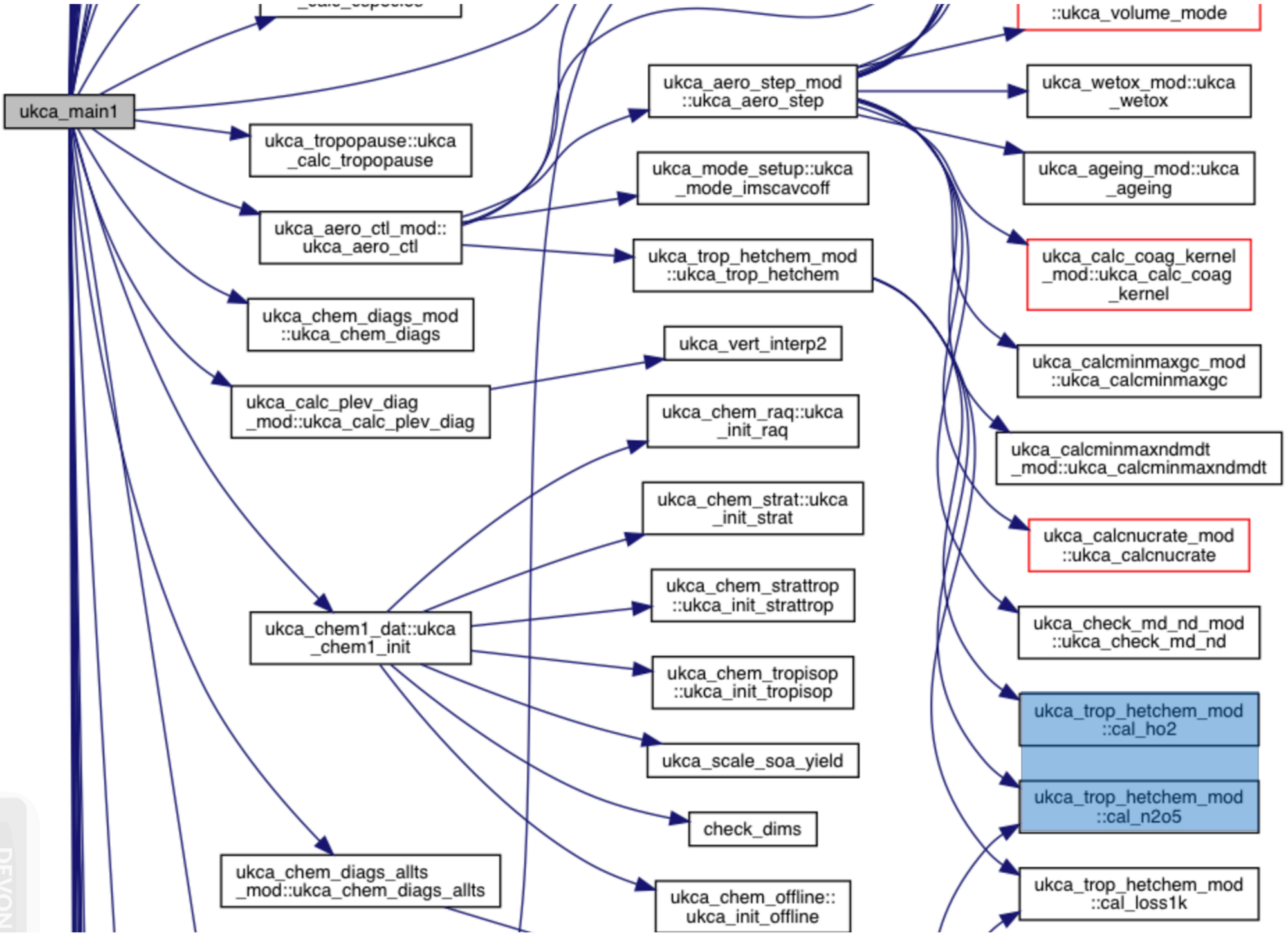
AERO_CTL calculates het rates using MODE aerosol



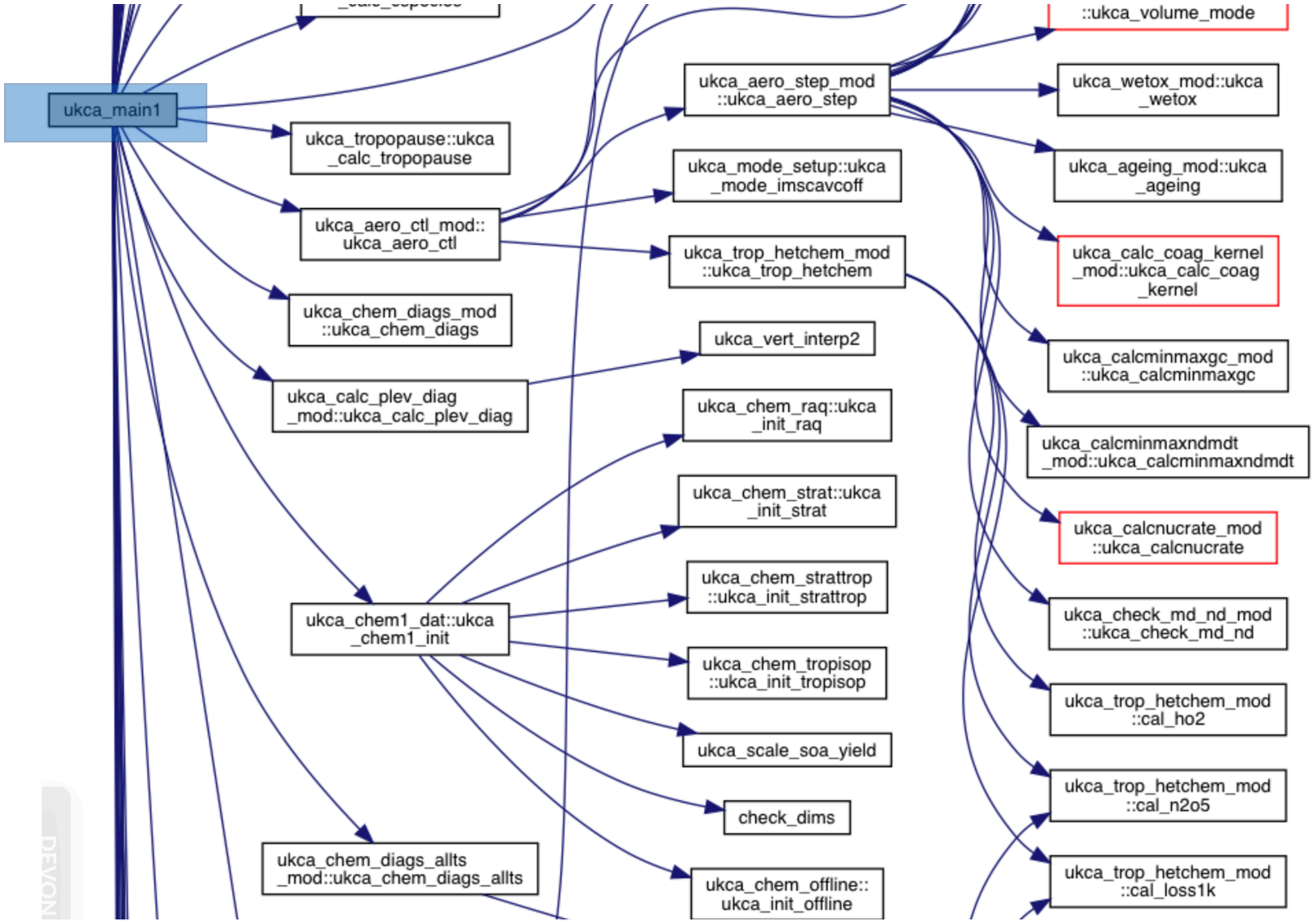
AERO_CTL calculates het rates using MODE aerosol



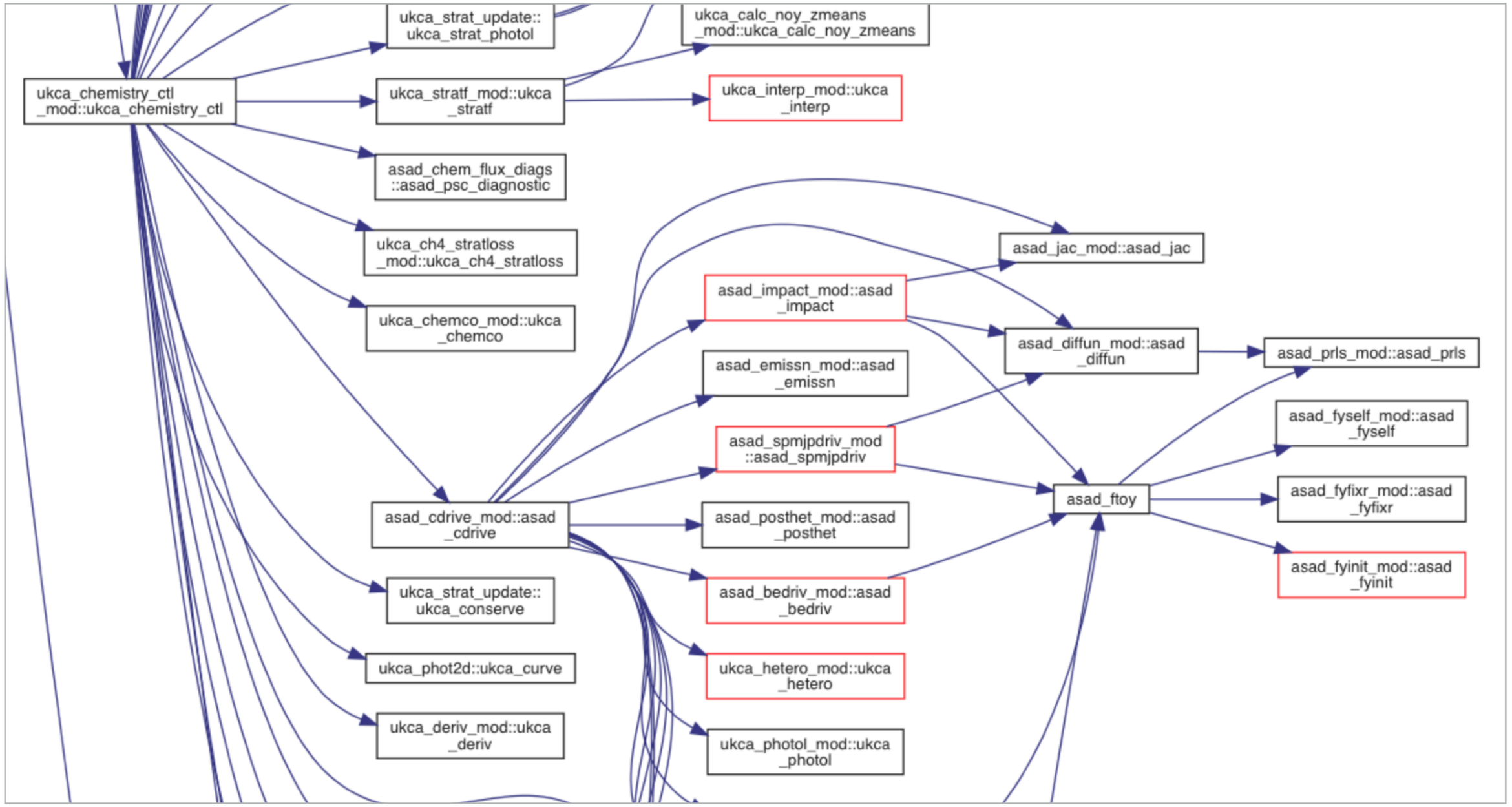
AERO_CTL calculates het rates using MODE aerosol



AERO_CTL calculates het rates using MODE aerosol



UKCA chemistry uses these rates in next timestep



Passing MODE heterogeneous rates into ASAD

UKCA/ukca_chem_master.F90

```
410   ! Tropospheric heterogenous reactions
411   rath_t1(9,'N2O5      ','          ','HONO2     ','          ', &
412   '          ', 2.000, 0.000, 0.000, 0.000, TI+R,TH,0,107),          &
413   ! Heterogenous
414   rath_t1(10,'HO2       ','          ','H2O2      ','          ', &
415   '          ', 0.500, 0.000, 0.000, 0.000, TI,TH,0,107)  /)
```

UKCA/ukca_chemistry_ctl.F90

```
649   !       Put pressure, temperature and tracer mmr into 1-D arrays
650   !       for use in ASAD chemical solver
651
652   zp(:) = RESHAPE(pres(:,:,k),(/theta_field_size/))
653   zt(:) = RESHAPE(temp(:,:,k),(/theta_field_size/))
```

```
737    ! tropospheric chemistry selected here. Use FAST-JX rates or previously
738    ! calculated 2-D rates.
739
740    IF (i_ukca_photol == i_ukca_fastjx) THEN
741      zprt = fastj_dj(:,:,k,:)
```

```
750    DO l=1,jppj
751      zprt1d(:,l) = RESHAPE(zprt(:,:,l),(/theta_field_size/))
752    END DO
753  END IF
```

UKCA/ukca_chemistry_ctl.F90

```
813     ! retrieve tropospheric heterogeneous rates from previous time step
814     ! for this model level (index k)
815     IF (L_ukca_trophet) THEN
816       ! N2O5
817       l = name2ntpindex(all_ntp, 'het_n2o5  ')
818       rc_het(:,1) = RESHAPE(all_ntp(l)%data_3d(:,:,k),            &
819                             (/theta_field_size/))
820       ! HO2+HO2
821       l = name2ntpindex(all_ntp, 'het_ho2   ')
822       rc_het(:,2) = RESHAPE(all_ntp(l)%data_3d(:,:,k),            &
823                             (/theta_field_size/))
824     ELSE
825       rc_het(:,:) = 0.0
826     END IF
827
```

Used in ASAD

```
790     CALL asad_cdrive(cdot, zftr, zp, zt, zq,                    &
791                      RESHAPE(cloud_frac(:,:,k),(/n_pnts/)),     &
792                      RESHAPE(qcl(:,:,k),(/n_pnts/)),            &
793                      k,zdryrt2, zwetrt3, rc_het,                &
794                      zprt1d, n_pnts, stratflag)
```

UKCA/asad_cdrive.F90

```
223   !       4.  Calculate reaction rate coefficients
224   !           ________ ________ ____ ____________
225
226   CALL asad_bimol (n_points)
227   CALL asad_trimol(n_points)
228
229   ! Calculate aqueous-phase SO2 oxdn. and tropospheric heterogenous rates
230   IF (L_ukca_nr_aqchem .OR. L_ukca_trophet)                          &
231     THEN
232       CALL asad_hetero(n_points, cld_f, cld_l, rc_het)
233     END IF
```

NB

```
331   REAL :: zfrdiss(row_length, rows, model_levels, jpdw, jpeq+1)
332   REAL :: rc_het(theta_field_size,2)                ! heterog rates for trop chem
333   REAL :: kp_nh(row_length, rows, model_levels)     ! Dissociation const
```

UKCA/asad_hetero.F90

```
217   ! Search for tropospheric heterogeneous reactions
218   IF (l_ukca_trophet) THEN
219     prods = (/'HONO2     ','          '/)
220     in2o5_h = asad_findreaction( 'N2O5      ', '          ',        &
221                                  prods, 2, sph, nhrkx, jphk+1, jpsph )
222     prods = (/'H2O2      ','          '/)
223     iho2_h = asad_findreaction( 'HO2       ', '          ',        &
224                                  prods, 2, sph, nhrkx, jphk+1, jpsph )
225
```

```
305   IF (L_ukca_trophet) THEN
306     ! N2O5 => HNO3 (heterogenous)
307     rk(:,in2o5_h) = rc_het(:,1)
308
309     ! HO2 + HO2 => H2O2 (heterogenous)
310     rk(:,iho2_h) = rc_het(:,2)
311   ELSE
312     IF (in2o5_h > 0) rk(:,in2o5_h) = 0.0
313     IF (iho2_h > 0)  rk(:,iho2_h) = 0.0
314   END IF
```

UKCA/ukca_chemistry_ctl.F90

```
790     CALL asad_cdrive(cdot, zftr, zp, zt, zq,                        &
791                      RESHAPE(cloud_frac(:,:,k),(/n_pnts/)),         &
792                      RESHAPE(qcl(:,:,k),(/n_pnts/)),                &
793                      k,zdryrt2, zwetrt3, rc_het,                    &
794                      zprt1d, n_pnts, stratflag)
```

```
853       IF (n_h2o < jpctr) THEN
854         DO l=n_h2o+1,jpctr
855           tracer(:,:,k,l) = RESHAPE(zftr(:,l),                      &
856                                     (/row_length,rows/))*c_species(l)
857         END DO
858       END IF
```

UKCA/ukca_main1-ukca_main1.F90

```
2161    CALL ukca_chemistry_ctl(i_month, i_day_number, i_hour,          &
2162         r_minute - timestep/60.0,                                  &
2163         REAL(chem_timestep),                                       &
2164         n_chem_tracers+n_aero_tracers,                             &
```

```
2315  CALL ukca_aero_ctl(i_month, i_day_number, i_hour,                 &
2316       INT(r_minute - timestep/60.0),                               &
2317       REAL(chem_timestep),                                         &
2318       rows, row_length,                                            &
```

```
2475  !     Return fields to D1
2476  CALL putd1flds()
2477
2478  ! Update the tracer_ukca_um and q_um arrays from the data used in
2479  ! chemistry and aerosol modules. These are then passed back
2480  ! to the UM.
2481  CALL ukca_all_tracers_copy_out(tracer_ukca_um, q_um)
```

Getting MODE heterogeneous rates

UKCA/ukca_aero_ctl.F90

```
3231   SUBROUTINE segment_data_allocate(seg, nbox, nchemg, nhet, nbudaer, nadvg)
3232   ! Allocates segment data, according to the passed array sizes.
3233
```

```
3273   ALLOCATE(seg%het_rates(nbox,nhet))
```

```
1977
1978   ! Calculate heterogeneous rate coeffs for tropospheric chemistry
1979   IF (L_UKCA_trophet) THEN
1980     CALL ukca_trop_hetchem(nbs, seg%t, seg%rh, seg%aird,     &
1981                            seg%pvol, seg%wetdp, seg%sarea, seg%het_rates)
1982     ! Now copy the het_rates into the all_ntp array
1983     i = name2ntpindex(all_ntp,'het_n2o5  ')
1984     CALL insert_seg(lb,ncs,nbs,stride_s,model_levels,        &
1985                     seg%het_rates(:,ihet_n2o5), all_ntp(i)%data_3d(1,1,1) )
1986     i = name2ntpindex(all_ntp,'het_ho2   ')
1987     CALL insert_seg(lb,ncs,nbs,stride_s,model_levels,        &
1988                     seg%het_rates(:,ihet_ho2_ho2), all_ntp(i)%data_3d(1,1,1))
1989   END IF
1990
```

UKCA/ukca_aero_ctl.F90

```
3231   SUBROUTINE segment_data_allocate(seg, nbox, nchemg, nhet, nbudaer, nadvg)
3232   ! Allocates segment data, according to the passed array sizes.
3233
```

```
3273   ALLOCATE(seg%het_rates(nbox,nhet))
```

```
1977
1978   ! Calculate heterogeneous rate coeffs for tropospheric chemistry
1979   IF (L_UKCA_trophet) THEN
1980     CALL ukca_trop_hetchem(nbs, seg%t, seg%rh, seg%aird,     &
1981                            seg%pvol, seg%wetdp, seg%sarea, seg%het_rates)
1982     ! Now copy the het_rates into the all_ntp array
1983     i = name2ntpindex(all_ntp,'het_n2o5  ')
1984     CALL insert_seg(lb,ncs,nbs,stride_s,model_levels,        &
1985                     seg%het_rates(:,ihet_n2o5), all_ntp(i)%data_3d(1,1,1) )
1986     i = name2ntpindex(all_ntp,'het_ho2   ')
1987     CALL insert_seg(lb,ncs,nbs,stride_s,model_levels,        &
1988                     seg%het_rates(:,ihet_ho2_ho2), all_ntp(i)%data_3d(1,1,1))
1989   END IF
1990
```

UKCA/ukca_aero_ctl.F90

Heterogeneous rates returned from het_chem routine

```
1977
1978  ! Calculate heterogeneous rate coeffs for tropospheri  chemistry
1979  IF (L_UKCA_trophet) THEN
1980    CALL ukca_trop_hetchem(nbs, seg%t, seg%rh, seg%aird,     &
1981                           seg%pvol, seg%wetdp, seg%sarea, seg%het_rates)
1982    ! Now copy the het_rates into the all_ntp array
1983    i = name2ntpindex(all_ntp,'het_n2o5  ')
1984    CALL insert_seg(lb,ncs,nbs,stride_s,model_levels,        &
1985                           seg%het_rates(:,ihet_n2o5), all_ntp(i)%data_3d(1,1,1) )
1986    i = name2ntpindex(all_ntp,'het_ho2   ')
1987    CALL insert_seg(lb,ncs,nbs,stride_s,model_levels,        &
1988                           seg%het_rates(:,ihet_ho2_ho2), all_ntp(i)%data_3d(1,1,1))
1989  END IF
1990
```

UKCA/ukca_aero_ctl.F90

Fill ALL_NTP array with het rates for use in next time step

```
1977
1978    ! Calculate heterogeneous rate coeffs
1979    IF (L_UKCA_trophet) THEN
1980      CALL ukca_trop_hetchem(nbs, seg%t, seg%rh, seg%ai,     &
1981                             seg%pvol, seg%wetdp, seg%sarea, seg%het_rates)
1982      ! Now copy the het_rates into the all_ntp array
1983      i = name2ntpindex(all_ntp,'het_n2o5  ')
1984      CALL insert_seg(lb,ncs,nbs,stride_s,model_levels,         &
1985                      seg%het_rates(:,ihet_n2o5), all_ntp(i)%data_3d(1,1,1) )
1986      i = name2ntpindex(all_ntp,'het_ho2   ')
1987      CALL insert_seg(lb,ncs,nbs,stride_s,model_levels,         &
1988                      seg%het_rates(:,ihet_ho2_ho2), all_ntp(i)%data_3d(1,1,1))
1989    END IF
1990
```

UKCA/ukca_aero_ctl.F90

```
3231   SUBROUTINE segment_data_allocate(seg, nbox, nchemg, nhet, nbudaer, nadvg)
3232   ! Allocates segment data, according to the passed array sizes.
3233
```

```
3273   ALLOCATE(seg%het_rates(nbox,nhet))
```

```
1977
1978   ! Calculate heterogeneous rate coeffs for tropospheric chemistry
1979   IF (L_UKCA_trophet) THEN
1980     CALL ukca_trop_hetchem(nbs, seg%t, seg%rh, seg%aird,     &
1981                            seg%pvol, seg%wetdp, seg%sarea, seg%het_rates)
1982     ! Now copy the het_rates into the all_ntp array
1983     i = name2ntpindex(all_ntp,'het_n2o5  ')
1984     CALL insert_seg(lb,ncs,nbs,stride_s,model_levels,        &
1985                     seg%het_rates(:,ihet_n2o5), all_ntp(i)%data_3d(1,1,1) )
1986     i = name2ntpindex(all_ntp,'het_ho2   ')
1987     CALL insert_seg(lb,ncs,nbs,stride_s,model_levels,        &
1988                     seg%het_rates(:,ihet_ho2_ho2), all_ntp(i)%data_3d(1,1,1))
1989   END IF
1990
```

UKCA/ukca_ntp_mod.F90

```
48   ! subroutines/functions which are public
49   PUBLIC ntp_init, name2ntpindex, stash2ntpindex, print_all_ntp, ntp_dealloc
50
51   ! The size of the all_ntp array is defined here.
52   ! If adding or removing entries remember to change
53   ! the size of dim_ntp
54   INTEGER, PARAMETER, PUBLIC :: dim_ntp = 73
```

```
174  ! Heterogeneous self reaction rate of HO2
175  CALL add_ntp_item(all_ntp, section=ukca_sect, item=973,          &
176    varname='het_ho2   ')
177
178  ! Heterogeneous loss rate of N2O5
179  CALL add_ntp_item(all_ntp, section=ukca_sect, item=974,          &
180    varname='het_n2o5  ')
181
```

UKCA/ukca_trop_hetchem.F90

```
67    ! Number of heterogeneous reaction rates
68    INTEGER, PARAMETER, PUBLIC :: nhet = 2
69
70    ! Indices for the location of each rate in the returned array.
71    ! 1. Index for heterogeneous hydrolysis of N2O5
72    INTEGER, PARAMETER, PUBLIC :: ihet_n2o5    = 1
73    ! 2. Index for self reaction of HO2 on surfaces
74    INTEGER, PARAMETER, PUBLIC :: ihet_ho2_ho2 = 2
```

Concluding remarks

- Adding new aerosol chemistry involves changes at a few places in the code.
- New tropospheric heterogeneous chemistry is very powerful.
- Can define uptake onto different aerosol modes so well worth effort.
- Big improvement over sulfate-only scheme.
- Box models can help in building up understanding of aerosol impact.
- Aerosols may enhance effective concentration and open up new pathways of reactivity, can recycle and transport reservoirs.