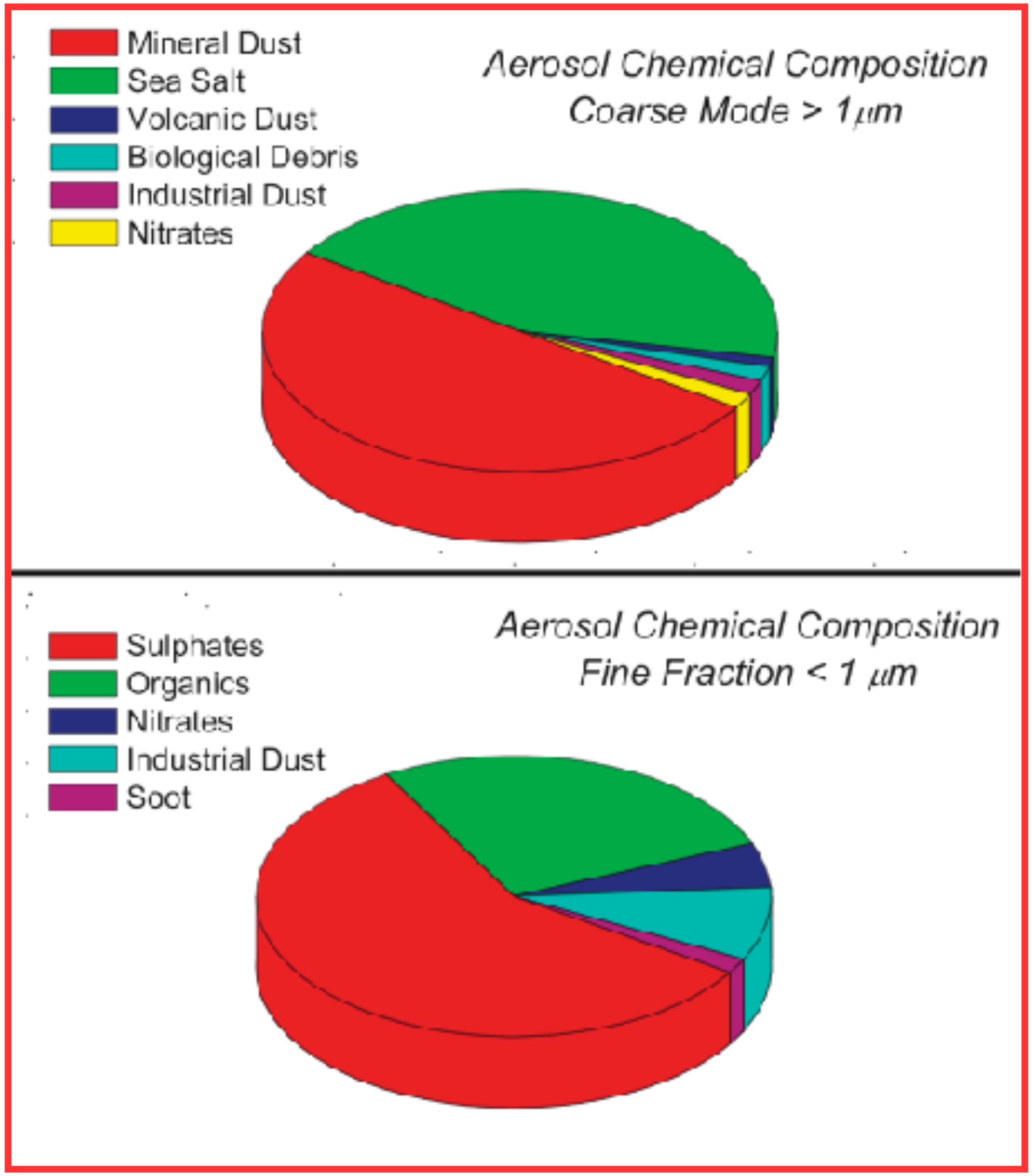
# Heterogeneous chemistry - how to get from the literature to UKCA model treatment

Paul Griffiths, NCAS Climate and Cambridge University

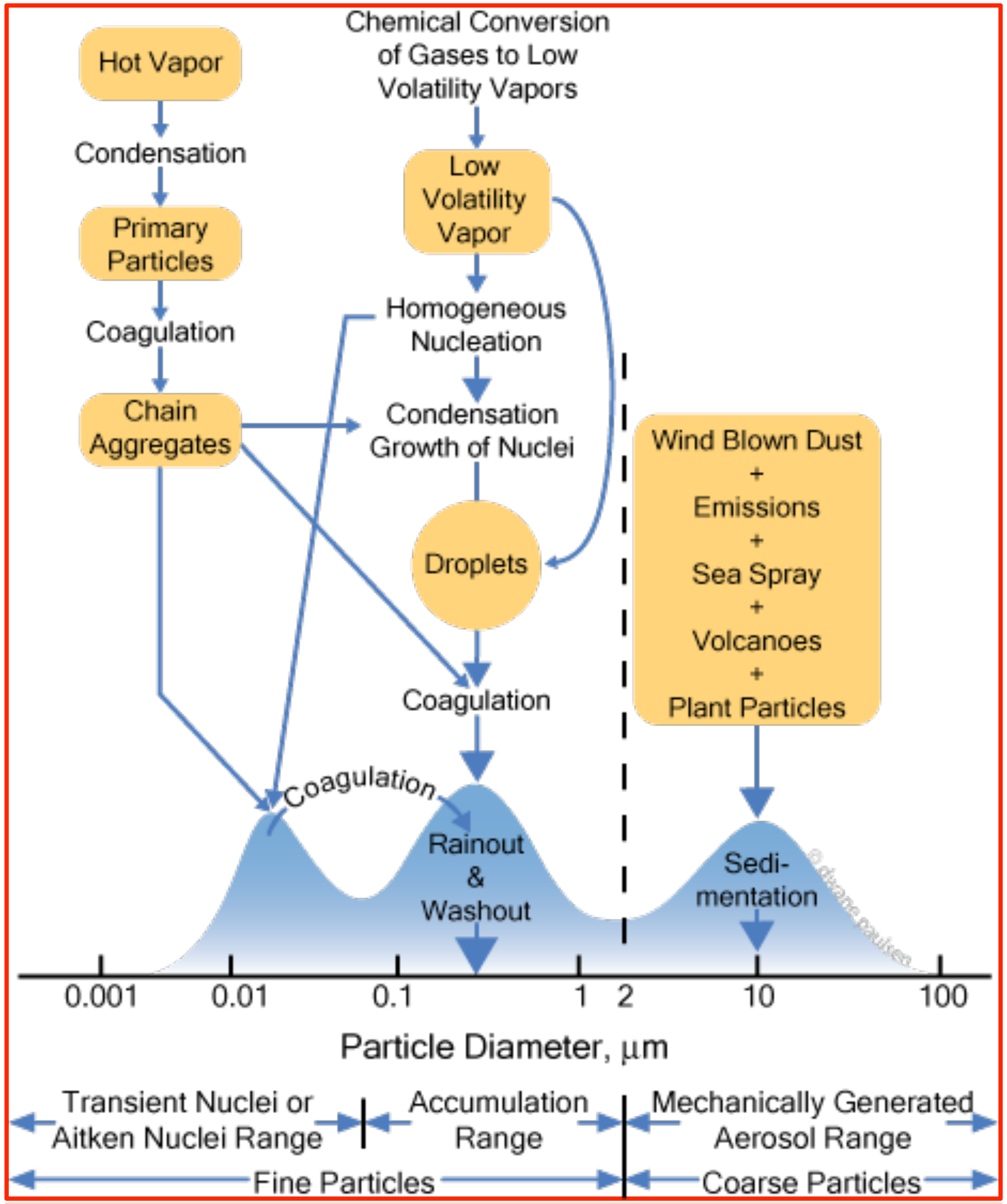
# Chemical composition of tropospheric aerosol

- 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.
- $NO_x$ → $HNO_3$ → aerosol nitrate
- $SO_2$ → $H_2SO_4$ → aerosol sulfate
- VOC → organics (carbon-rich)

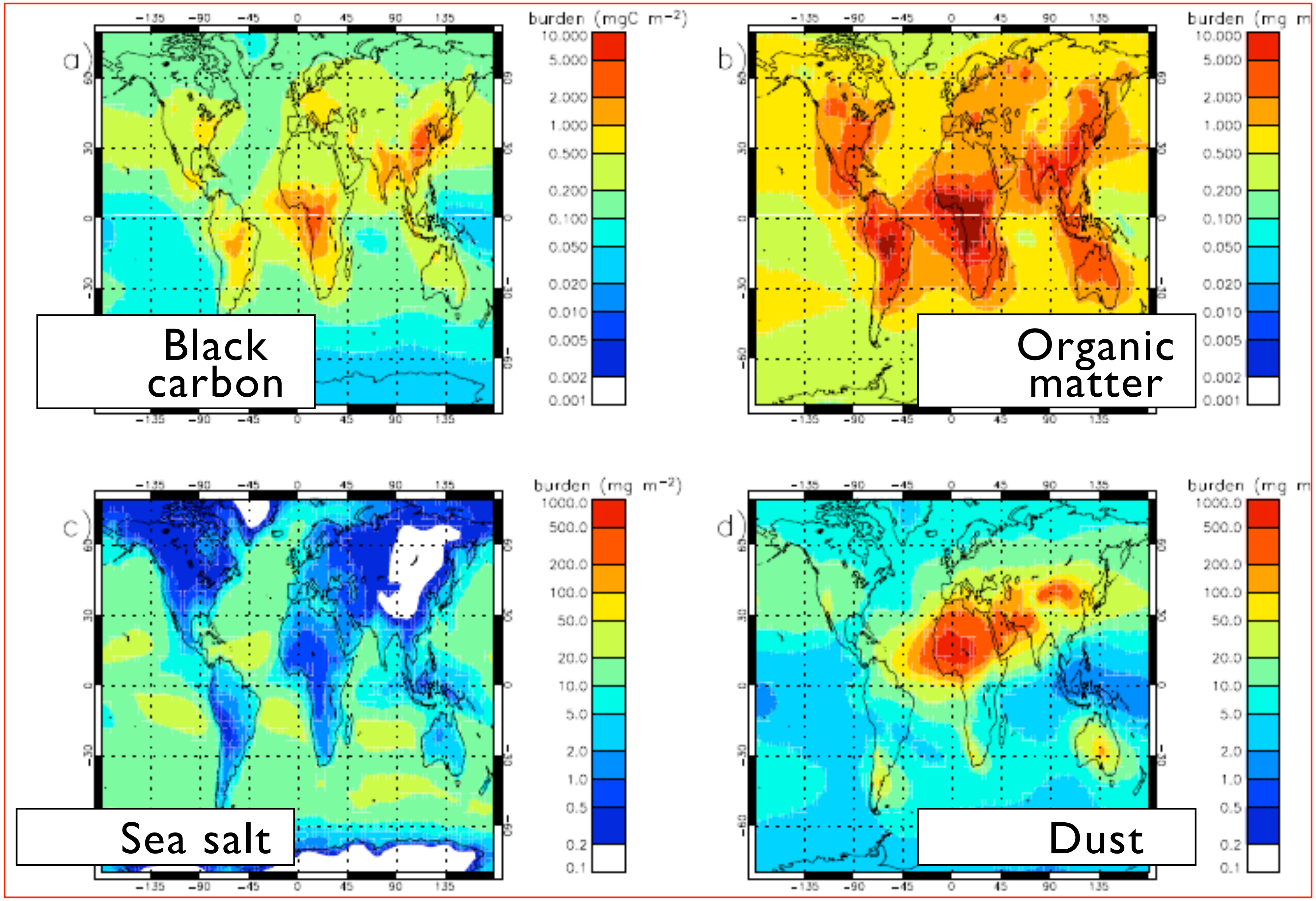


# Size range spanned by atmospheric aerosol

- 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.

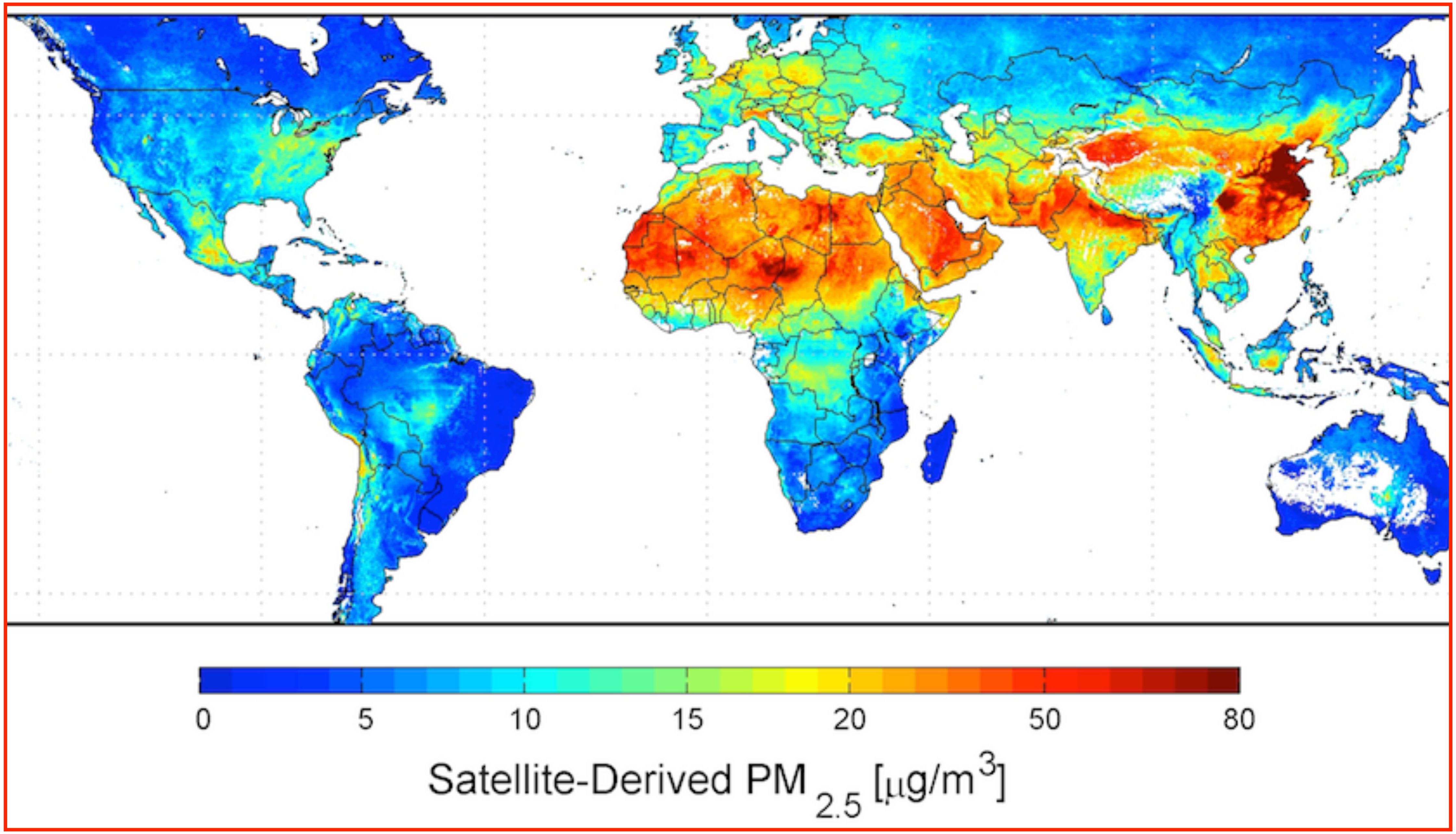


# Current work - aerosol chemistry on a global scale



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

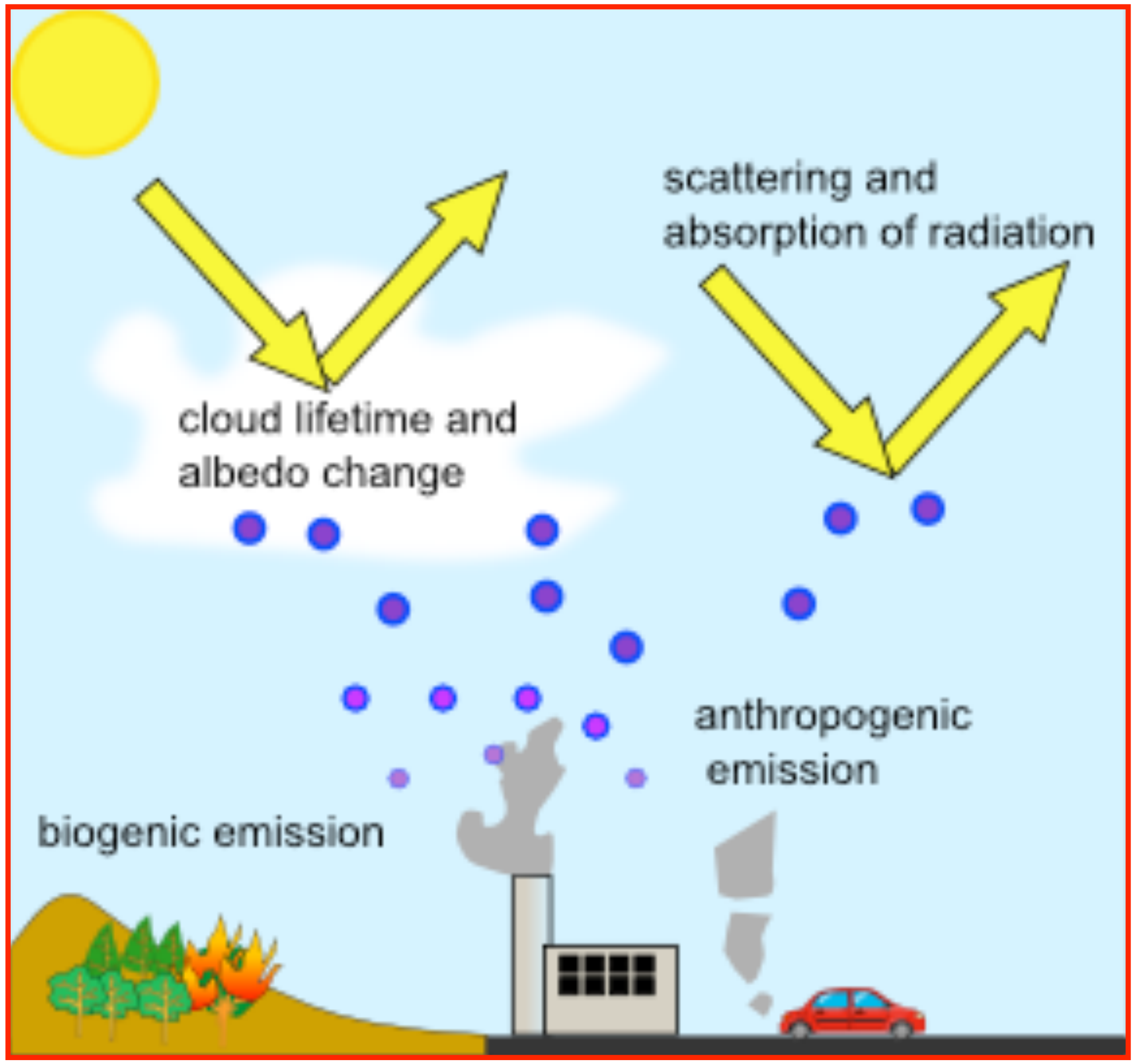
# Global near-surface distribution of aerosol



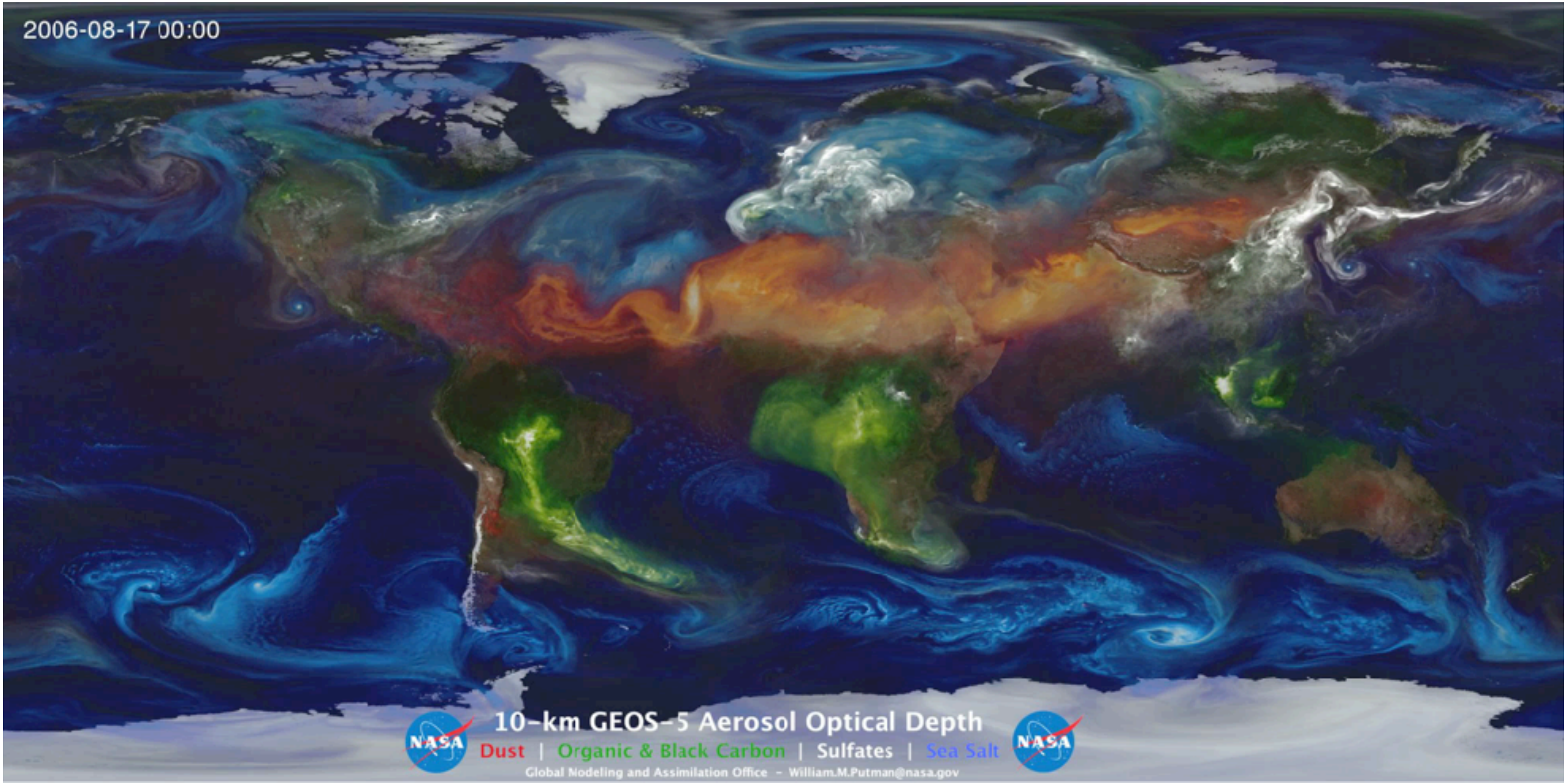
Total (mass) particulate matter is shown (NB no measurements over oceans)

# 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.



# Global distribution of aerosol



White: sulfate blue: sea salt red: dust green: soot

https://gmao.gsfc.nasa.gov/research/aerosol/modeling/nr1_movie/

# Coupling between aerosol and oxidation

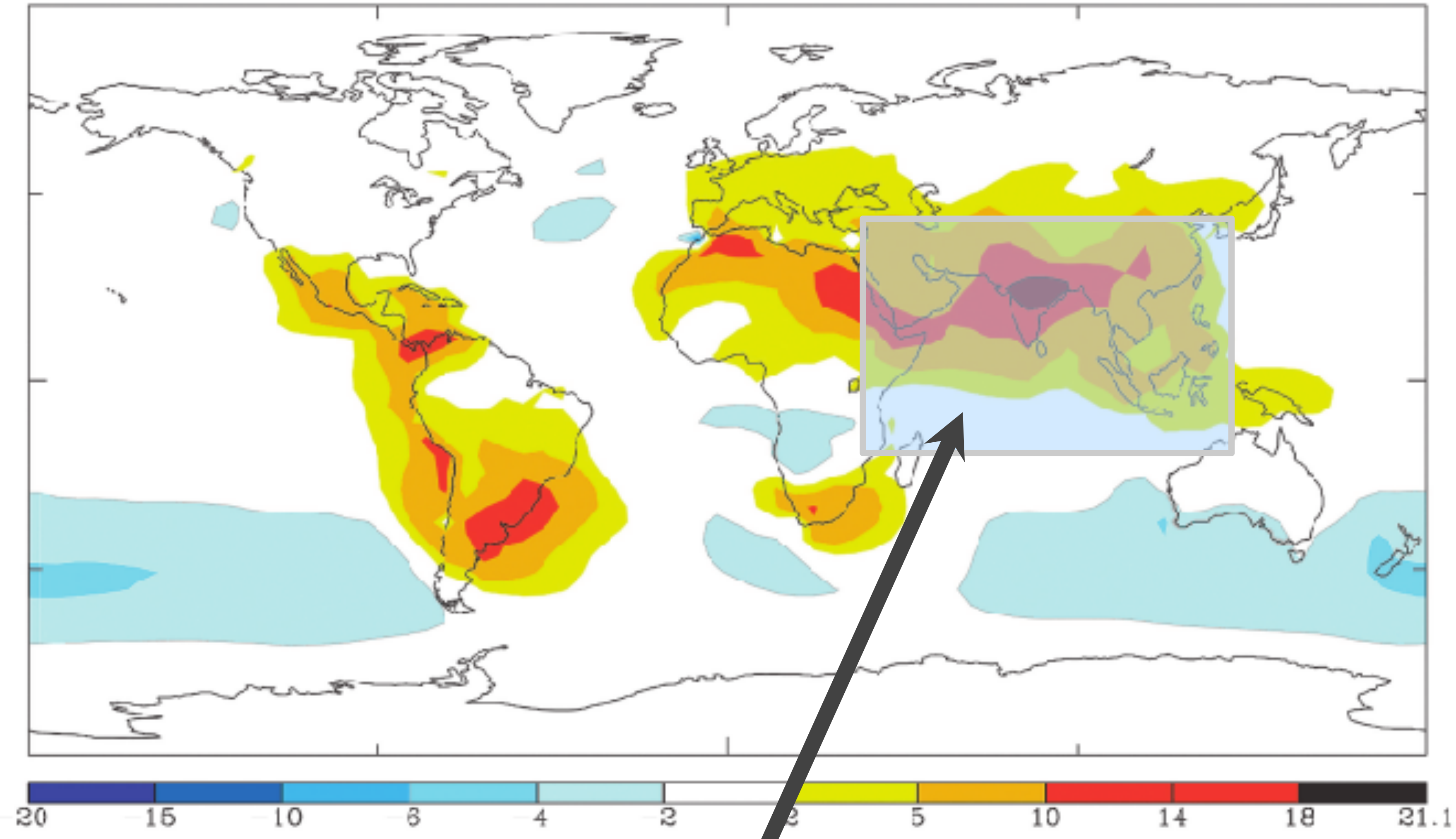


**Fig. 1.** Percentage difference in surface sulfate mixing ratio between future control simulation (2030C) and sensitivity simulation with future $SO_2$ emissions but present-day $O_3$ precursor emissions (2030$SO_4$) [i.e., 100 × (2030C − 2030$SO_4$)/2030C].

Regional variations in impact: higher future NOx emissions lead to large increase in [OH], more OH+SO2 reaction, more sulfate.
More aerosol means a decrease in solar radiation, moderating climate change.

# Aerosols and their effect on ozone

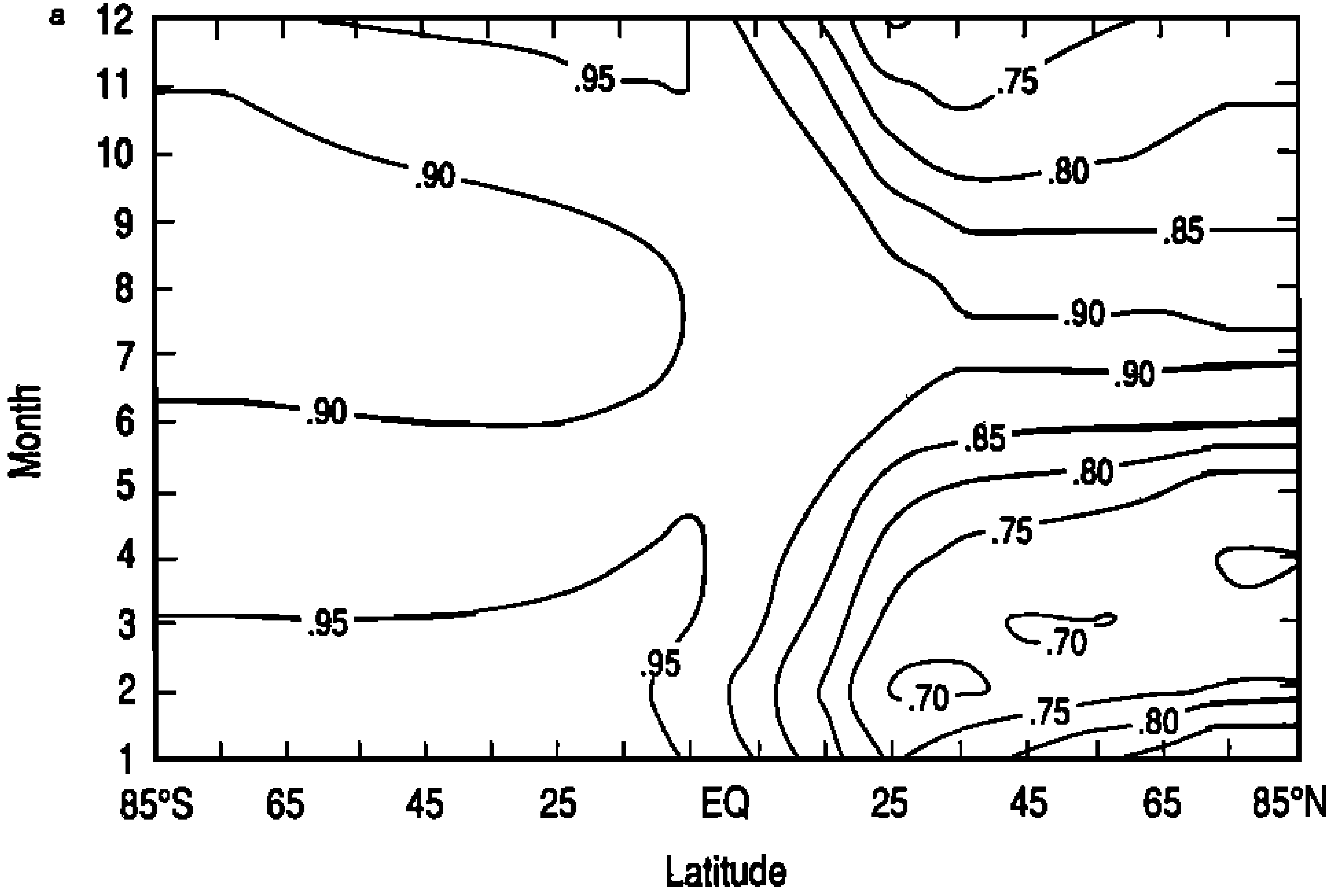


Fig. 9 from Dentener and Crutzen, 1993. The zonal mean monthly average ratio of O3 concentrations with aerosol reactions to those without for all months at 1000 hPa

# 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 rate of reaction - open up new pathways of reactivity.

# Prognostic equation for reaction of aerosol with gas X

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

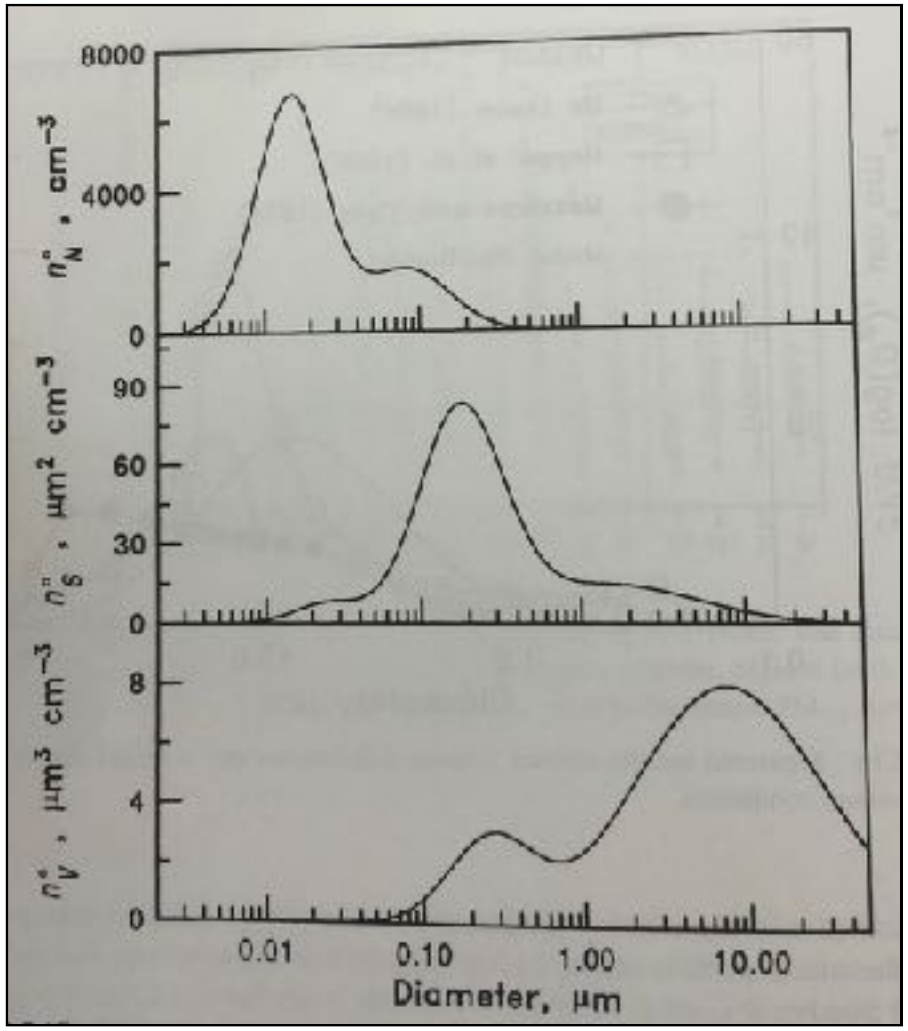
$$k_{het} = \gamma S_a c/4$$

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

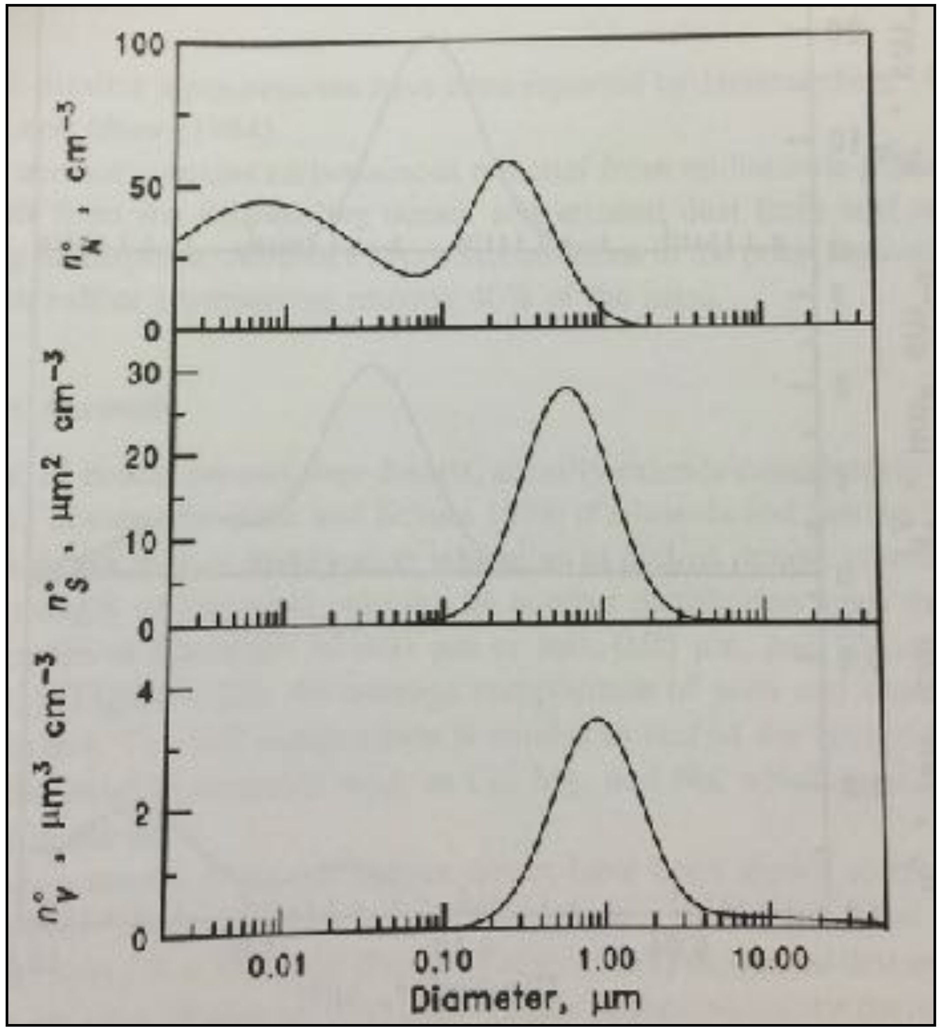
- Parameterise reaction/uptake via uptake coefficient, γ, $(0 < \gamma \leq 1)$
- Represents the probability that the gas phase species X is lost per collision with the aerosol surface.
- Make sure units of surface area density ($m^2\ m^{-3}$) and c (mean molecular speed of gas phase X, $ms^{-1}$) match.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

# Representative aerosol number, SA and mass distributions

## Rural continental

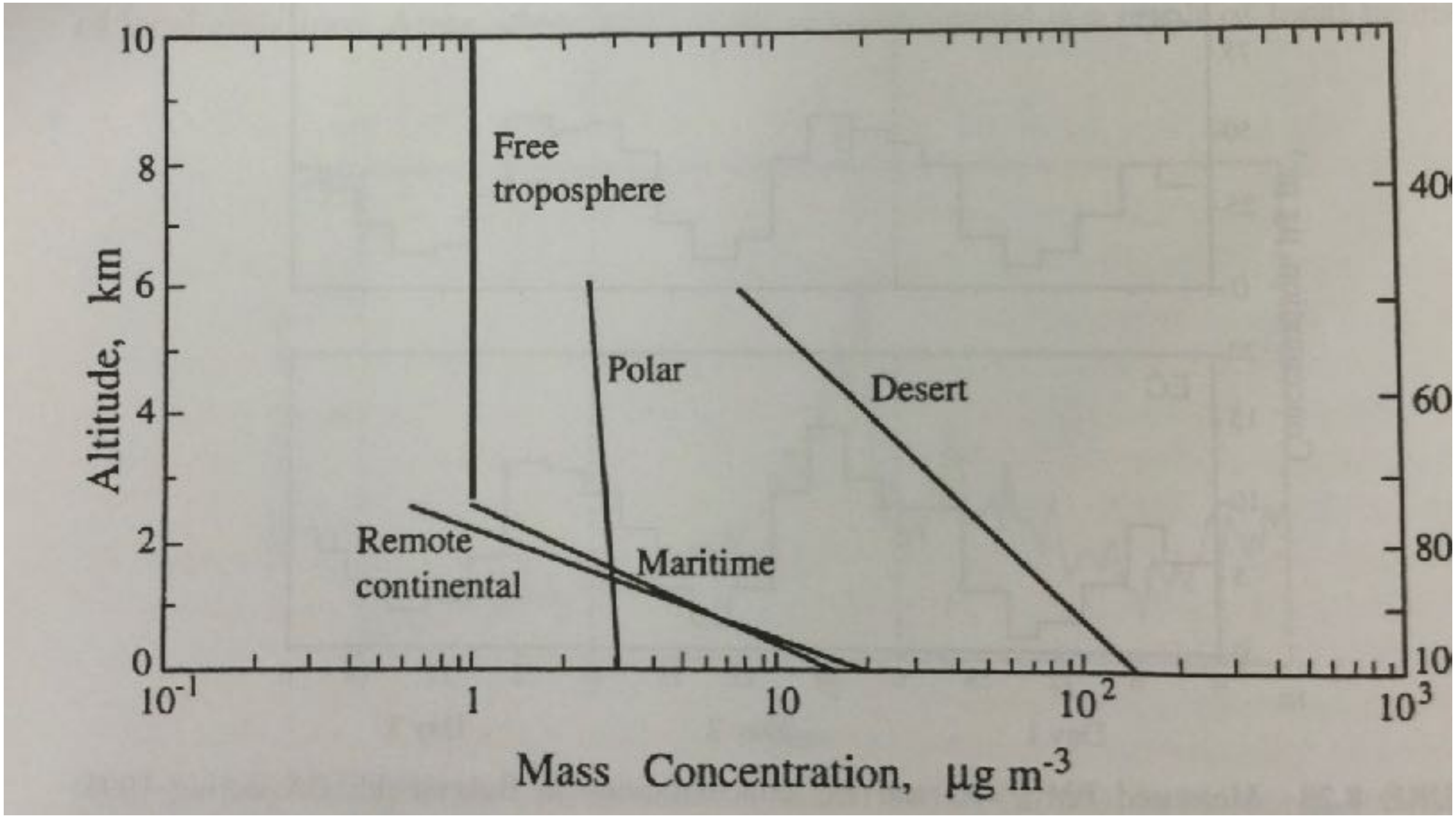


## Free troposphere



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

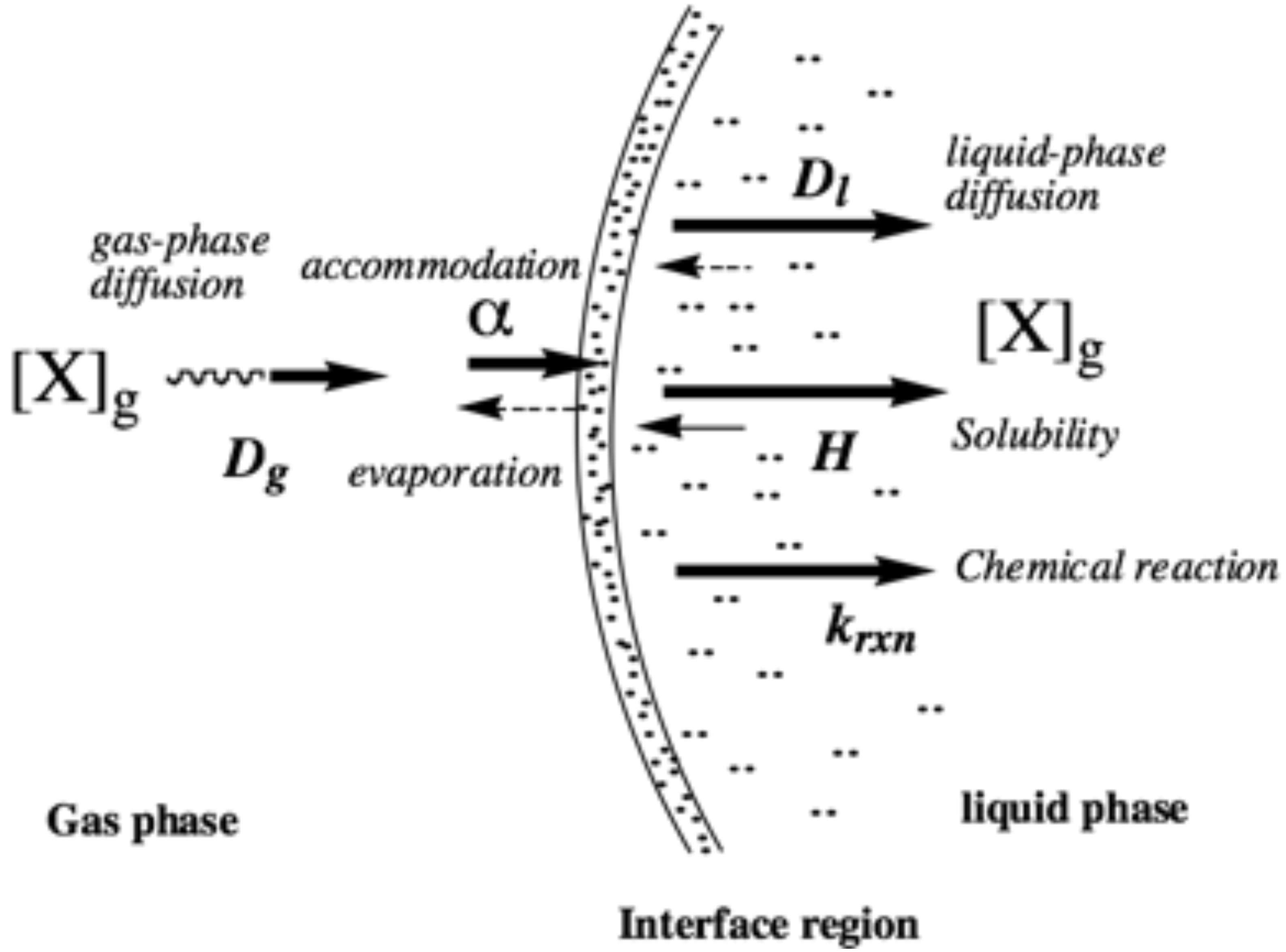
$$\frac{d[X]}{dt} = -k_{het}[X]$$

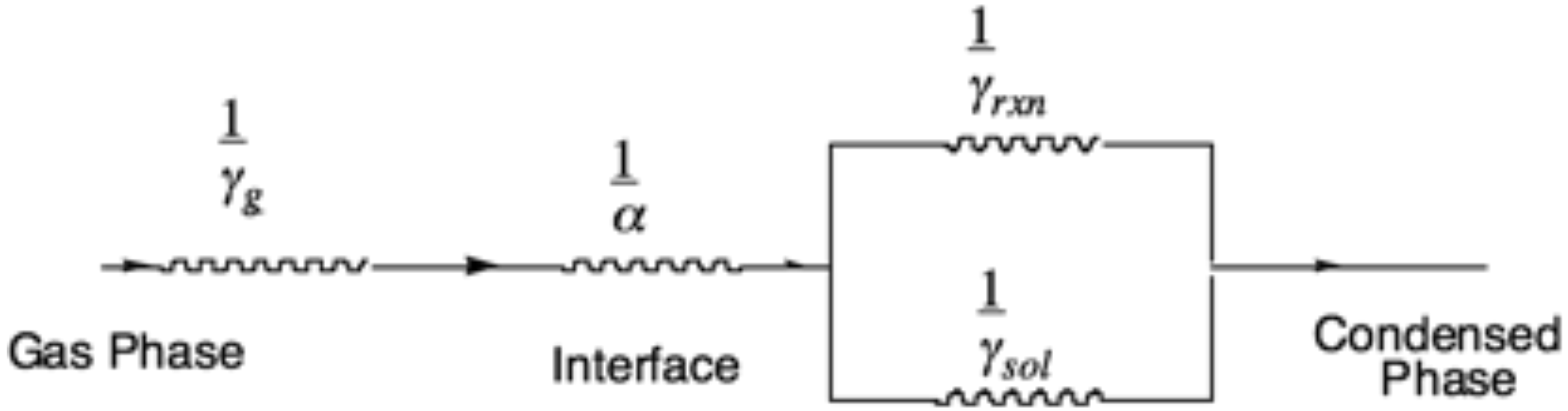
$$k_{het} = \gamma S_a c/4$$

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

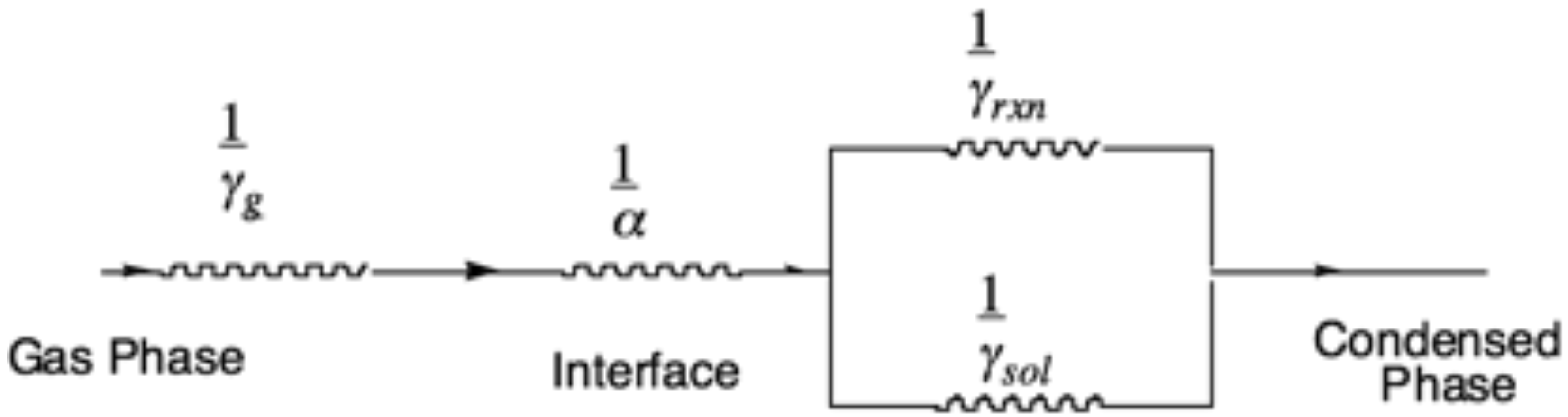
- The uptake coefficient, γ, contains the physical chemistry that you need to think about.
- This is generally what the experimentalists report.
- Tempting just to take the number from the paper and put it into the model, but there's usually scope to add a bit of value.
- The resistor framework provides 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

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

- $\gamma_g$ 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

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

- $\alpha$ 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 ($\gamma_{rxn}$ is large) the accommodation step may again be the slowest step and control $\gamma$ (so-called ‘accommodation-controlled uptake’)

# Trace gas uptake as a series of coupled steps

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

- $\gamma_{sol}$ 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

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

- $\gamma_{rxn}$ 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)

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

- $k_{rxn}$ 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.

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

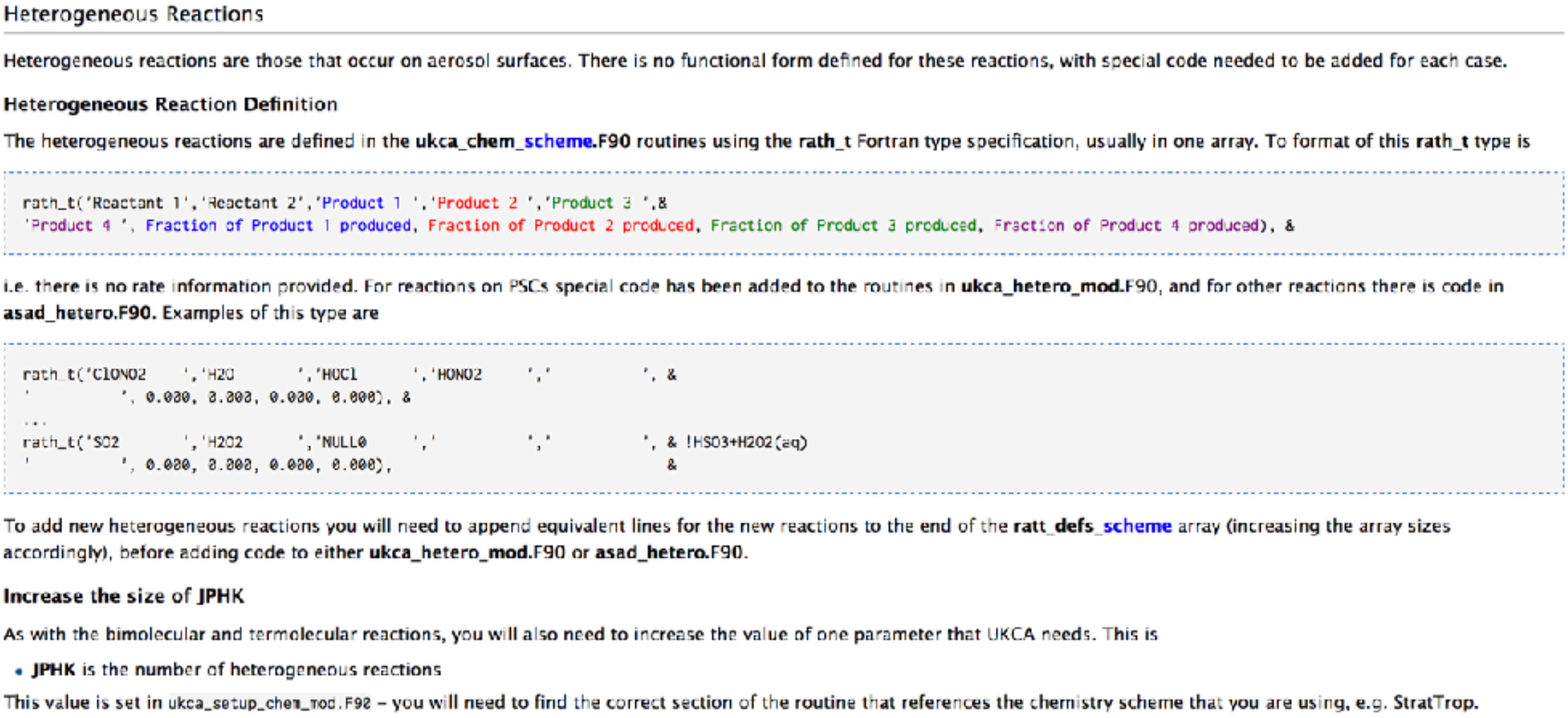
- For more information see the IUPAC website, http://iupac.pole-ether.fr/htdocs/supp_info/NewHetIntroOct2009.pdf

# 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_vn10.4_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_scheme.F90** routines using the **rath_t** Fortran type specification, usually in one array. To format of this **rath_t** type is

```
rath_t('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), &
```

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.** Examples of this type are

```
rath_t('ClONO2    ','H2O       ','HOCl      ','HONO2     ','          ', &
'          ', 0.000, 0.000, 0.000, 0.000), &
...
rath_t('SO2       ','H2O2      ','NULL0     ','          ','          ', & !HSO3+H2O2(aq)
'          ', 0.000, 0.000, 0.000, 0.000),                              &
```

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

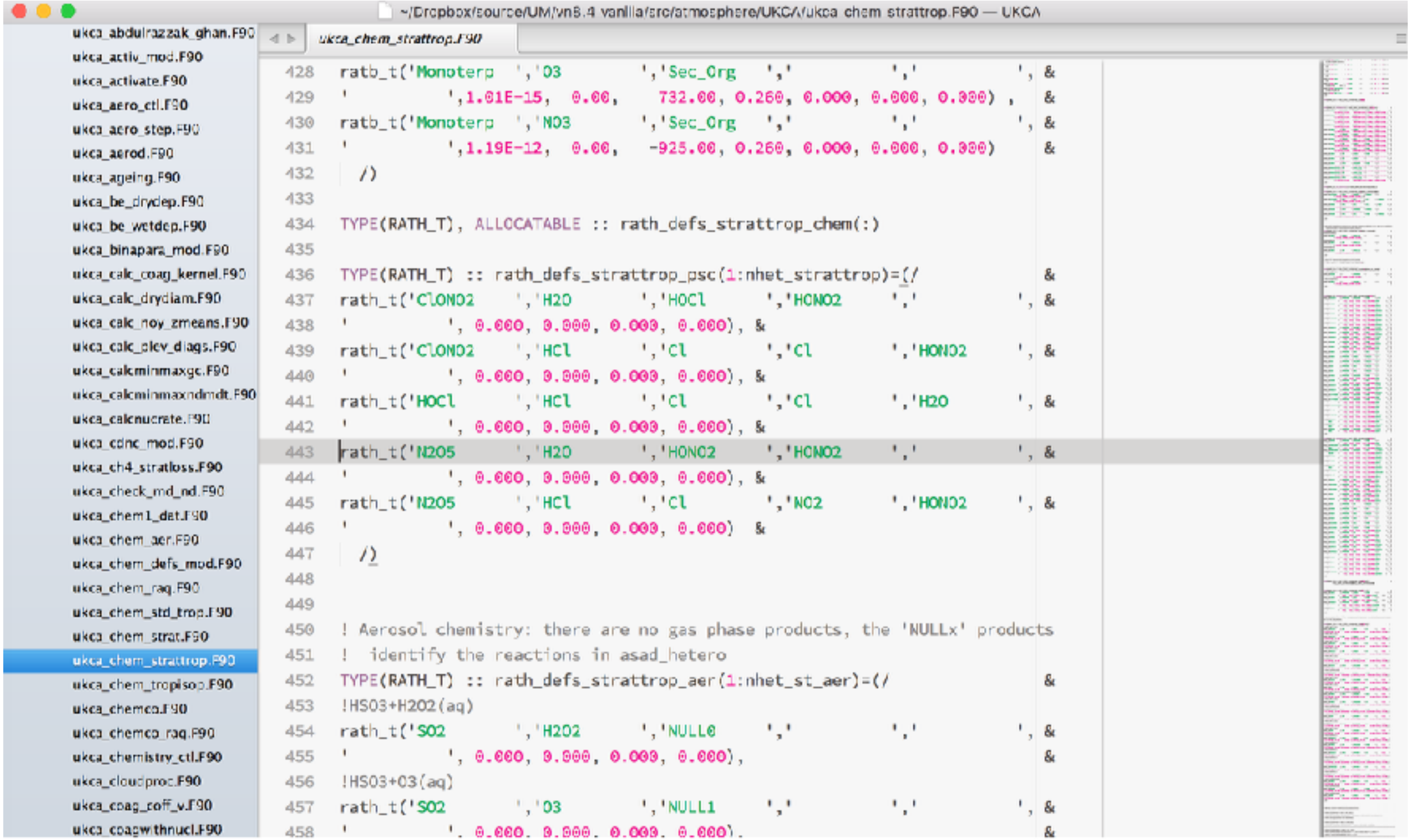
### Increase the size of JPHK

As with the bimolecular and termolecular reactions, you will also need to increase the value of one parameter that UKCA needs. This is

- **JPHK** is the number of heterogeneous reactions

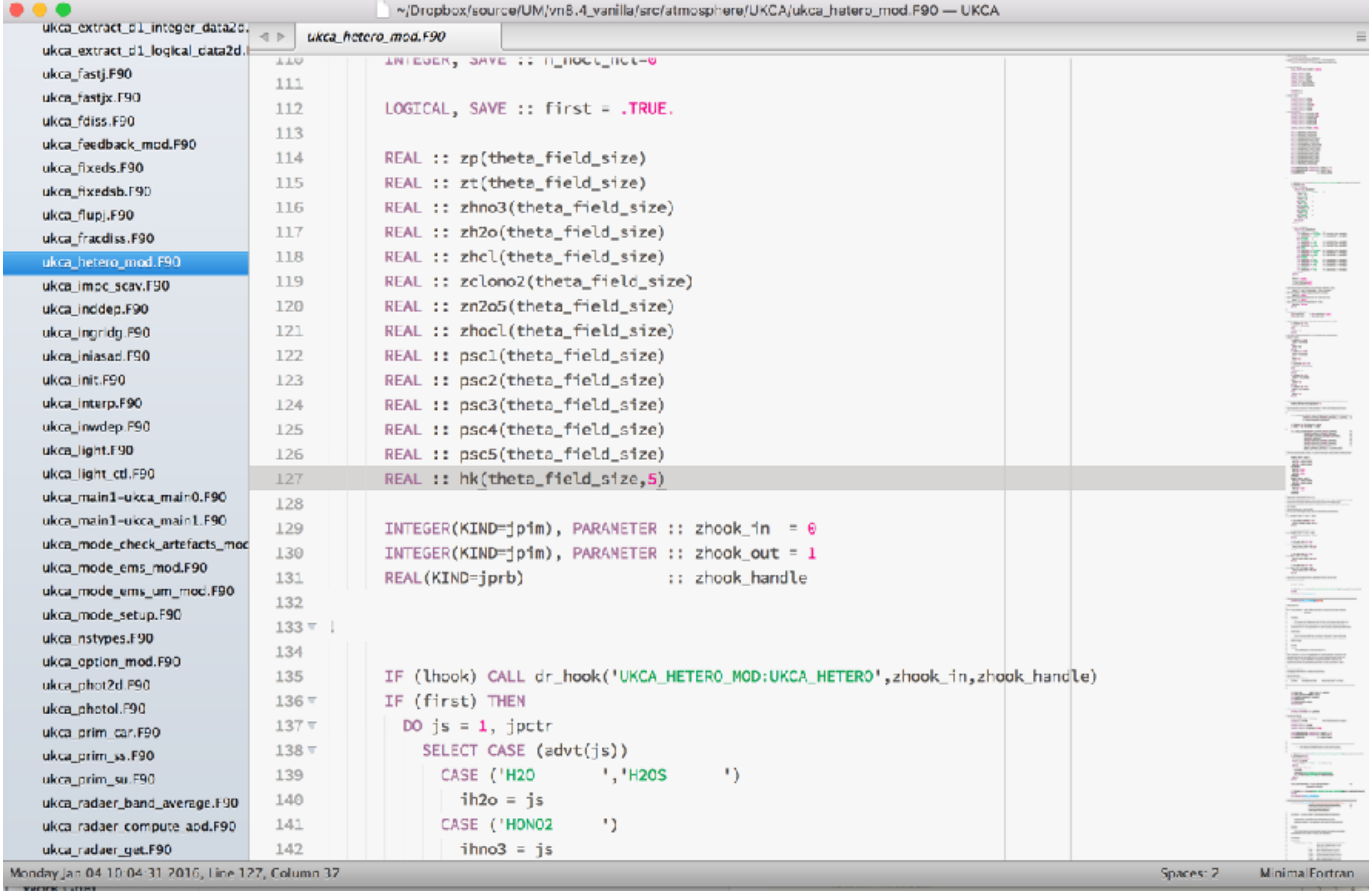
This value is set in `ukca_setup_chem_mod.F90` – you will need to find the correct section of the routine that references the chemistry scheme that you are using, e.g. StratTrop.

# UKCA/ukca_chem_strattrop.F90



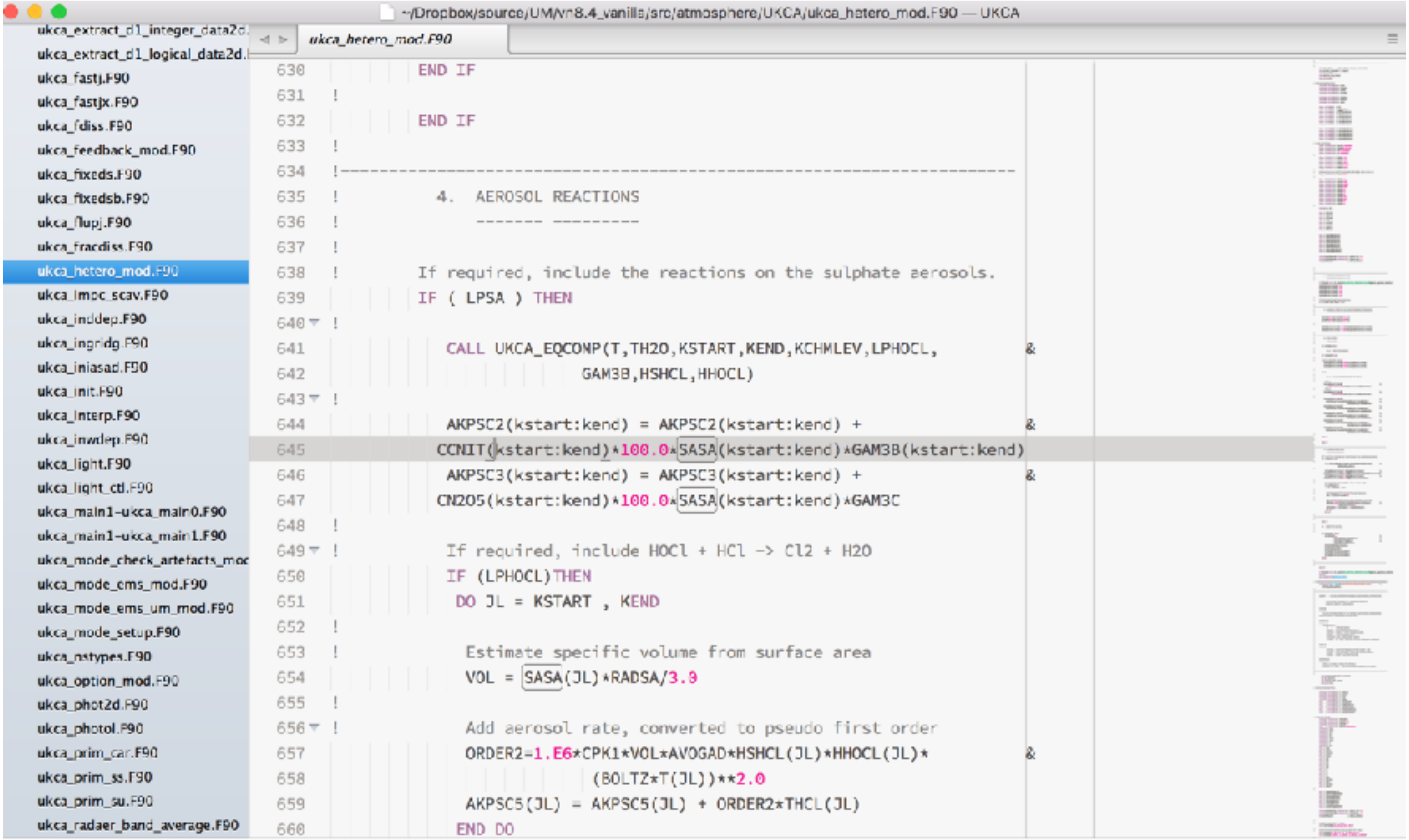
```fortran
ratb_t('Monoterp  ','O3        ','Sec_Org   ','          ','          ', &
'          ',1.01E-15,  0.00,    732.00, 0.260, 0.000, 0.000, 0.300) ,  &
ratb_t('Monoterp  ','NO3       ','Sec_Org   ','          ','          ', &
'          ',1.19E-12,  0.00,   -925.00, 0.260, 0.000, 0.000, 0.300)    &
  /)

TYPE(RATH_T), ALLOCATABLE :: rath_defs_strattrop_chem(:)

TYPE(RATH_T) :: rath_defs_strattrop_psc(1:nhet_strattrop)=(/              &
rath_t('ClONO2    ','H2O       ','HOCl      ','HONO2     ','          ', &
'          ', 0.000, 0.000, 0.000, 0.000), &
rath_t('ClONO2    ','HCl       ','Cl        ','Cl        ','HONO2     ', &
'          ', 0.000, 0.000, 0.000, 0.000), &
rath_t('HOCl      ','HCl       ','Cl        ','Cl        ','H2O       ', &
'          ', 0.000, 0.000, 0.000, 0.000), &
rath_t('N2O5      ','H2O       ','HONO2     ','HONO2     ','          ', &
'          ', 0.000, 0.000, 0.000, 0.000), &
rath_t('N2O5      ','HCl       ','Cl        ','NO2       ','HONO2     ', &
'          ', 0.000, 0.000, 0.000, 0.000)  &
  /)


! Aerosol chemistry: there are no gas phase products, the 'NULLx' products
!  identify the reactions in asad_hetero
TYPE(RATH_T) :: rath_defs_strattrop_aer(1:nhet_st_aer)=(/                 &
!HSO3+H2O2(aq)
rath_t('SO2       ','H2O2      ','NULL0     ','          ','          ', &
'          ', 0.000, 0.000, 0.000, 0.000),                              &
!HSO3+O3(aq)
rath_t('SO2       ','O3        ','NULL1     ','          ','          ', &
'          ', 0.000, 0.000, 0.000, 0.000),                              &
```

# UKCA/ukca_hetero_mod.F90



```fortran

LOGICAL, SAVE :: first = .TRUE.

REAL :: zp(theta_field_size)
REAL :: zt(theta_field_size)
REAL :: zhno3(theta_field_size)
REAL :: zh2o(theta_field_size)
REAL :: zhcl(theta_field_size)
REAL :: zclono2(theta_field_size)
REAL :: zn2o5(theta_field_size)
REAL :: zhocl(theta_field_size)
REAL :: psc1(theta_field_size)
REAL :: psc2(theta_field_size)
REAL :: psc3(theta_field_size)
REAL :: psc4(theta_field_size)
REAL :: psc5(theta_field_size)
REAL :: hk(theta_field_size,5)

INTEGER(KIND=jpim), PARAMETER :: zhook_in  = 0
INTEGER(KIND=jpim), PARAMETER :: zhook_out = 1
REAL(KIND=jprb)               :: zhook_handle

!

IF (lhook) CALL dr_hook('UKCA_HETERO_MOD:UKCA_HETERO',zhook_in,zhook_handle)
IF (first) THEN
  DO js = 1, jpctr
    SELECT CASE (advt(js))
      CASE ('H2O       ','H2OS      ')
        ih2o = js
      CASE ('HONO2     ')
        ihno3 = js
```

# UKCA/ukca_hetero_mod.F90



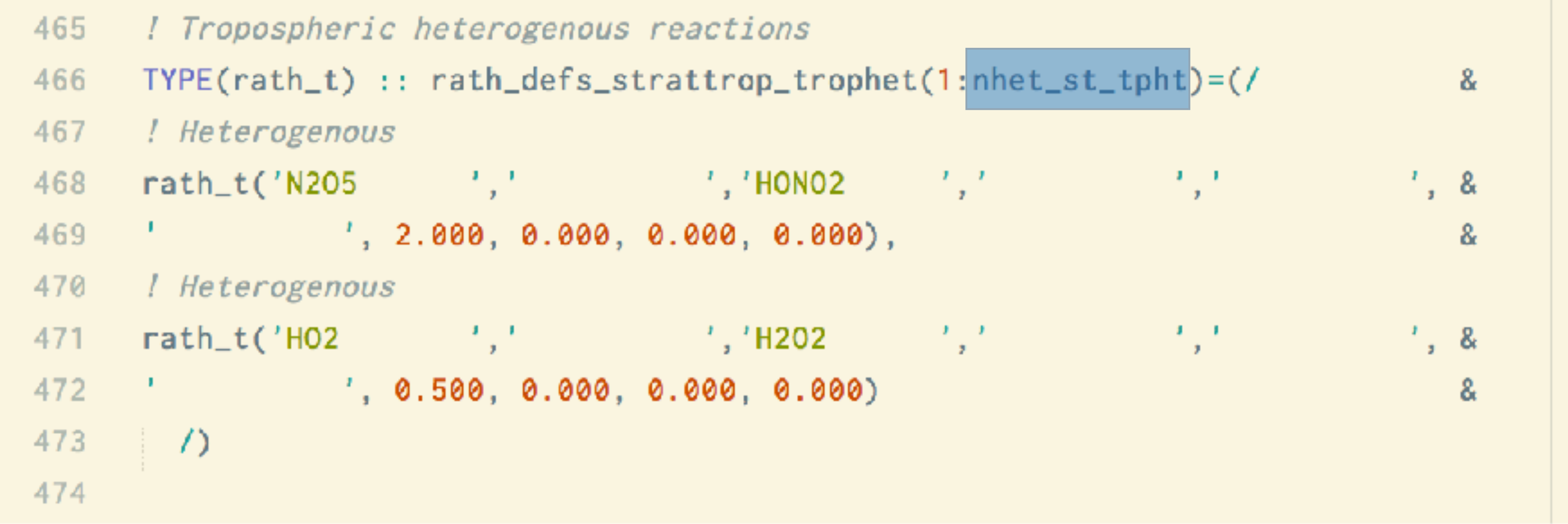
```
         END IF
!
         END IF
!
!-----------------------------------------------------------------------
!          4.  AEROSOL REACTIONS
!              ------- ---------
!
!        If required, include the reactions on the sulphate aerosols.
         IF ( LPSA ) THEN
!
            CALL UKCA_EQCOMP(T,TH2O,KSTART,KEND,KCHMLEV,LPHOCL,                 &
                          GAM3B,HSHCL,HHOCL)
!
            AKPSC2(kstart:kend) = AKPSC2(kstart:kend) +                         &
           CCNIT(kstart:kend)*100.0*SASA(kstart:kend)*GAM3B(kstart:kend)
            AKPSC3(kstart:kend) = AKPSC3(kstart:kend) +                         &
           CN2O5(kstart:kend)*100.0*SASA(kstart:kend)*GAM3C
!
!           If required, include HOCl + HCl -> Cl2 + H2O
            IF (LPHOCL)THEN
             DO JL = KSTART , KEND
!
!             Estimate specific volume from surface area
              VOL = SASA(JL)*RADSA/3.0
!
!             Add aerosol rate, converted to pseudo first order
              ORDER2=1.E6*CPK1*VOL*AVOGAD*HSHCL(JL)*HHOCL(JL)*                  &
                           (BOLTZ*T(JL))**2.0
              AKPSC5(JL) = AKPSC5(JL) + ORDER2*THCL(JL)
             END DO
```

# UKCA/ukca_hetero_mod.F90

```
!
      END IF
!
!-----------------------------------------------------------------------
!          4.  AEROSOL REACTIONS
!              -------- ---------
!
!     If required, include the reactions on the sulphate aerosols.
      IF ( LPSA ) THEN
!
        CALL UKCA_EQCOMP(T,TH2O,KSTART,KEND,KCHMLEV,LPHOCL,         &
                         GAM3B,HSHCL,HHOCL)
!
        AKPSC2(kstart:kend) = AKPSC2(kstart:kend) +                 &
       CCNIT(kstart:kend)*100.0*SASA(kstart:kend)*GAM3B(kstart:kend)
        AKPSC3(kstart:kend) = AKPSC3(kstart:kend) +                 &
       CN2O5(kstart:kend)*100.0*SASA(kstart:kend)*GAM3C
!
!       If required, include HOCl + HCl -> Cl2 + H2O
        IF (LPHOCL)THEN
         DO JL = KSTART , KEND
!
!          Estimate specific volume from surface area
           VOL = SASA(JL)*RADSA/3.0
!
!          Add aerosol rate, converted to pseudo first order
           ORDER2=1.E6*CPK1*VOL*AVOGAD*HSHCL(JL)*HHOCL(JL)*         &
                  (BOLTZ*T(JL))**2.0
           AKPSC5(JL) = AKPSC5(JL) + ORDER2*THCL(JL)
         END DO
```

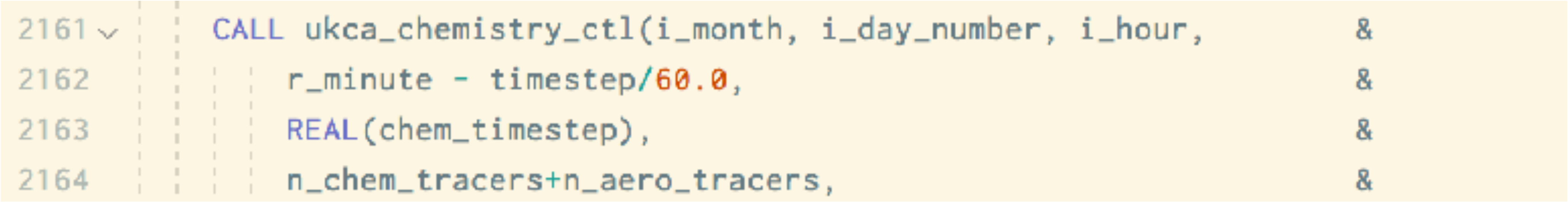
# The MODE aerosol chemistry - slightly different

# UKCA/ukca_chem_strattrop.F90

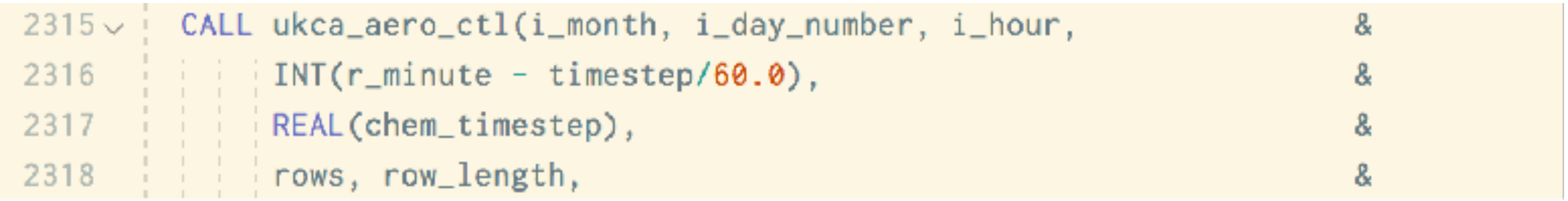


```fortran
! Tropospheric heterogenous reactions
TYPE(rath_t) :: rath_defs_strattrop_trophet(1:nhet_st_tpht)=(/          &
! Heterogenous
rath_t('N2O5      ','          ','HONO2     ','          ','          ', &
'          ', 2.000, 0.000, 0.000, 0.000),                              &
! Heterogenous
rath_t('HO2       ','          ','H2O2      ','          ','          ', &
'          ', 0.500, 0.000, 0.000, 0.000)                               &
  /)

```

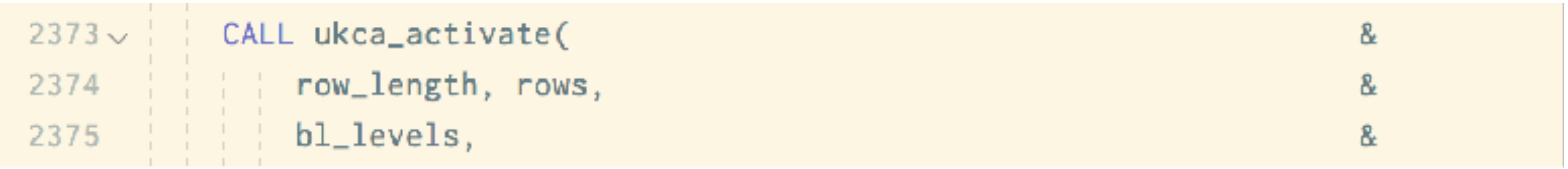
# UKCA/ukca_main1-ukca_main1.F90



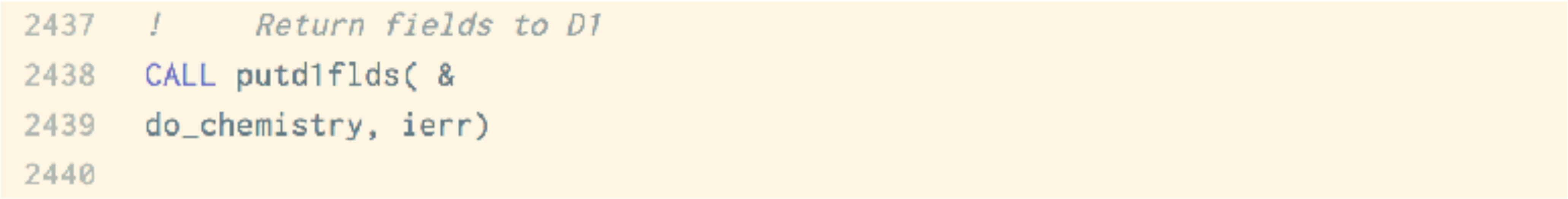
```
CALL ukca_chemistry_ctl(i_month, i_day_number, i_hour,        &
    r_minute - timestep/60.0,                                 &
    REAL(chem_timestep),                                      &
    n_chem_tracers+n_aero_tracers,                            &
```



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

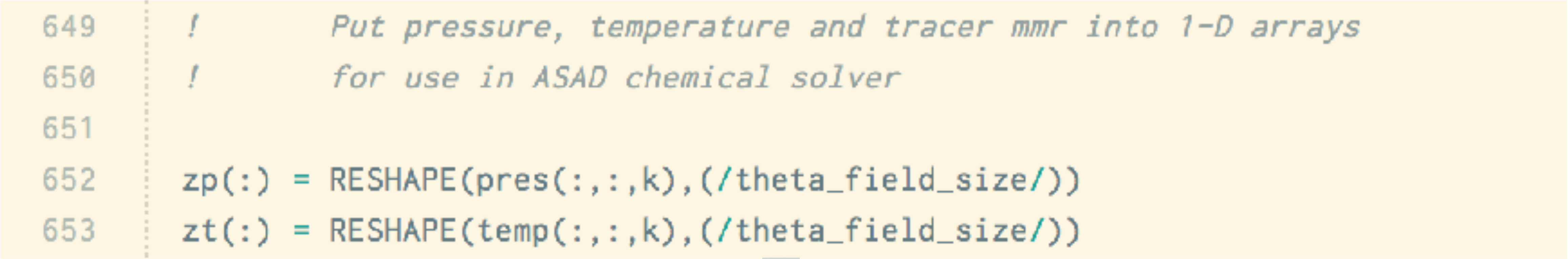


```
CALL ukca_activate(                                           &
    row_length, rows,                                         &
    bl_levels,                                                &
```

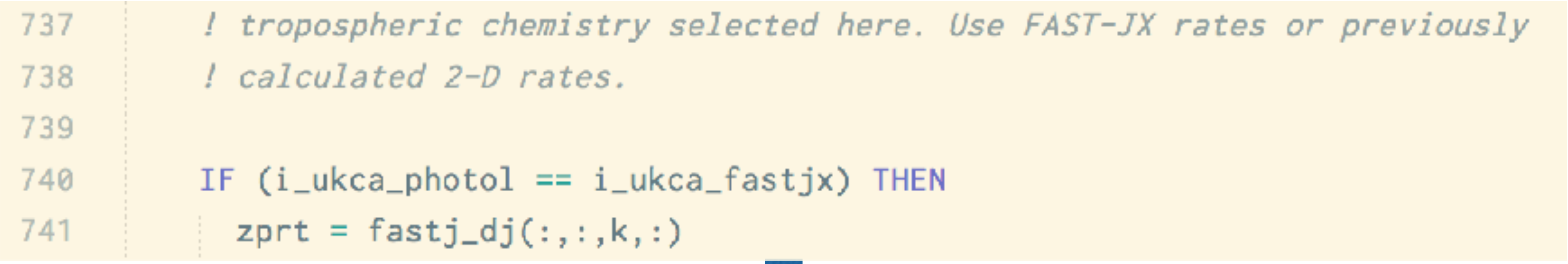


```
!     Return fields to D1
CALL putd1flds( &
do_chemistry, ierr)

```

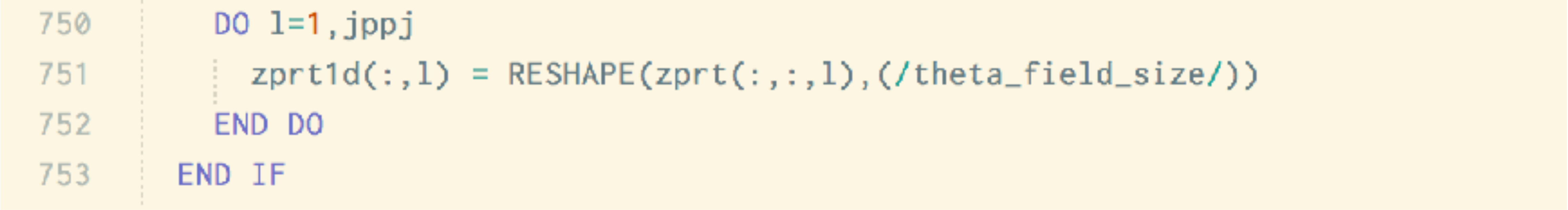
# UKCA/ukca_chemistry_ctl.F90



```
!         Put pressure, temperature and tracer mmr into 1-D arrays
!         for use in ASAD chemical solver

zp(:) = RESHAPE(pres(:,:,k),(/theta_field_size/))
zt(:) = RESHAPE(temp(:,:,k),(/theta_field_size/))
```

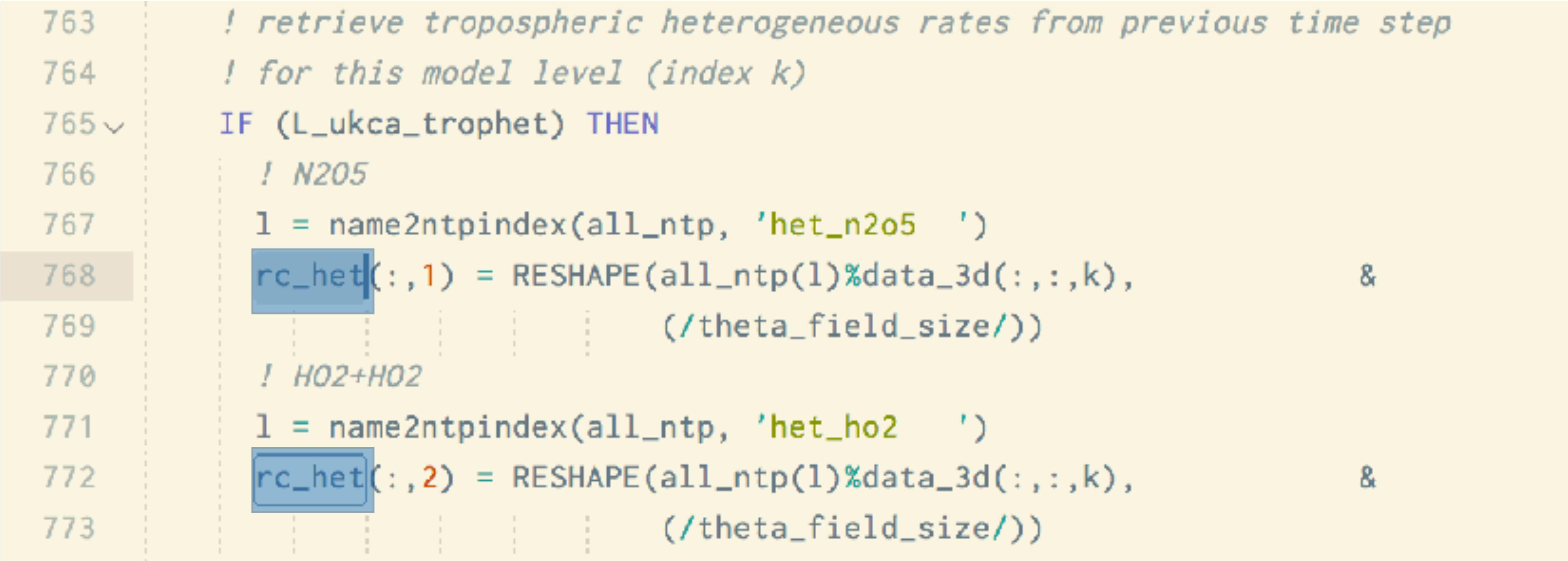


```
! tropospheric chemistry selected here. Use FAST-JX rates or previously
! calculated 2-D rates.

IF (i_ukca_photol == i_ukca_fastjx) THEN
  zprt = fastj_dj(:,:,k,:)
```

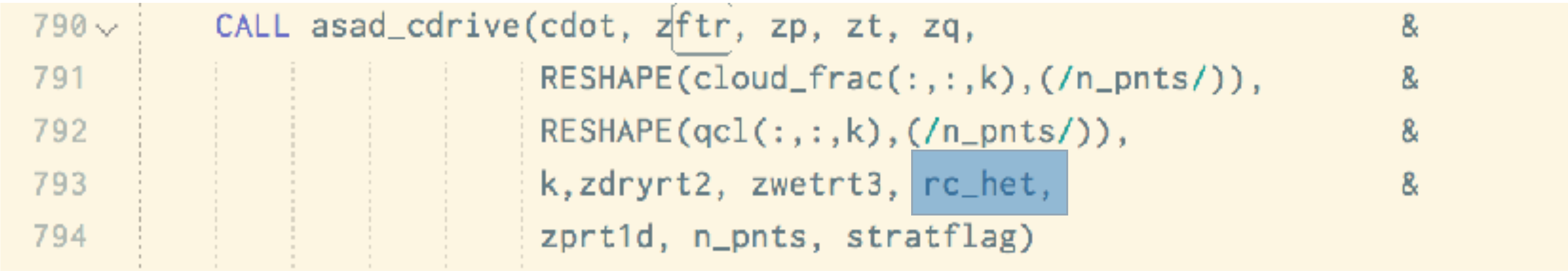


```
  DO l=1,jppj
    zprt1d(:,l) = RESHAPE(zprt(:,:,l),(/theta_field_size/))
  END DO
END IF
```

# UKCA/ukca_chemistry_ctl.F90

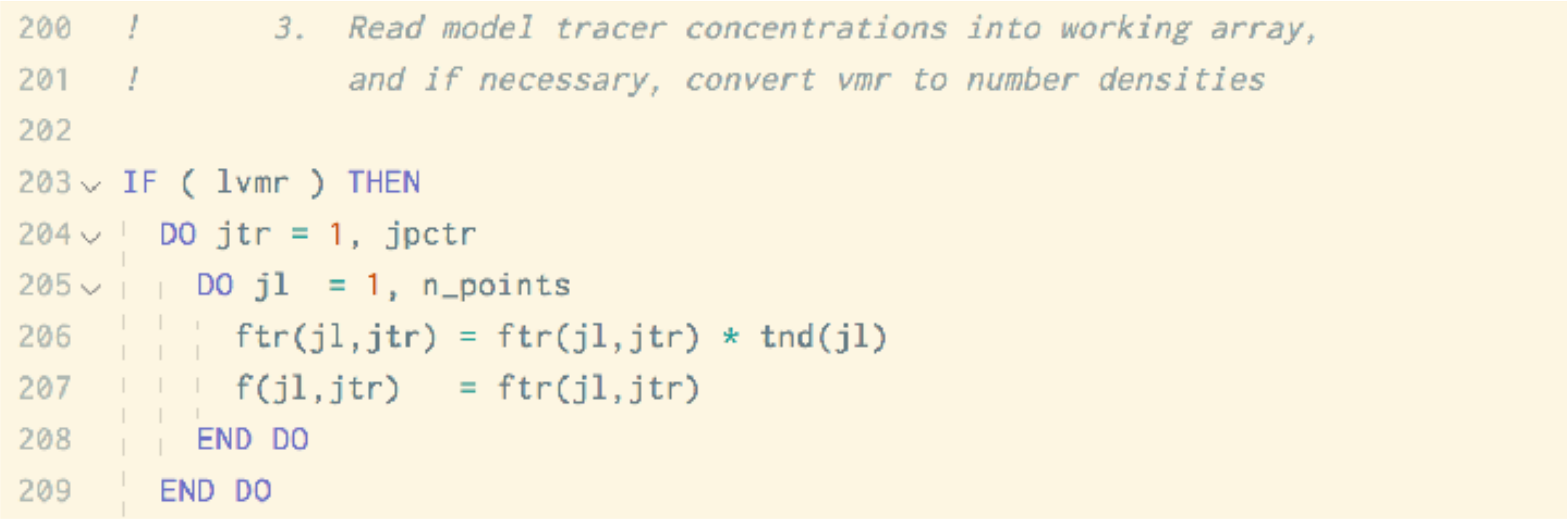


```
! retrieve tropospheric heterogeneous rates from previous time step
! for this model level (index k)
IF (L_ukca_trophet) THEN
  ! N2O5
  l = name2ntpindex(all_ntp, 'het_n2o5  ')
  rc_het(:,1) = RESHAPE(all_ntp(l)%data_3d(:,:,k),     &
                        (/theta_field_size/))
  ! HO2+HO2
  l = name2ntpindex(all_ntp, 'het_ho2   ')
  rc_het(:,2) = RESHAPE(all_ntp(l)%data_3d(:,:,k),     &
                        (/theta_field_size/))
```

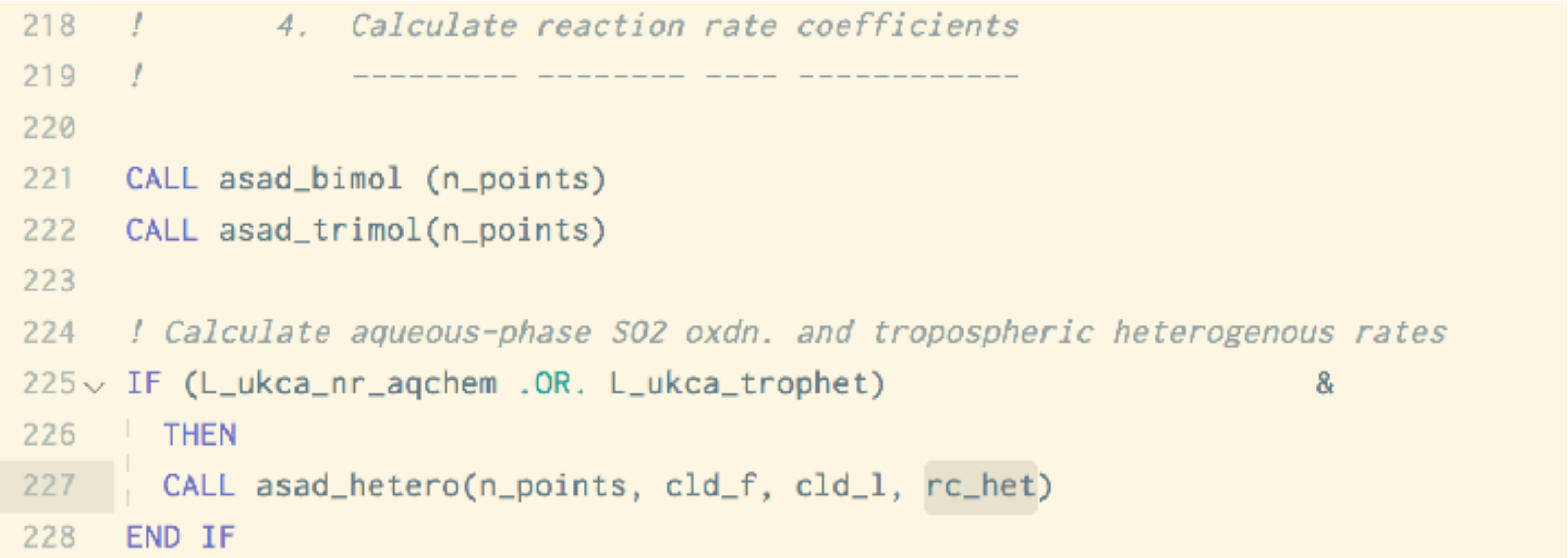


```
CALL asad_cdrive(cdot, zftr, zp, zt, zq,                        &
                 RESHAPE(cloud_frac(:,:,k),(/n_pnts/)),         &
                 RESHAPE(qcl(:,:,k),(/n_pnts/)),                &
                 k,zdryrt2, zwetrt3, rc_het,                    &
                 zprt1d, n_pnts,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

# UKCA/asad_cdrive.F90

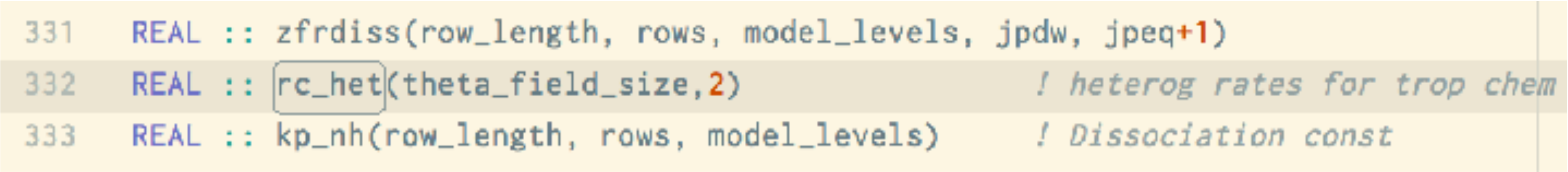


```
!        3.   Read model tracer concentrations into working array,
!             and if necessary, convert vmr to number densities

IF ( lvmr ) THEN
  DO jtr = 1, jpctr
    DO jl  = 1, n_points
      ftr(jl,jtr) = ftr(jl,jtr) * tnd(jl)
      f(jl,jtr)   = ftr(jl,jtr)
    END DO
  END DO
```



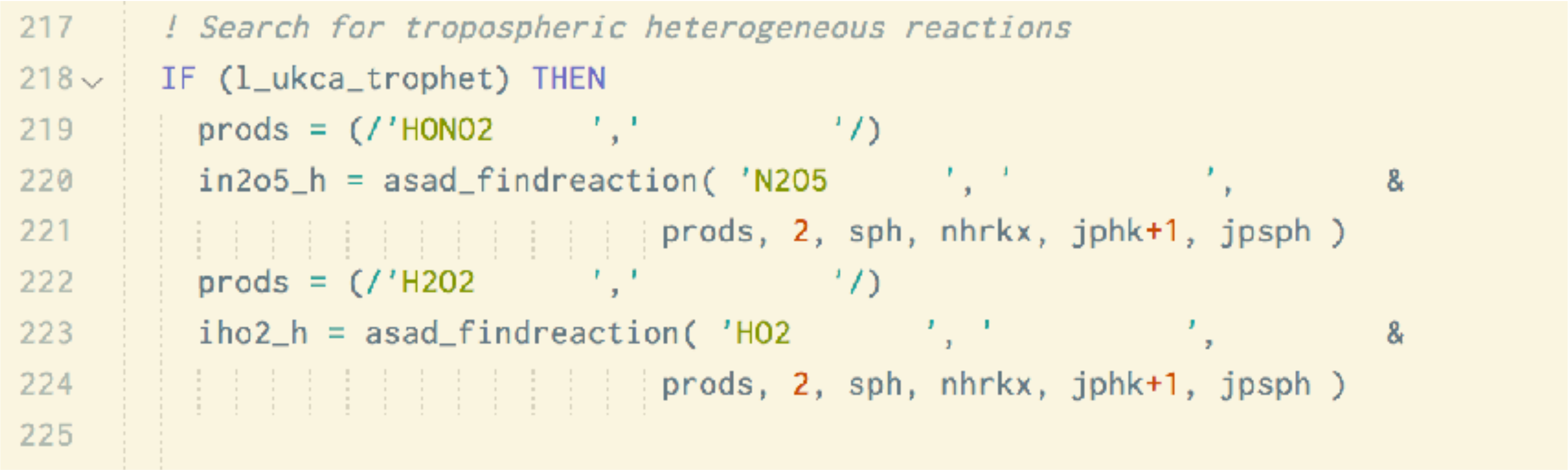
```
!        4.   Calculate reaction rate coefficients
!             --------- -------- ---- ------------

CALL asad_bimol (n_points)
CALL asad_trimol(n_points)

! Calculate aqueous-phase SO2 oxdn. and tropospheric heterogenous rates
IF (L_ukca_nr_aqchem .OR. L_ukca_trophet)                            &
  THEN
  CALL asad_hetero(n_points, cld_f, cld_l, rc_het)
END IF
```

NB

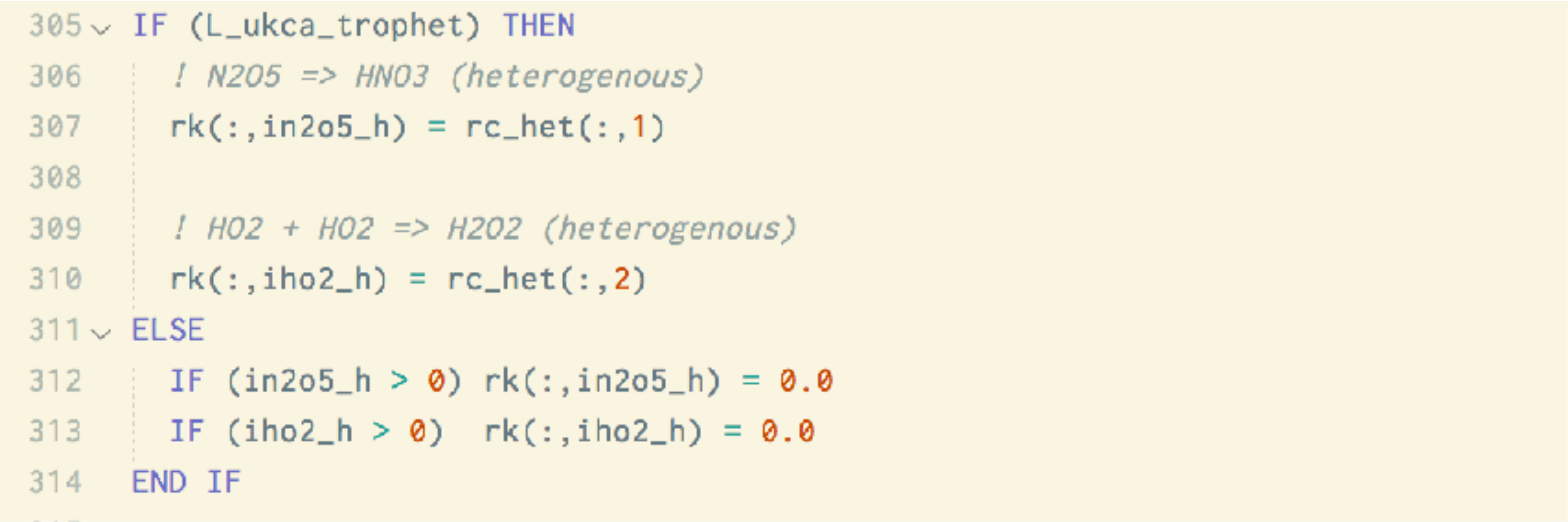


```
REAL :: zfrdiss(row_length, rows, model_levels, jpdw, jpeq+1)
REAL :: rc_het(theta_field_size,2)                   ! heterog rates for trop chem
REAL :: kp_nh(row_length, rows, model_levels)        ! Dissociation const
```

# UKCA/asad_hetero.F90

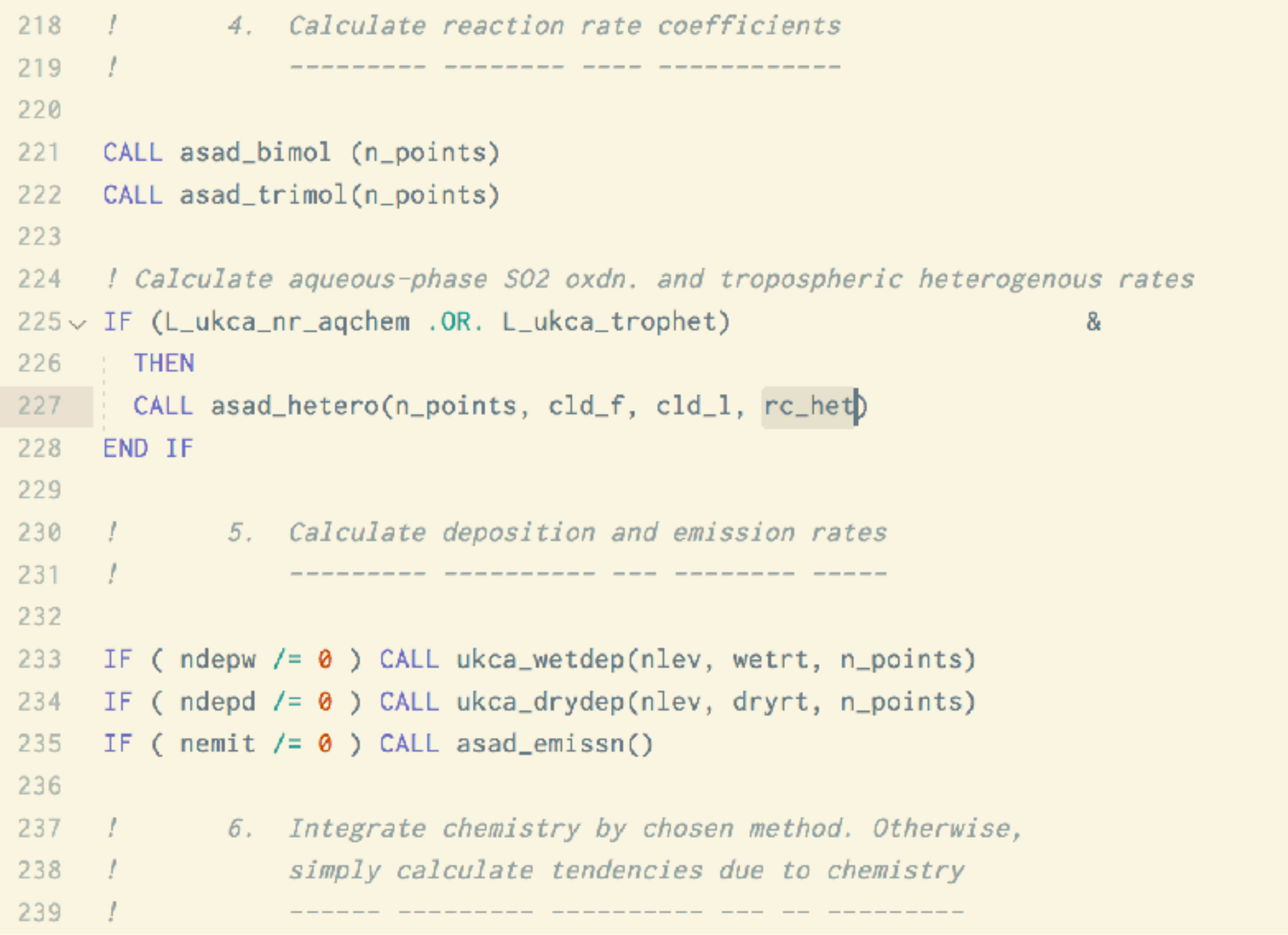


```fortran
  ! Search for tropospheric heterogeneous reactions
  IF (l_ukca_trophet) THEN
    prods = (/'HONO2     ','          '/)
    in2o5_h = asad_findreaction( 'N2O5      ', '          ',         &
                         prods, 2, sph, nhrkx, jphk+1, jpsph )
    prods = (/'H2O2      ','          '/)
    iho2_h = asad_findreaction( 'HO2       ', '          ',          &
                         prods, 2, sph, nhrkx, jphk+1, jpsph )

```



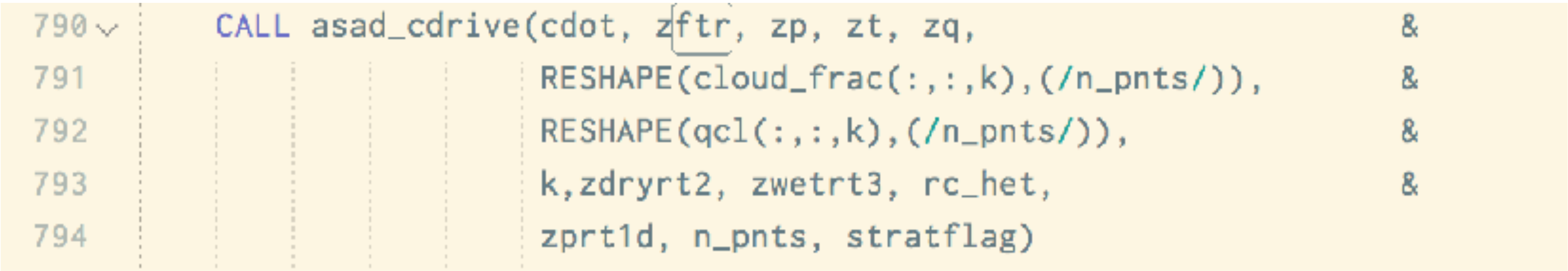
```fortran
IF (L_ukca_trophet) THEN
  ! N2O5 => HNO3 (heterogenous)
  rk(:,in2o5_h) = rc_het(:,1)

  ! HO2 + HO2 => H2O2 (heterogenous)
  rk(:,iho2_h) = rc_het(:,2)
ELSE
  IF (in2o5_h > 0) rk(:,in2o5_h) = 0.0
  IF (iho2_h > 0)  rk(:,iho2_h) = 0.0
END IF
```

# UKCA/asad_cdrive.F90

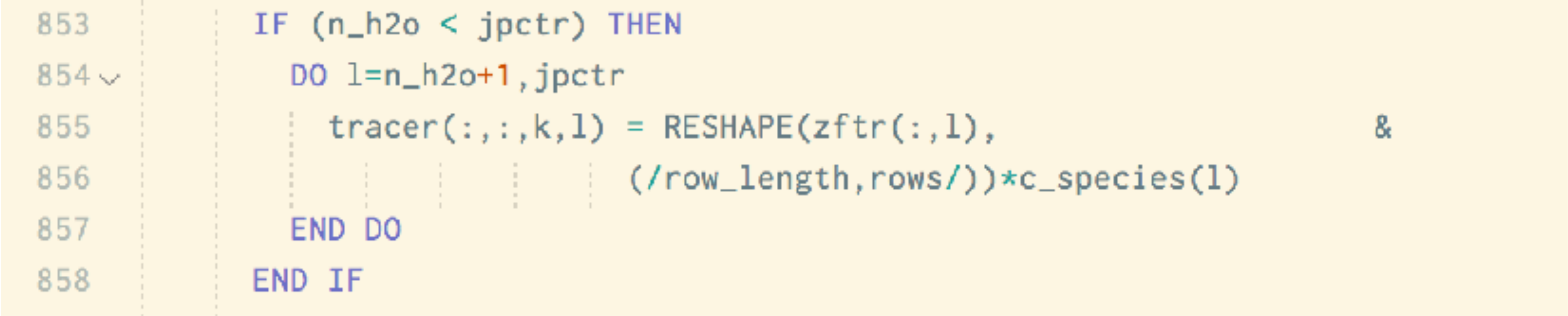


```
!       4.   Calculate reaction rate coefficients
!            --------- -------- ---- ------------

CALL asad_bimol (n_points)
CALL asad_trimol(n_points)

! Calculate aqueous-phase SO2 oxdn. and tropospheric heterogenous rates
IF (L_ukca_nr_aqchem .OR. L_ukca_trophet)                        &
  THEN
  CALL asad_hetero(n_points, cld_f, cld_l, rc_het)
END IF

!       5.   Calculate deposition and emission rates
!            --------- ---------- --- -------- -----

IF ( ndepw /= 0 ) CALL ukca_wetdep(nlev, wetrt, n_points)
IF ( ndepd /= 0 ) CALL ukca_drydep(nlev, dryrt, n_points)
IF ( nemit /= 0 ) CALL asad_emissn()

!       6.   Integrate chemistry by chosen method. Otherwise,
!            simply calculate tendencies due to chemistry
!            ------ --------- ---------- --- -- ---------
```

# UKCA/ukca_chemistry_ctl.F90

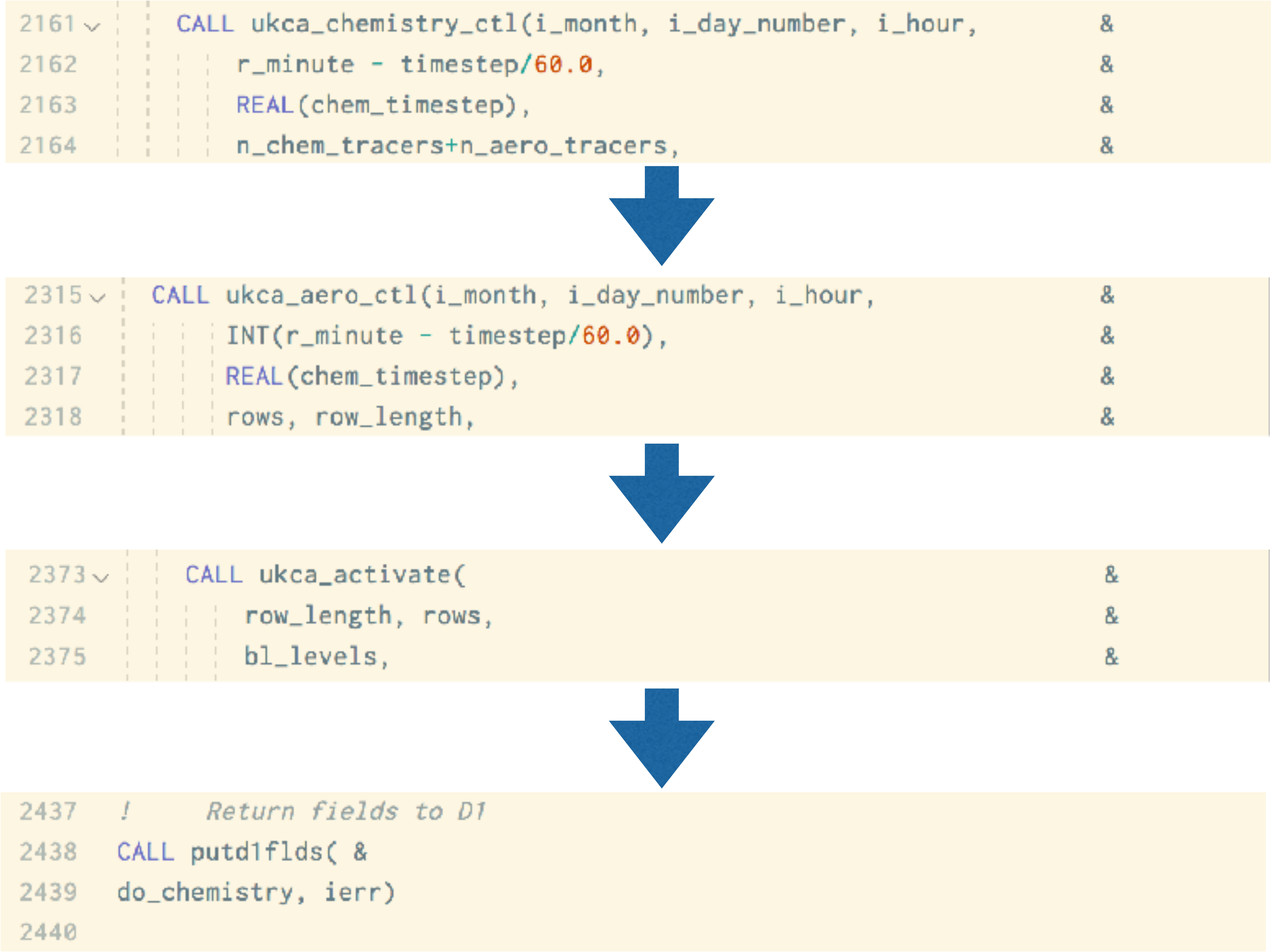


```
    CALL asad_cdrive(cdot, zftr, zp, zt, zq,                      &
                     RESHAPE(cloud_frac(:,:,k),(/n_pnts/)),       &
                     RESHAPE(qcl(:,:,k),(/n_pnts/)),              &
                     k,zdryrt2, zwetrt3, rc_het,                  &
                     zprt1d,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



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

# UKCA/ukca_main1-ukca_main1.F90



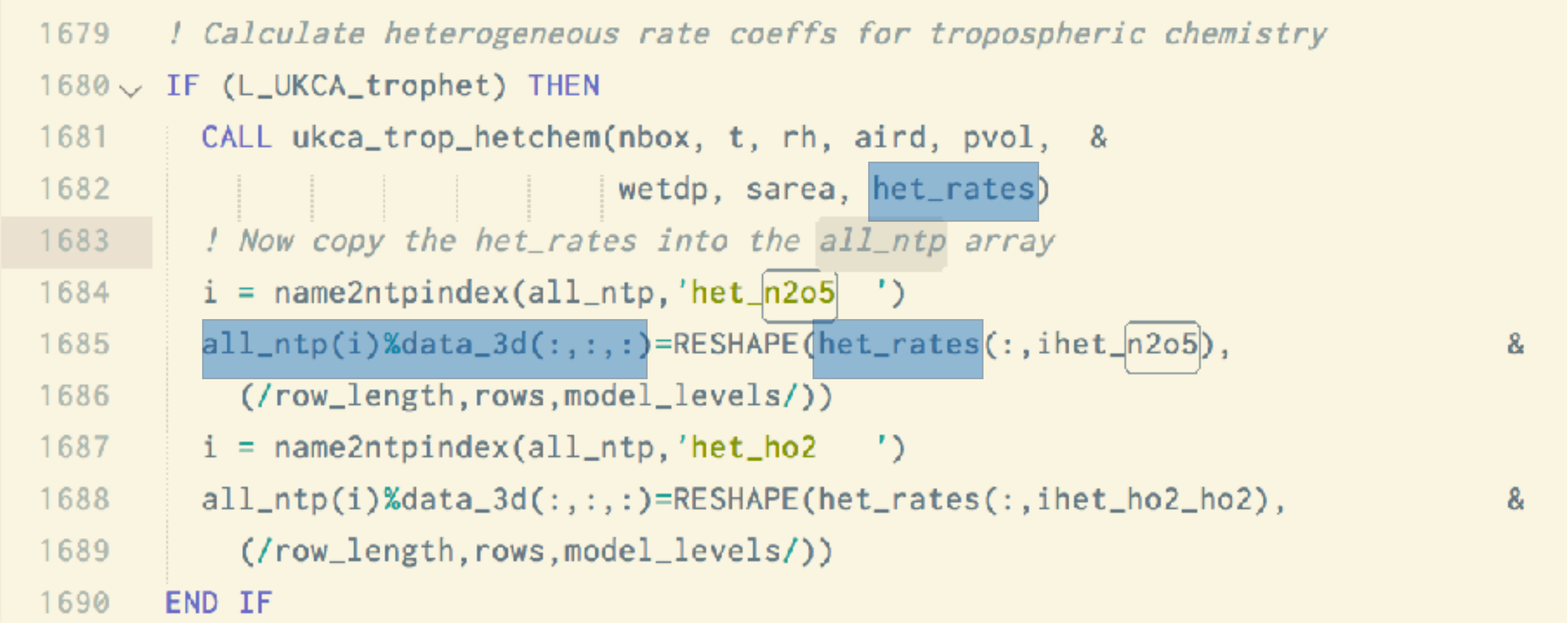
```
CALL ukca_chemistry_ctl(i_month, i_day_number, i_hour,        &
    r_minute - timestep/60.0,                                 &
    REAL(chem_timestep),                                      &
    n_chem_tracers+n_aero_tracers,                            &
```

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

```
CALL ukca_activate(                                           &
    row_length, rows,                                         &
    bl_levels,                                                &
```

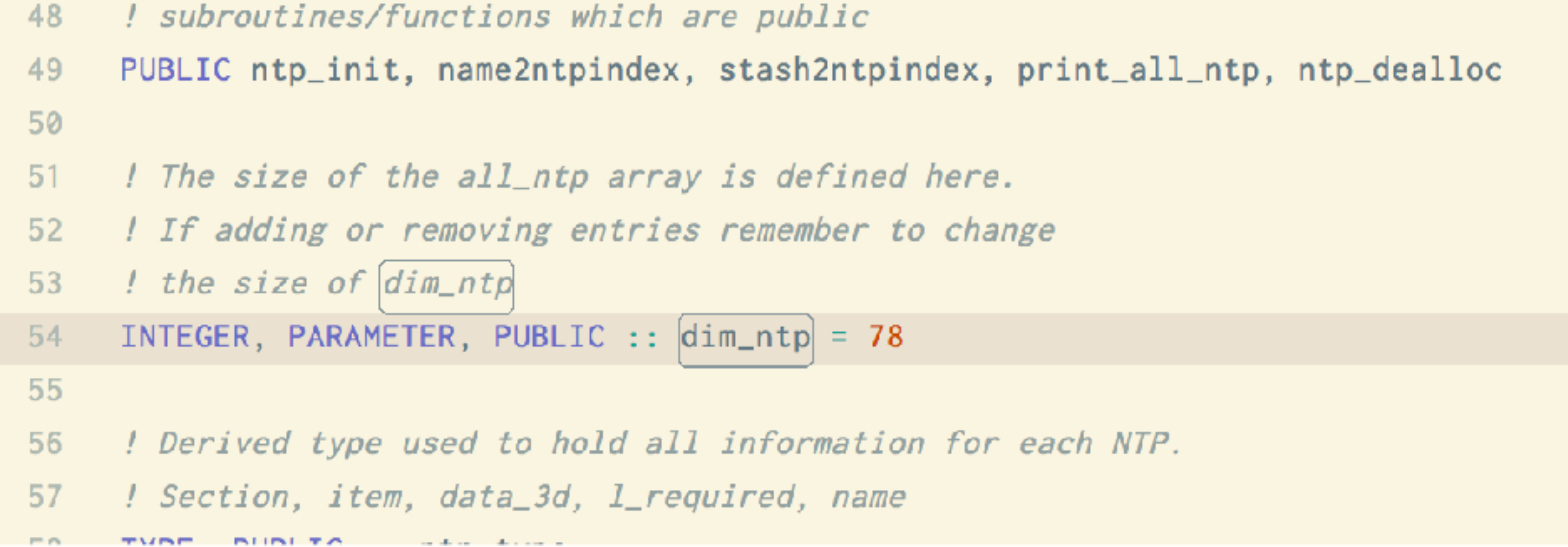
```
!     Return fields to D1
CALL putd1flds( &
do_chemistry, ierr)

```

# UKCA/ukca_aero_ctl.F90

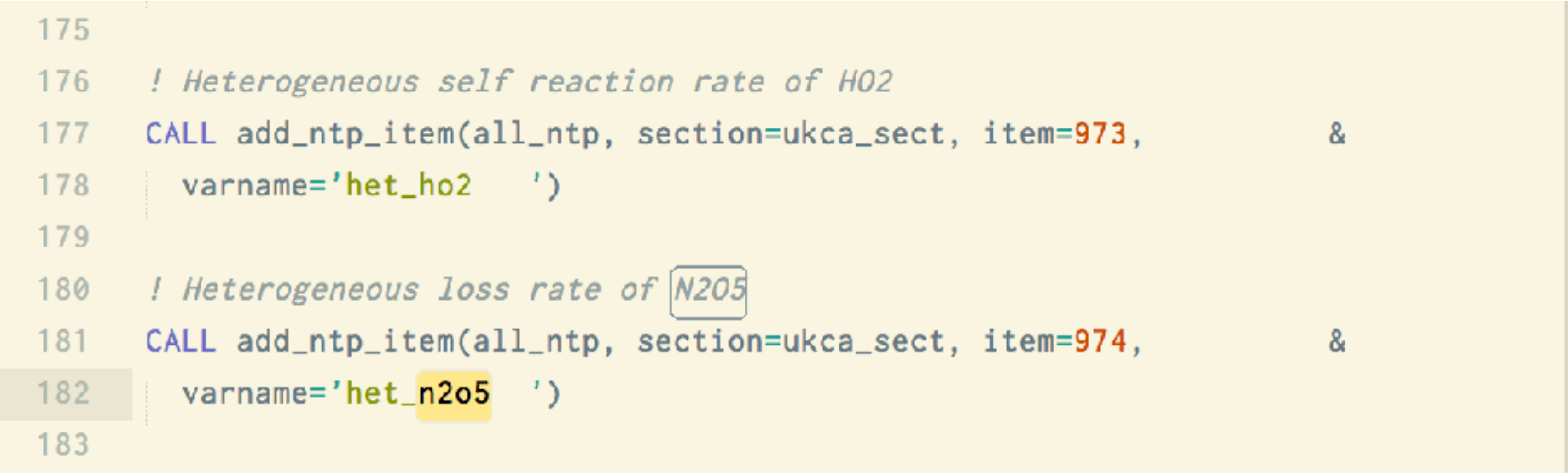


```
! Calculate heterogeneous rate coeffs for tropospheric chemistry
IF (L_UKCA_trophet) THEN
  CALL ukca_trop_hetchem(nbox, t, rh, aird, pvol,  &
                         wetdp, sarea, het_rates)
  ! Now copy the het_rates into the all_ntp array
  i = name2ntpindex(all_ntp,'het_n2o5  ')
  all_ntp(i)%data_3d(:,:,:)=RESHAPE(het_rates(:,ihet_n2o5),               &
    (/row_length,rows,model_levels/))
  i = name2ntpindex(all_ntp,'het_ho2   ')
  all_ntp(i)%data_3d(:,:,:)=RESHAPE(het_rates(:,ihet_ho2_ho2),            &
    (/row_length,rows,model_levels/))
END IF
```

# UKCA/ukca_ntp_mod.F90

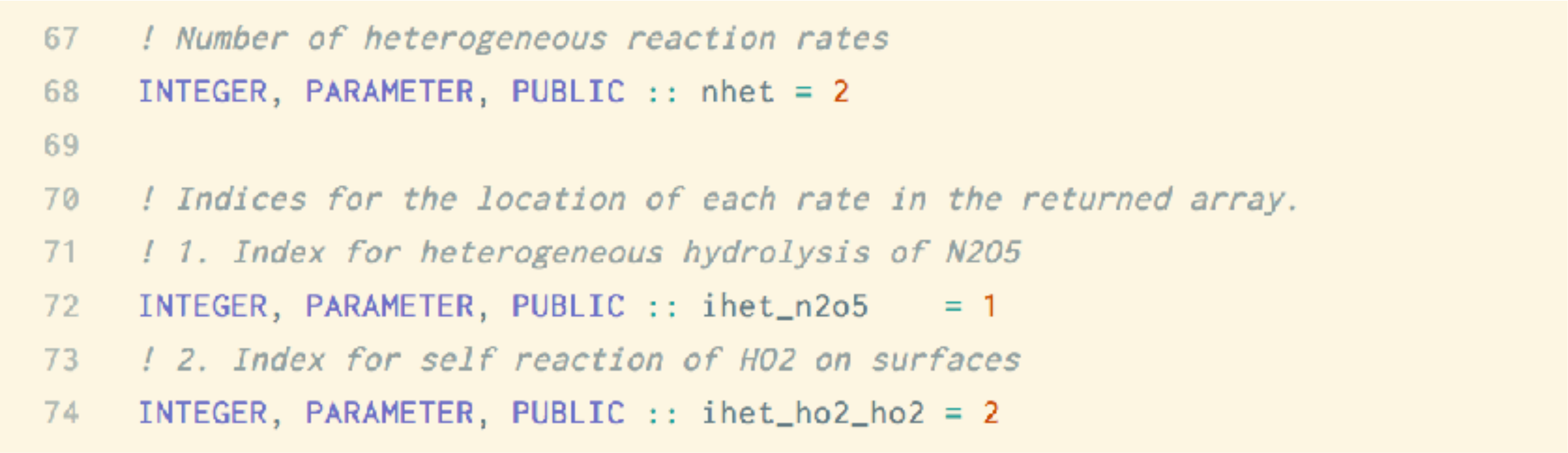


```fortran
! subroutines/functions which are public
PUBLIC ntp_init, name2ntpindex, stash2ntpindex, print_all_ntp, ntp_dealloc

! The size of the all_ntp array is defined here.
! If adding or removing entries remember to change
! the size of dim_ntp
INTEGER, PARAMETER, PUBLIC :: dim_ntp = 78

! Derived type used to hold all information for each NTP.
! Section, item, data_3d, l_required, name
TYPE, PUBLIC :: ntp_type
```



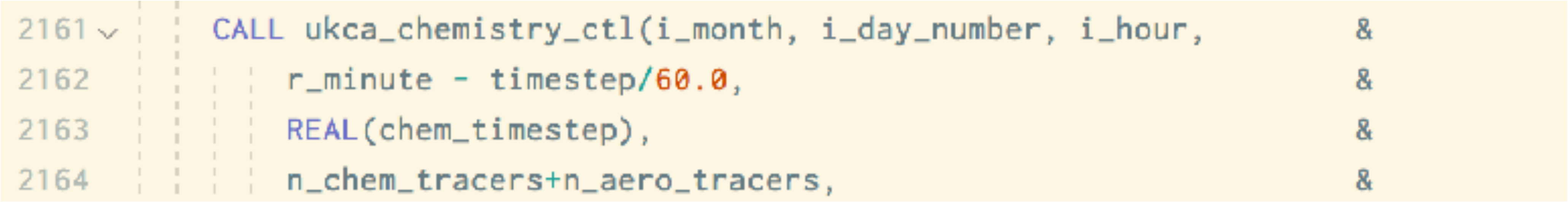
```fortran

! Heterogeneous self reaction rate of HO2
CALL add_ntp_item(all_ntp, section=ukca_sect, item=973,          &
  varname='het_ho2   ')

! Heterogeneous loss rate of N2O5
CALL add_ntp_item(all_ntp, section=ukca_sect, item=974,          &
  varname='het_n2o5  ')

```

# UKCA/ukca_trop_hetchem.F90

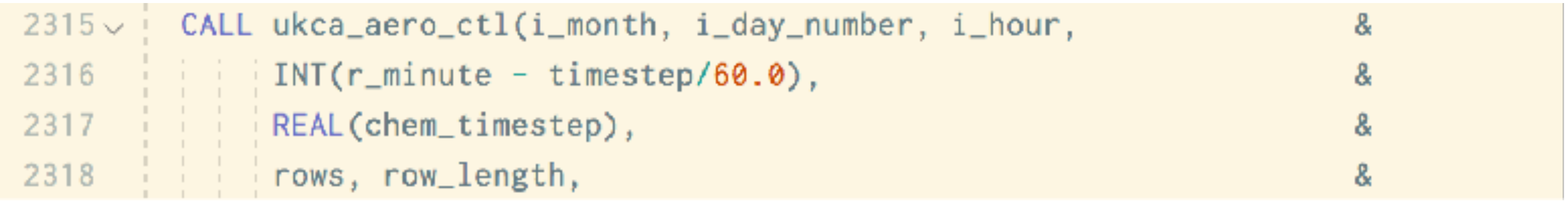


```fortran
! Number of heterogeneous reaction rates
INTEGER, PARAMETER, PUBLIC :: nhet = 2

! Indices for the location of each rate in the returned array.
! 1. Index for heterogeneous hydrolysis of N2O5
INTEGER, PARAMETER, PUBLIC :: ihet_n2o5    = 1
! 2. Index for self reaction of HO2 on surfaces
INTEGER, PARAMETER, PUBLIC :: ihet_ho2_ho2 = 2
```

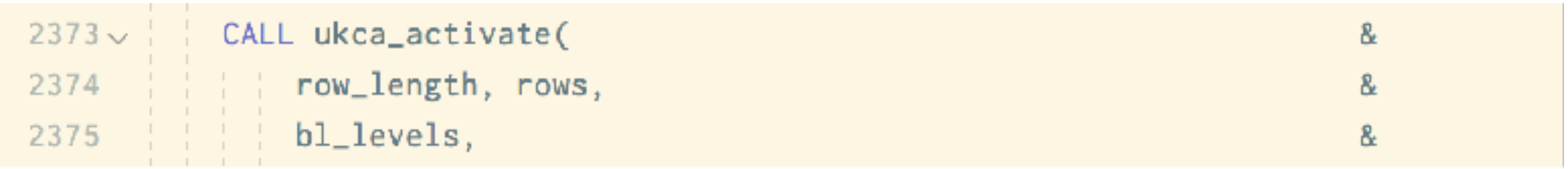
# UKCA/ukca_main1-ukca_main1.F90



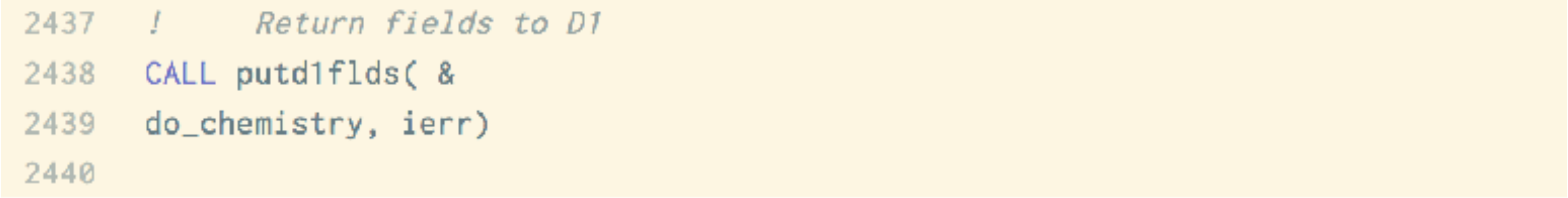
```fortran
    CALL ukca_chemistry_ctl(i_month, i_day_number, i_hour,        &
        r_minute - timestep/60.0,                                 &
        REAL(chem_timestep),                                      &
        n_chem_tracers+n_aero_tracers,                            &
```



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



```fortran
    CALL ukca_activate(                                           &
        row_length, rows,                                         &
        bl_levels,                                                &
```



```fortran
!     Return fields to D1
CALL putd1flds( &
do_chemistry, ierr)

```

# 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.