# Supplement of "The MESSy chamber DWARF: a box model for simulating chamber experiments (MESSy v2.55.2)"

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## S1. MESSy's submodels

In order to employ MESSy's submodels in the chamber DWARF for the purpose of simulating chamber processes, it is necessary to configure the namelist syntax of individual submodels accordingly. The subsequent section will present an example and the syntax configuration for each submodel.

### S1.1. Submodel PTRACINI

Submodel PTRACINI (Prognostic TRACer INItialisation) initializes tracer to a value at one specific point in time or it permanently nudges tracers to a given value(Kerkweg et al., 2025). The value can be either a constant (set in the namelist) or it can be provided by a channel object (which name ist provided in the namelist). Chamber DWARF uses this submodel to describe the chemical point-in-time injection of an experiment and constrains a variable to existing data.

PTRACINI submodel also constrains a tracer to observed data provided by other channel object example of `TRINI(2)` in Fig. S1.

```
!------------------------------------------------------------------------------
! -*- f90 -*-
&CPL
!The following lines for emissions and nudging have been derived from star data automatically:
TRINI(1)%INI1STEP = T
TRINI(1)%EVENT_START = 2022,04,06,08,00,0
TRINI(1)%EMIS_IOEVENT  = 1,'steps','first',0
TRINI(1)%TRACER = 'O3','','','','','','','','','',
TRINI(1)%CRIT(1)='','','IF',20E-9,'',''

TRINI(2)%INI1STEP = T
TRINI(2)%EVENT_START = 2022,04,06,08,00,0
TRINI(2)%EMIS_IOEVENT  = 1,'steps','first',0
TRINI(2)%TRACER = 'NO','','','','','','','','','',
TRINI(2)%CRIT(1)='scalc','NO_constrain','IF',,'',''
/
!------------------------------------------------------------------------------
```

**Figure S1.** Example namelist file `ptracini.nml` for the MESSy submodel PTRACINI. `TRINI(1)` establishes an injection at 06 April 2022 08:00 (`TRINI(1)%EVENT_START`) in one time step (`INI1STEP = T`). This injection sets the mixing ratio of Ozone (`O3`) to $20 \cdot 10^{-9}$ mol mol$^{-1}$. In TRINI(2), the `NO` mixing ratio is constrained to `NO_constrain` variable provided by SCALC submodel (TRINI(2)%CRIT(1)).

### S1.2. Submodel TREXP

In 3D simulations, the MESSy submodel TREXP is used to define new tracers (including one degradation reaction) and point sources of tracers via a namelist (Jöckel et al., 2010). MESSy's submodel TREXP (Tracer Release EXperiments from Point sources) is used to define new tracers (including one degradation reaction) and point sources of tracers via namelist (Jöckel et al., 2010). The degradation reaction of a tracer can be either first-order or second-order decay.

TREXP is used for the simulation of two processes in the chamber DWARF. On the one hand side. the dilution, which is a processes, that can be treated as the first order of decay, is simulated via this submodel. On the other hand side, the continuous injection of a chemical into a chamber is described by the point sources emission of tracers function. This function is useful for steady-state chambers in which the chemicals are continuously released into the chamber.

In Figure S2, ozone (`TR(1)`) is diluted with a decay rate of 0.00025 mol s$^{-1}$. Additionally, a continuous injection of $\alpha$-pinene from 06 April 2022, 12:00:00 to 14 April 2022, 16:00:00 proceeds with an injection rate of 3 x $10^{-10}$ mol s$^{-1}$. Continuous injection is identified by starting key "POINT(1)" which follow up with longitude, latitude, level and height (from the ground to chamber level).

```
!------------------------------------------------------------------
! -*- f90 -*-
&CPL
! ### O : ORDER
!         = 0 : dx/dt = -ka * x       + p , [ka] = 1/s , Ta = 0
!         = 1 : dx/dt = -ka * x * [Y] + p , [ka] = cm3/s
!         = -1: dx/dt = -k  * x * [Y] + p , [ka] = cm3/s
!               k = ka + c_air*kb           [kb] = cm6/s, [c_air] = 1/cm3
!         = -2: CH4 + OH : k = 1.85E-20 * exp(2.82*log(T) - 987/T)
!         = -3: SO2 + OH : K = k_3rd(T,cair,3.3E-31,4.3,1.6E-12,0.,0.6)
!         (p: production, x: mixing ratio, Y: reaction partner)
! ### Ta: O=0 : Ta=0
!         O=1 : ACTIVATION TEMPERATURE      [Ta] = K
!         O=-1: PRESSURE DEPENDENCE         [Ta] = cm6/s
!                                                      ONLY FOR ORDER=1
!                                                    |==================|
! 'tracer-set(s);', 'tracer-name[_subname]', ORDER, ka, Ta, 'channel', 'object'
TR(1) = 'gp', 'O3', 0, 0.00025,0,'','' ,
! ### LIST OF RELEASE POINTS AND TIME
! LON [-180 ... 180], LAT [-90 ... 90], LEV [hPa], MASS [kg],
! YYYY, MM, DD, HH, MI, SE, YYYY, MM, DD, HH, MI, SE, tracer_list
POINT(1) = 3,  6.411,50.909,
           10., 'm AGL', 3E-10, 'mol/s', 2022, 04,
           06, 12, 00, 00, 2022, 04, 14, 16, 00, 00,
           '','','', 1.0,
           'gp', 'APINENE',
/
!-----------------------------------------------------------
```

**Figure S2.** Example namelist file `trexp.nml` for the MESSy submodel TREXP. `TR(1)` establishes a first order decay reaction of ozone (O3) with a constant rate of 0.0025. `POINT(1)` introduces an injection point located at 50.909 $^o$ N, 6.411$^o$ E, 10 m height from the ground, the injection rate of tracer APINENE is 3 x $10^{-10}$ mol $s^{-1}$ for a period of time from 06 April 2022, 12:00:00 to 14 April 2022, 16:00:00.

### S1.3. Submodel SCALC

The MESSy submodel, SCALC (Simple CALCulations) provides the functionality to apply simple math operations with "channel objects" (Jöckel et al., 2016). In the chamber DWARF, SCALC can be used to create missing photolysis rates by scaling of others or profile of chemicals from measurement. An application example for the SCALC submodel is illustrated by scaling the inorganic mass from observation (`CALC(2)` entry in Fig. S3). The estimated scaling factor is given by Eq. (S1).

```
!-------------------------------------------------------------------------------
! -*- f90 -*-
&CPL
CALC(1) = 'temp','import_grid:inp3d_xlm1%0.;import_ts:temp%1.', 'MULT1D', 'messy_init_tracer;messy_global_start',
!-------------------------------------------------------------------------------
CALC(2) = 'HRSO4','import_grid:inp3d_xlm1%0.;import_ts:HRSO4%1.04E-2', 'MULT1D', 'messy_init_tracer;messy_global_start',
/
!-------------------------------------------------------------------------------
```

**Figure S3.** Example namelist file `scalc.nml` for the MESSy submodel SCALC. `CALC(1)` simply maps the 0D time series as read in by IMPORT_TS (`import_ts:temp%1.`) to the model internally required 3D grid (done by multiplifcation with the 3D field `import_grid:inp3d_xlm1`) which is multiplied by zero to provide the grid, but to not influence the result. `CALC(2)` applies this regridding and additionally scales the`HRSO4` object provided by IMPORT_TS with the factor $1.04e^{-2}$.

$$C_{inorg\_scaled}(t) = \frac{C^0_{inorg}}{N^0_p} * N_p(t) \tag{S1}$$

Furthermore, SCALC is used for a numerical trick. As MESSy is mostly used for 3-dimensional simulations, the internal dimensions are always 3-dimensional. As the input data from a chamber experiment is just 0-dimensional, SCALC is used to enlarge the data from scalar to three dimensions. This is achieved with the marker `MULT1D` as in the namelist entries `CALC(1)` in Fig. S3.

### S1.4. Submodel MECCA

The most essential element of the chamber DWARF is the submodel MECCA (Module Efficiently Calculating the Chemistry of the Atmosphere). This atmospheric chemistry module incorporates a comprehensive chemical mechanism encompassing tropospheric and stratospheric chemistry of both the gas and aqueous phases, as referenced in Sander et al. (2019). The Fig. S4 illsutrates the configuration of `mecca.nml` for simulating chamber experiment.

#### S1.4.1. Chamber gas wall loss

In order to apply the gas wall loss (GWL) to the simulation, it is necessary to use the `modenumber` '0' (Fig. S4: `modenumber(2) = 0`). The type of gas wall loss can be defined by the variable `def_wall`. The initial option is designated as `'reference'`, representing the wall loss rate from the CUEC chamber (Krechmer et al., 2016, 2020). This option enables the assessment of chamber gas wall loss with a reference loss constant rate, applicable to Teflon chambers ranging from size 6 to 20 $m^3$. In contrast, the `'STAR'` option is customized for GWL of SAPHIR-STAR chamber. The third option (`'custom'`) is for customizing individual chamber experiment. If the `'custom'` option is selected, the forward and backward chamber wall exchange coefficients of the gas species ($RO_2$, LVOCs, SVOCs)

```
&CTRL_KPP
icntrl(3) = 4
/
&CTRL
l_chamexp = T
/
&CPL_CHAMEXP
aerosol_module = 'chamber',
!define aerosol:
str_number = 'import_ts:num1,num1'
inp_aerosol_wetradius = 'import_ts','wetradius'
inp_aerosol_dryradius = 'import_ts','dryradius'
inp_aerosol_sigma     = 'import_ts','sigma'
!Aerosol phase and chamber wall
modenumber(1)  = 1
modenumber(2)  = 0  !Mode number 0 represent chamber wall
def_wall = 'STAR' !'reference': wall loss rate from CUEC chamber
        !'STAR': wall loss rate from for SAPHIR-STAR study
        !'custom' set constant value of GWL
        !'' no GWL apply
!Set 'custom' exchange rate with chamber wall
!       kf_wall: rate forward to wall
!  kb_wall: rate backward from wall
!     k*_wall = 'RO2, LVOCs, SVOCs'
kf_wall = 5.83E-3, 5.83E-3, 0
kb_wall = 0E-3, 0., 0.0
precursor = 'TERP'
density_method = 'UManSysProp' !'UManSysProp': based on UManSysProp
                    !'HC_OC': based on H/C and O/C ratio
lwc_method = 'growth_factor'
! 'V_solutes':use volume of solutes (aqueous: SO4mm, HSO4m, NO3m, NH4p, [organic])
! 'growth_factor': use growth factor
l_vol_org  = F   !Organic volume as dry volume
gf_method = 'estimation' !'estimation' (only for ammonium sulfate) or 'constant'
gf_inorg = 1.3    !Inorganic's growth factor
gf_org =  1.0         !Organic's growth factor
TAG_SPEC(1) = 'LAPINABO2','','G40203'
TAG_SPEC(2) = 'LAPINABO2','NO','G40201a, G40201b'
TAG_SPEC(3) = 'LAPINABO2','HO2','G40202a, G40202b'
/
```

**Figure S4.** Example namelist file `scalc.nml` for the MESSy submodel SCALC.

need to be provided in that order in the namelist (`kf_wall` and `kb_wall`, respectively). All the exchange coefficients should be provided in 1/s.

The `precursor` variable is used in the conversion of Henry coefficients to volatility (C*). The `precursor` variable can be selected from six possible options: 'ARO1' (toluene); 'ARO2' (xylenes); 'OLE1' (C12 internal olefins); 'OLE2' (C12 external olefins); 'ALK4' (C8 n-alkane); 'ALK5' (C18 n-alkane); and 'TERP' (a mixture of $\alpha$-pinene, $\beta$-pinene, and limonene) (Hodzic et al., 2014).

### S1.4.2. Growth factor calculation

Two possible ways of growth factor (gf) calculation are currently implemented in the model. The growth factor for ammonium sulfate seed is estimated during the simulation by choosing the growth factor calculation method (`gf_method`) as `'estimation'`.

$$k_e = exp(\frac{4MW_w\sigma_{sol}}{RT\rho_w D_p}) \tag{S2}$$

$$a_w = \frac{RH}{K_e} \tag{S3}$$

$$GF_{AS} = [1 + (a + b * a_w + c * a_w^2) * \frac{a_w}{1 - a_w}]^{\frac{1}{3}} \tag{S4}$$

Where $K_e$ is the corrected factor for the Kelvin term, $MW_w$ is molecular weight of water of water, R is the universal gas constant, T is temperature. The $\sigma_{sol}$ is the surface tension of the solution and assumed to equal to that of pure water ($\sigma_{sol}$=$\sigma_w$=0.072 J $m^{-2}$). The $a_w$ is water activity of the solution droplet, RH is relative humidity. The fitting constants for GF-aw relationship a, b, c for ammonium sulfate with Kelvin corrected from the work of (Kreidenweis et al., 2005) is used.

If the `gf_method` is selected as `'constant'`, users can directly provide the growth factor of inorganic matter from the experiment via the variable `gf_inorg`. The growth factor of organic matter (`gf_org`) is a constant parameter. In this study, it is assumed that textttgf_org represents organic matter that does not absorb water.

As illustrated in Figure S5, the model demonstrates the outcomes of employing alternative methods to estimate LWC and organic density. The LWC estimation derived from the application of the growth factor was found to be less than that obtained from the utilization of solute volume. The two methods demonstrate a dependence on inorganic mass (ammonium and sulfate) by predicting an increase in LWC as inorganic mass rises. In this $\alpha$-pinene photooxidation experiment, the elemental method predicted organic aerosol density of approximately 1.38 $gcm^{-3}$ under high $NO_x$ condition. This method shows the lower organic aerosol density with decreasing $NO_x$ levels. On the other hand, the organic density estimated from the UManSysProp method remained stable throughout the experiment. Given that, the mean predicted density of aerosol is consistent across the two methods. This phenomenon

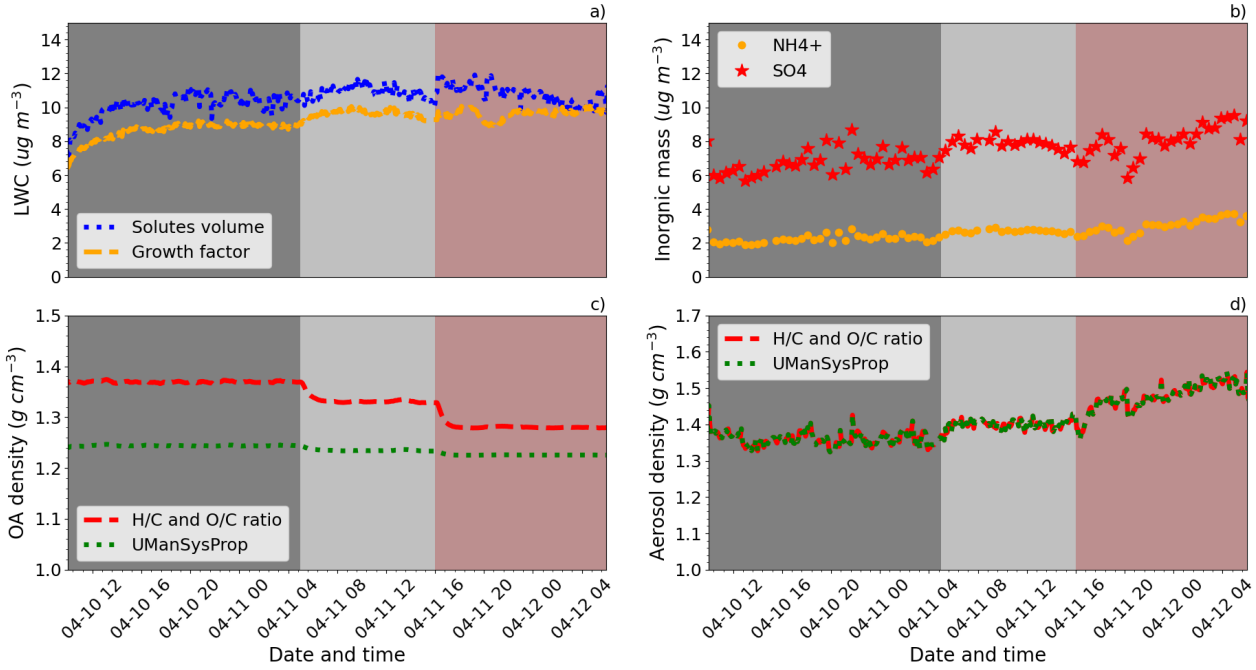


**Figure S5.** Model results of organic density and aerosol density by using element method and UManSysProp method. The inorganic masses are measured data from AMS measurement. OA density is mean density of organic component in aqueous phase. Aerosol density is the liquid aerosol accounting inorganic, organic compounds and water. An increase in aerosol density is observed as the experiment progresses, despite the increases in organic mass. The reason is that the amount of inorganic matter that was injected also increased accordingly.

can be attributed to the fraction of organic mass present within the total aerosol mass. In this experiment, the organic mass constituted approximately 12 to 13% of the total aerosol mass. Consequently, the discrepancy in the estimated organic aerosol density between the two simulations was negligible.

### S1.4.3. Chemical loss diagnostic

A function for tracking the loss tendencies of a species has been implemented. The `TAG_SPC()` function in `mecca.nml` triggers the book-keeping of a species' loss tendency to another reactant. In MECCA all reactions are labeled with so-called equation tags. These are used here to identify the reaction, which should be taken into account. As illustrated in figure S4, `TAG_SPEC(1)` tags the loss tendency of LAPINABO2 in its reaction with other $RO_2$, as defined by the reaction tag name `G40203`. The function also allows for the estimation of the total loss due to multiple reactions with the same reactant. The tags `TAG_SPEC(2)` and `TAG_SPEC(3)` illustrate the syntax for estimating the loss tendency of LAPINABO2 to NO, as indicated by the reaction tags `G40201a` and `G40201b`. Similarly, they demonstrate the loss to reaction with $HO_2$, as specified by the reaction tags `G40202a` and `G40202b`.

## S2. Teflon wall emission

Teflon film (FEP) is commonly used as a wall's material in many environment chambers such as the SAPHIR chamber and the BATCH chamber. The Teflon wall can emit precursors (HONO, HCHO...) into the chamber during light exposure experiments (Rohrer et al., 2005). We take this factor into account when simulating SAPHIR. Photochemical reactions of artificial species namely SHONO, SHCHO are added on top of the actual chemical mechanism to mimic emissions of respective species (HONO, HCHO, ...) from chamber wall Eq. (R1)-(R8). The artificial reaction coefficients depend on the photolysis frequency of $NO_2$, relative humidity and temperature. We assume that the reactive chemicals are constantly emitted from the chamber wall during irradiation. The concentration of artificial species is constant and can be modified for fitting model prediction with observation.

$$\mathrm{SHONO} + \mathrm{hv} \rightarrow \mathrm{HONO} \quad \text{(R1)}$$

$$\mathrm{SHCHO} + \mathrm{hv} \rightarrow \mathrm{HCHO} \quad \text{(R2)}$$

$$\mathrm{SCH_3CHO} + \mathrm{hv} \rightarrow \mathrm{CH_3CHO} \quad \text{(R3)}$$

$$\mathrm{SNO} + \mathrm{hv} \rightarrow \mathrm{NO} \quad \text{(R4)}$$

$$\mathrm{SACETOL} + \mathrm{hv} \rightarrow \mathrm{ACETOL} \quad \text{(R5)}$$

$$\mathrm{SMGLYOX} + \mathrm{hv} \rightarrow \mathrm{MGLYOX} \quad \text{(R6)}$$

$$\mathrm{SACETONE} + \mathrm{hv} \rightarrow \mathrm{ACETONE} \quad \text{(R7)}$$

$$\mathrm{SHCOOH} + \mathrm{hv} \rightarrow \mathrm{HCOOH} \quad \text{(R8)}$$

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