



The atmospheric chemistry box model CAABA/MECCA-4.0



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We present version 4.0 of the atmospheric chemistry box model CAABA/MECCA which now includes a number of new features: skeletal mechanism reduction; the MOM chemical mechanism for terpenes and aromatics; an option to include reactions from The Master Chemical Mechanism (MCM) and other chemical mechanisms; updated isotope tagging; improved photolysis modules (updated JVAL, RADJIMT). Another new feature can be used when MECCA is connected to a global model: coexisting multiple chemistry mechanisms (Polymecca/CHEMGLUE). Additional changes have been implemented to make the code more user-friendly and to facilitate the analysis of the model results. Like earlier versions, CAABA/MECCA-4.0 is a community model published under the GNU General Public License.

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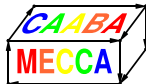
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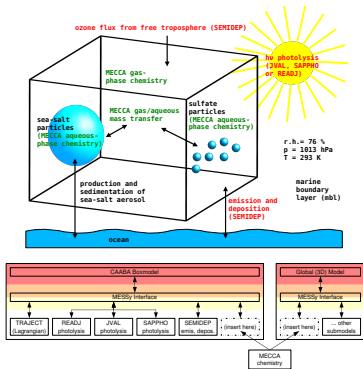


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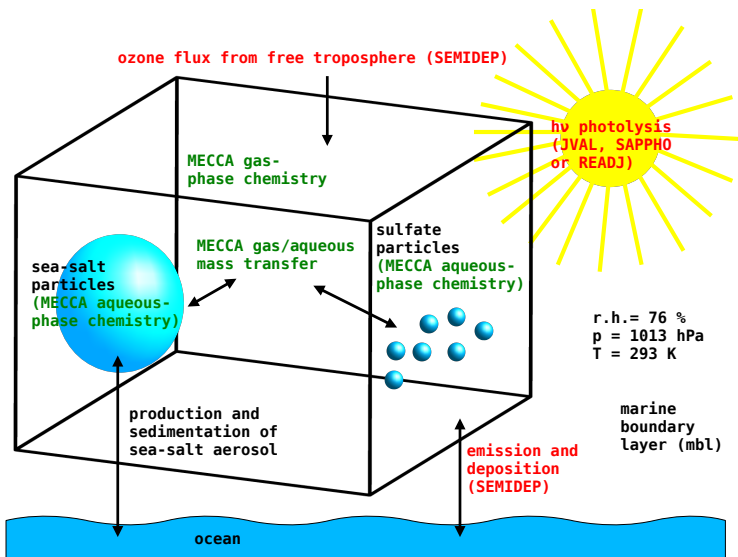


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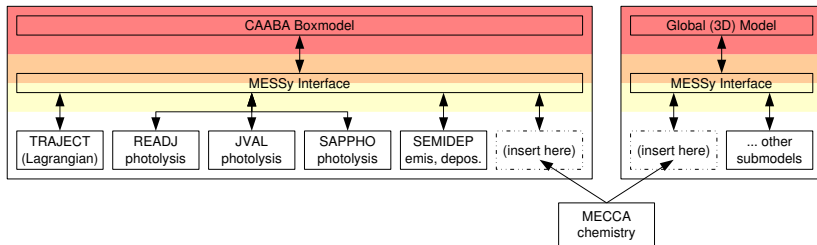
- ▶ Chemical mechanism MOM for terpenes and aromatics
- ▶ Include reactions from The Master Chemical Mechanism (MCM)
- ▶ Other chemical mechanisms: CB05BASCOE, MOZART, JAM002
- ▶ Skeletal mechanism reduction
- ▶ Updated isotope tagging
- ▶ Improved photolysis modules (updated JVAL, RADJIMT).
- ▶ Updated trajectory model
- ▶ Global model: coexisting multiple chemistry mechanisms (Polymecca/CHEMGLUE)
- ▶ Chemical property database (CHEMPROP)



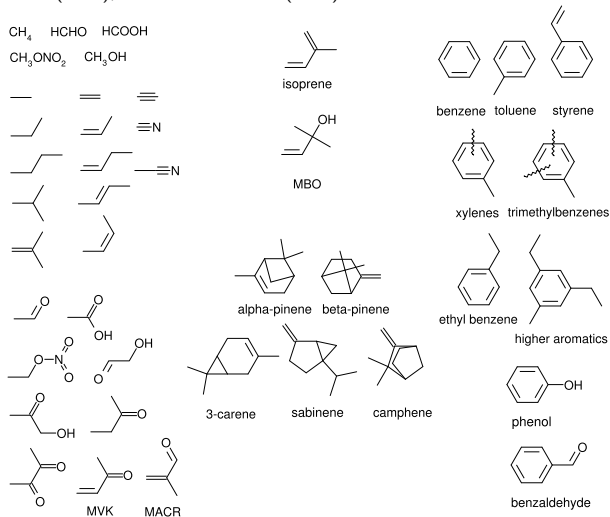
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- ▶ The CAABA boxmodel can be run with several, user-selected submodels.
- ▶ The MECCA chemistry can be used in the CAABA boxmodel or plugged into another model (via the MESSy interface)



The current MOM code is a further development of the versions used by Lelieveld et al. (2016) and Cabrera-Perez et al. (2016). It also includes developments from Taraborrelli et al. (2012), Hens et al. (2014), and Nölscher et al. (2014).



The screenshot shows the homepage of the Master Chemical Mechanism (MCM) website. The header features the logos for the University of Leeds, the National Centre for Atmospheric Science (Natural Environment Research Council), and the University of York. The main title is "The Master Chemical Mechanism" with "VERSION 3.3.1" and a link to the "MCMv3.2 Archive site". A search bar is located on the right. A navigation menu includes links for Home, Browse, Search, Extract, Download, Construction method, AiChem, Tools, Feedback, Links, Citation, Contributors, Funding, MCMv3.2, and CRI. A "Mark List" button is present, with a message stating "No species are marked." Below this is a "Welcome to the MCM website" section with introductory text about the mechanism's scope and its use in modeling studies.

The Master Chemical Mechanism (MCM) describes in detail the tropospheric degradation of more than a hundred VOCs (Jenkin et al., 1997; Saunders et al., 2003). It is widely used as the reference mechanism for modeling studies of atmospheric processes. Although the standard organic chemistry mechanism in MECCA (MOM, described above) is sufficient for many model applications, a more explicit mechanism can be necessary when studying specific VOCs. For example, the fate of limonene ($C_{10}H_{16}$) emitted from boreal forests is not included in the standard MECCA mechanism. To use MCM reactions inside MECCA, a new tool has been added which converts an extracted subset from the MCM web page (<http://mcm.leeds.ac.uk/MCM>) to a KPP equation file that is compatible with MECCA.

CB05BASCOE

- ▶ 99 species, 211 gas-phase and 10 heterogeneous reactions
- ▶ tropospheric chemistry from CB05 (Carbon Bond mechanism 2005) by Yarwood et al. (2005) ⇒ extended to include C₁ – C₃ (Williams et al., 2013), SO₂, DMS, MSA and NH₃ (Huijnen et al., 2010)
- ▶ stratospheric chemistry from BASCOE (Belgian Assimilation System for Chemical Observations) by Errera et al. (2008) ⇒ complete description for multi-decadal simulations with ozone-depleting species, greenhouse gases, reservoir and short-lived species
- ▶ More information: Huijnen et al. (2016)

MOZART

- ▶ 117 gas-phase species, 65 photolysis, 247 gas-phase reactions
- ▶ tropospheric chemistry based on MOZART-3 (Kinnison et al., 2007), additions from MOZART-4 (Emmons et al., 2010) and the Community Atmosphere Model (CAM4-chem) by Lamarque et al. (2012) ⇒ updated isoprene oxidation scheme, volatile organic compounds, degradation of C₁, C₂, C₃, C₄, C₅, C₇, and C₁₀ species
- ▶ stratospheric chemistry based on Kinnison et al. (2007), Lamarque et al. (2012) and Tilmes et al. (2016) ⇒ chlorine, bromine, heterogeneous processes on liquid sulfate aerosols and polar stratospheric clouds (Considine et al., 2000)

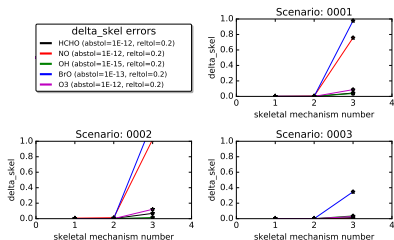
JAM002

- ▶ 246 species, 733 reactions, 142 photolysis reactions
- ▶ stratospheric chemistry from the Whole Atmosphere Chemistry Climate Model (WACCM) by Kinnison et al. (2007)
- ▶ tropospheric chemistry from the Model of OZone And Related Tracers (MOZART4) by Emmons et al. (2010)
- ▶ enhanced by Mainz Isoprene Mechanism 2 (MIM2) by Taraborrelli et al. (2009) ⇒ 1,6 H-shift reactions (Peeters et al., 2009), epoxide formation (Paulot et al., 2009), hydroperoxyenals (Wolfe et al., 2012)
- ▶ explicit pathways for peroxy radical reactions with HO₂, CH₃O₂, and CH₃COO₂ (peroxy acetyl)
- ▶ More information: Schultz et al. (2017)



- ▶ Adopted from fuel combustion research
- ▶ Several methods to create a simplified (“skeletal”) chemical mechanism (e.g., Tomlin and Turányi, 2013)
- ▶ DRGEP (Directed Relation Graph with Error Propagation) by (Pepiot-Desjardins and Pitsch, 2008)
- ▶ now implemented in CAABA/MECCA, making skeletal reduction available for atmospheric chemistry

- ▶ Target: Important species, for which the skeletal mechanism produces similar results as the full mechanism.
- ▶ Sample points: A set of environmental conditions ($c(X)$, T , p)
- ▶ Overall interaction coefficient (OIC): The maximum importance of a chemical species for any of the sample points, between 0 (unimportant) and 1 (important)
- ▶ Normalized error δ_{skeletal} : Difference between skeletal mechanism and full mechanism. OK if $\delta_{\text{skeletal}} < 1$ for all targets and sample points. Depends on acceptable tolerance (abs. and rel.) of individual targets.
- ▶ OIC threshold ε_{ep} : A chemical species is considered important if $\text{OIC}(\text{species}) > \varepsilon_{\text{ep}}$. The final ε_{ep} calculated by DRGEP is the maximum value for which $\delta_{\text{skeletal}} < 1$ still holds.



We have updated the sub-submodel MECCA-TAG (Gromov et al., 2010), which had been introduced in version 3.0 of CAABA. Several improvements to the kinetic tagging technique were implemented.

- ▶ Selectable composition transfer mode: Depending on the research question, prescribed-, molecular- or element-weighted composition transfer may be selected. These modes determine the shares with which each reactant contributes to the products in the tagged chemical reactions: according to user-specified weightings, proportional to the reacting molecules count, or following the given element (e.g., C or H) content, respectively. Whilst the latter mode is intrinsic to isotope tagging, the others may be used for custom tagging configurations, e.g., product yield calculations.
- ▶ Diagnostics for unaccounted production or loss of elemental composition: MECCA-TAG optionally adds passive diagnostic species to the tagged reactions with unbalanced transfer of the element of interest. This helps to quantify the amount of atoms the chemical mechanism receives from or loses to “nothing”, including the isotope composition of such mass-balance violations.
- ▶ The new “class shifting” tagging mode: This mode allows migration of molecules between the tagging classes in specified reactions, which allows quantifying various exchange processes in the mechanism. For instance, one can distinguish oxidation generations: in reactions of reactants with given oxidants the products become “promoted” to the tagging class of the next oxidation generation. Another application of “class shifting” is quantifying the efficiency of recycling chains. In essence, such is the “online” implementation of the approach similar to that of Lehmann (2004), with the number of tagging classes defining the maximum of the recycling sequences it is possible to follow.

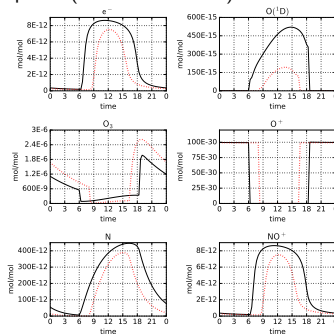
JVAL

The submodel JVAL inside the CAABA/MECCA model calculates J -values using the method of Landgraf and Crutzen (1998). It was first updated to the version described by Sander et al. (2014), and then additional changes were made. Many new photolysis reactions have been added, most of them related to either species from the MOM mechanism (CH₃NO₃, CH₃O₂NO₂, CH₃ONO, CH₃O₂, HCOOH, C₂H₅NO₃, NOA, MEKNO₃, BENZAL, HOC₆H₄NO₂, CH₃COCO₂H, IPRCHO₂HCO, C₂H₅CHO₂HCO, C₃H₇CHO₂HCO, PeDIONE₂₄, PINAL₂HCO) or organic halogen compounds (CF₂CICFCI₂, CH₃CFCl₂, CF₃CF₂Cl, CF₂CICF₂Cl, CHF₂Cl, CHCl₃, CH₂Cl₂). Besides, bugfixes were necessary regarding incorrect temperature dependencies of the ozone and OCS cross sections in the input data.

Right: Model-calculated mixing ratios from an upper atmosphere simulation with MECCA and RADJIMT: Diurnal cycles for 4 January for the equator (black) and a latitude of 50° N (red).

RADJIMT

RADJIMT is a new submodel that provides dissociation and ionization rates due to absorption of light and energetic photoelectrons in the mesosphere and thermosphere. It is part of the upper atmosphere extension of MESSy initially described by Baumgaertner et al. (2013), which was partly based on the implementations from the middle and upper atmosphere model CMAT2 (Harris, 2001; Dobbin, 2005; Dobbin and Aylward, 2008). For upper atmosphere simulations, MECCA was extended by the relevant chemical species (electrons and ions) and reactions.



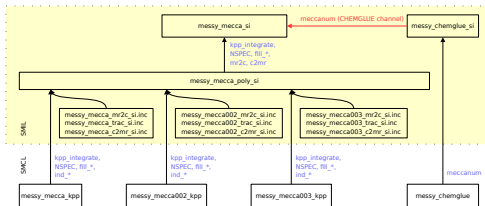
The TRAJECT submodel by Riede et al. (2009) allows simulations of atmospheric chemistry along pre-calculated Lagrangian trajectories. For this purpose, the air parcel simulated by CAABA is moved through space and time along a trajectory taken from an external input file, while simulating atmospheric photochemistry with the MECCA and JVAL submodels. More generally, the TRAJECT submodel allows to prescribe physical boundary conditions for CAABA box model simulations. A typical application is the simulation of atmospheric trajectories (balloon measurements or backward trajectories). However, laboratory conditions (e.g., in a flow reactor) can also be prescribed. The previous TRAJECT version, described by Sander et al. (2011), has been updated. The output is now more consistent with the trajectory input file, as physical information is now written out beginning with the first time step instead of the second. In general, an integration time step of chemical kinetics is always performed with the physical parameters given for the end of the time step. In that way, the mixing ratios written out at the end of a time step are consistent with the physical conditions at that point. Also, solar zenith angle and local time at the end of a time step are now consistent with the given longitude and latitude for that trajectory point. In addition to the trajectory input file, an external input file with J-values for NO₂ can be used to scale all J-values with the factor:

$$jfac = \frac{J(\text{NO}_2, \text{external})}{J(\text{NO}_2, \text{JVAL})} \quad (1)$$

To facilitate the analysis of the scaling impact, jfac is now written to output. Scaling thresholds have been implemented to prevent artifacts that would occur when $J(\text{NO}_2, \text{JVAL})$ is very small and the calculation of jfac approaches a division by zero.

Polymecca

Normally, the MESSy submodel MECCA contains one chemical mechanism that is used for all grid boxes of the base model. This ensures a consistent chemistry simulation from the surface to the upper atmosphere. However, in some cases, it may be preferable to allow different mechanisms in different boxes, e.g., terpene chemistry only in the troposphere and ion chemistry only in the mesosphere. With the script `xpolymecca`, several independent chemical MECCA mechanisms can be produced. The first mechanism has the name "mecca", as usual. Additional mechanisms are labeled with a three-digit suffix. For example, the code of mechanism 2 is contained in `messy_mecca002_kpp.f90` and related files.



CHEMGLUE

To select an appropriate mechanism at each point in space and time, the MESSy submodel CHEMGLUE has been written. The name of the submodel was chosen because CHEMGLUE also "glues" together different chemical mechanisms at the border where a chemical species is included in one mechanism but not in the other. CHEMGLUE defines the new channel object "meccanum" which contains the mechanism number for each grid point. These values can either be selected statically, e.g., depending on the model level number or the sea-land fraction mask. Alternatively, a dynamic (time-dependent) selection based on chemical or meteorological variables is possible, e.g., pressure, temperature, or the concentrations of ozone or isoprene. Note that even when different boxes of a global model simulation use different chemistry mechanisms, the set of tracers contains all species from all mechanisms for all boxes.

Chemical properties of the species in the reaction mechanism are needed at many locations in the model, e.g., molar mass (M), Henry's law constants (H), accommodation coefficients (α), acidity constants (K_A), and ion charge number (z). These constants have so far been stored at different locations in the code (gas.tex, messy_cmn_gasaq.f90, and elsewhere). Because maintaining data that are spread over several source files is tedious and error-prone, the new CHEMPROP database has been created, which stores all values centrally in the ASCII table messy_main_tracer_chemprop.tbl. MECCA (and other submodels) can access these chemical property data via MESSy tracer containers, as described by Jöckel et al. (2008).

<CHEMPROP>	S_casrn	R_molarmass	R_Henry_T0	R_Henry_Tdep	R_Sechenov	R_alpha_T0
<LATEX>	CAS-RN	Formula	< \Henry\$	\HTdep\$ >	< Sk_{\rm s}\$ >	< \alpha_{\text{minius}}
<DEFAULT>	?	0.	-9.99999	-9.99999	9.99999	0.1 {&SN}
ONE		1.0				
O		O				
O2	7782-44-7	O2	1.3E-3 {&190}	1500.		0.01 {&SN}
O3	10028-15-6	O3	1.03E-2 {&3245}	2830.		0.002 {&826}
H	12385-13-6	H				
H2	1333-74-0	H2				
OH	3352-57-6	OH	3.0E1 {&515}	4300.		0.01 {&1047}
H02	3170-83-0	H02	3.9E3 {&515}	5900.		0.5 {&1864}
H2O	7732-18-5	H2O	BIG_DP {&SN}	0.		0.0 {&SN}
H2O2	7722-84-1	H2O2	1.E5 {&311}	6338.		0.077 {&32}
N		N				
N2D		N				
N2		N2				
NH3	7664-41-7	NH3	60.2 {&3245}	4160.		0.06 {&826}
N2O		N2O				
NO	10102-43-9	NO	1.9E-3 {&449}	1480.		5.0E-5 {&448}
NO2	10102-44-0	NO2	1.2E-2 {&3245}	2360.		0.0015 {&176}
NO3	12033-49-7	NO3	3.8E-2 {&3245}	2000. {&763}		0.04 {&1048}
N2O5	10102-03-1	N2O5	BIG_DP {&SN}	0.		
HONO	7782-77-6	HONO	4.9E1 {&449}	4780.		0.04 {&826}
HN03	7697-37-2	HN03	2.45E6/1.5E1 {&530}	8694.		0.5 {&930}
HN04	26404-66-0	HN04	1.26E4 {&797}	6900.		

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[HOME](#)[MOM](#)[MCM](#)[Other](#)[Skeleton](#)[TAG](#)[h_v](#)[TRAJECT](#)[Polymecca](#)[Chemprop](#)[Refs](#)

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