Multiphase processing of tropospheric halogen species: Mechanism development and modelling

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Introduction and Motivation

Halogens play a key role in the marine multiphase chemistry. Their main source is the ocean either by emission of sea salt particles and the activation and release of reactive halogen species from bromide and chloride or by direct emission of halogenated hydrocarbons. Because of their high reactivity halogens interact with almost all species and reaction cycles. Among the most important reactions is the depletion of ozone in catalytic cycles. Thus halogens do influence the oxidation capacity of the atmosphere making them of special interest for the scientific community. Research was carried out and is still going on in all fields either by field measurements (e.g. Pszenny et al., 2007), laboratory experiments (e.g. Burkholder et al., 2004) or modelling studies (e.g. von Glasow et al., 2002).

Although many modelling studies exist does each work reflect some restrictions. The aim of this study is to provide a comprehensive halogen mechanism, which can be braodly used in many different scenarios or case studies. The halogen module 2.0 was developed as an update of the halogen module 1.0 (Herrmann et al., 2003) for the use together with the multiphase mechanism RACM-MIM2ext/CAPRAM 3.0i (Tilgner and Herrmann, 2009).

Simulations were carried out for an open ocean scenario with non-permanent clouds (Tilgner and Herrmann, 2009) with the model SPACCIM (Wolke et al., 2005). Besides this base run (HM2) several sensitivity studies have been performed omitting iodine chemistry (HM2$_{CLBR}$) and both iodine and bromine chemistry (HM2$_{CL}$). In other runs no halogen chemistry at all was calculated (woHALO) and the formation of clouds was suppressed (woCLOUD).
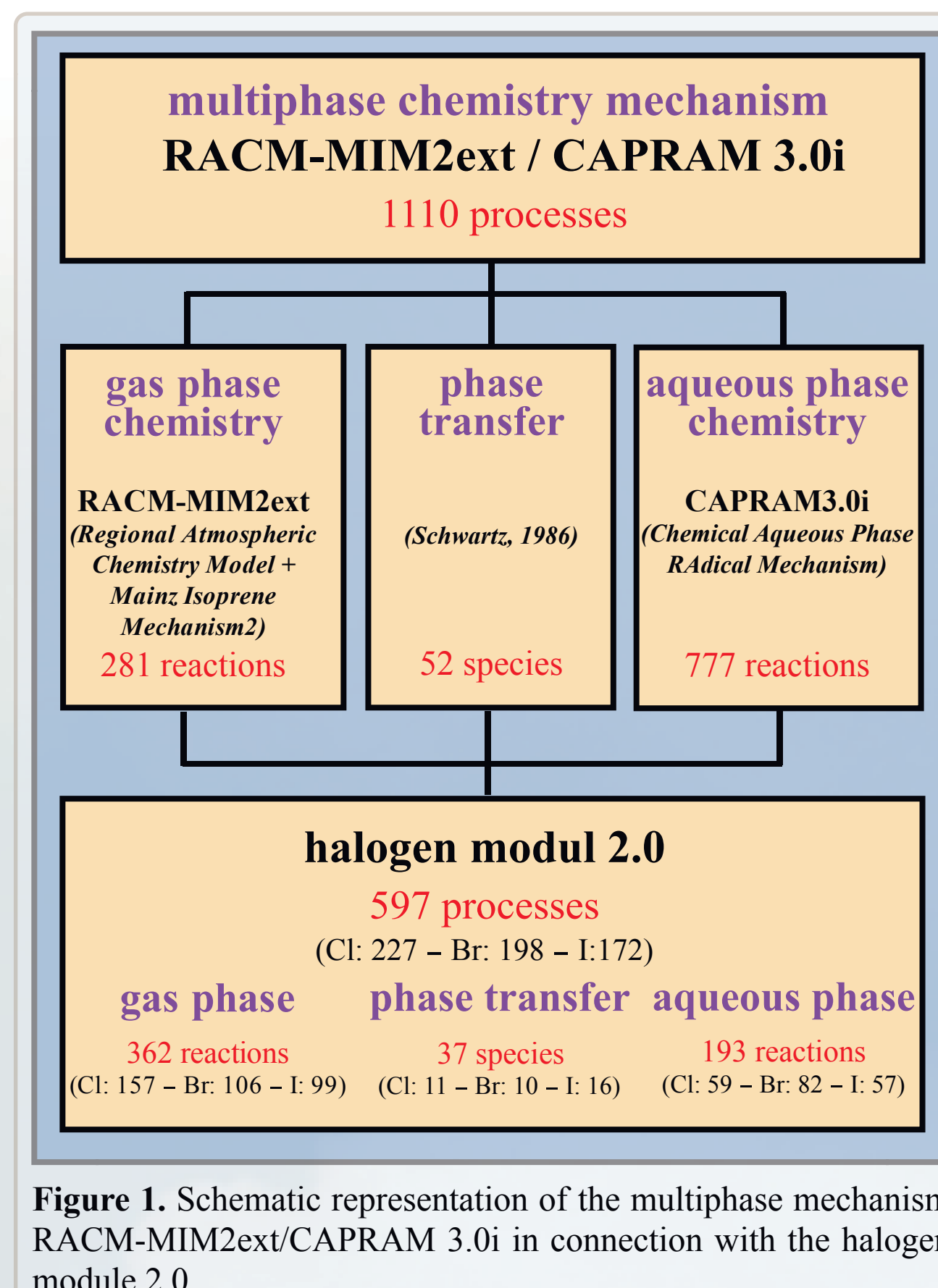
Mechanism development

➤ Developement of the mechanism is based on the halogen module 1.0 (Herrmann et al., 2003) and the work of von Glasow et al. (2002).

➤ When availlable, kinetic data was taken from latest IUPAC or JPL recommendations (Atkinson et al., 2007 and Sander et al., 2006, respectively), otherwise most recent literature data was used.

➤ A near explicite oxidation scheme of alkyl halides is based on MCMv3 (Pilling et al., 2008).

➤ Photodissociations are calculated offline.

➤ In the overall mechanism RACM-MIM2ext/CAPRAM 3.0i together with the halogen module 2.0 1707 processes and 699 species are included of which 597 reactions and 204 species belong to the halogen module 2.0 (Fig. 1).

Figure 1. Schematic representation of the multiphase mechanism RACM-MIM2ext/CAPRAM 3.0i in connection with the halogen module 2.0.

Figure 2. Simplified scheme of the most important processes implemented in the halogen module 2.0.
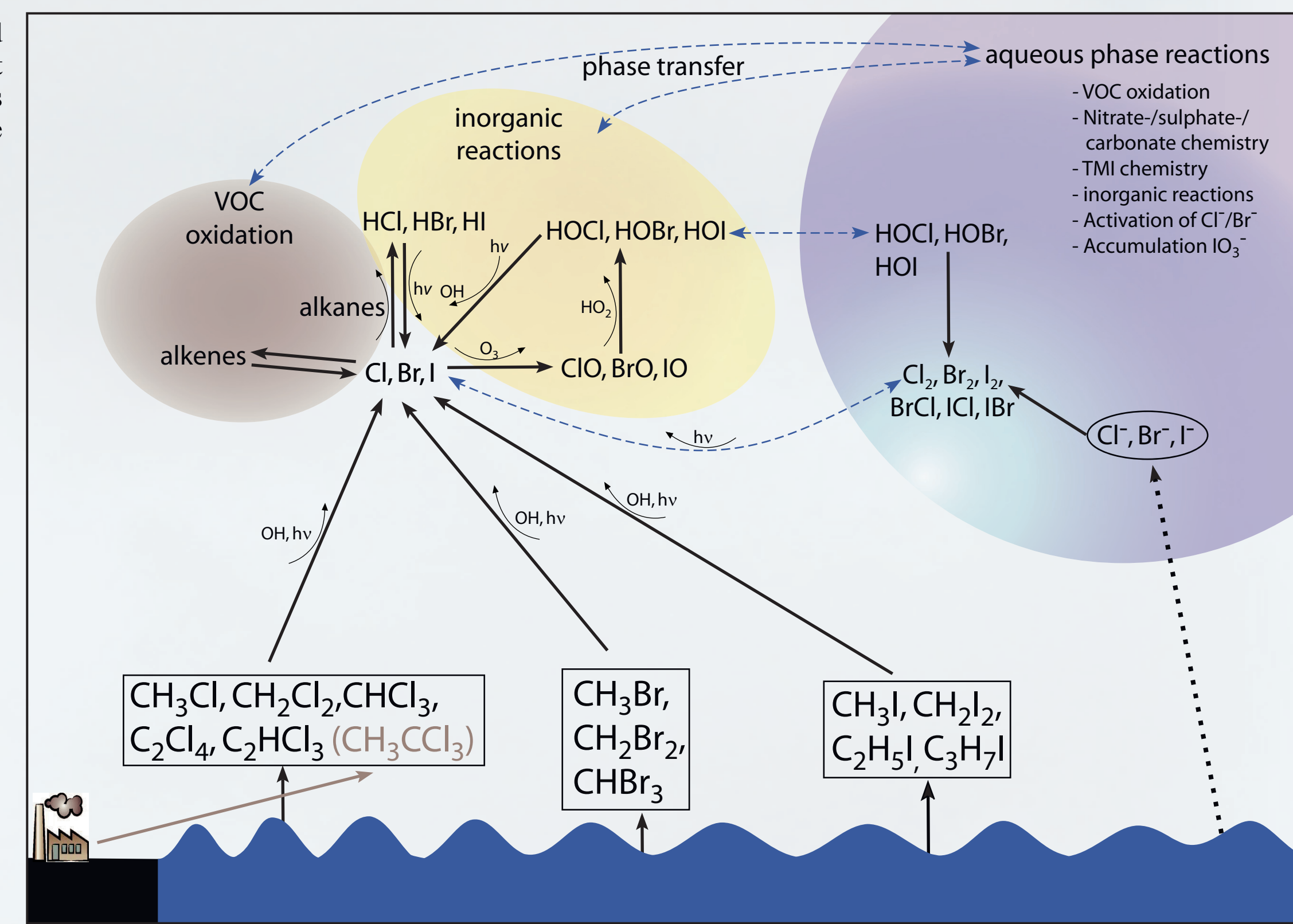
Results and Discussion

Chlorine chemistry

➤ Inferred Cl concentrations of measurements by Pszenny et al. (2007) of 2.2 – 5.6·10⁴ molecules cm⁻³ could be reproduced in the base run HM2 (Fig. 3).

➤ Omitting iodine chemistry lowers Cl concentrations dramatically (to 24% and 5% in the runs HM2$_{CLBR}$ and HM2$_{CL}$, respectively).

➤ Clouds lower Cl concentrations significantly in the base run (Cl maximum concentrations are 5.2·10⁴ molecules cm⁻³ before and 1.5·10⁴ molecules cm⁻³ after the cloud phase for the scenario HM2 and 8.4·10⁴ molecules cm⁻³ calculating no cloud chemistry in the sensitivity run woCLOUD).
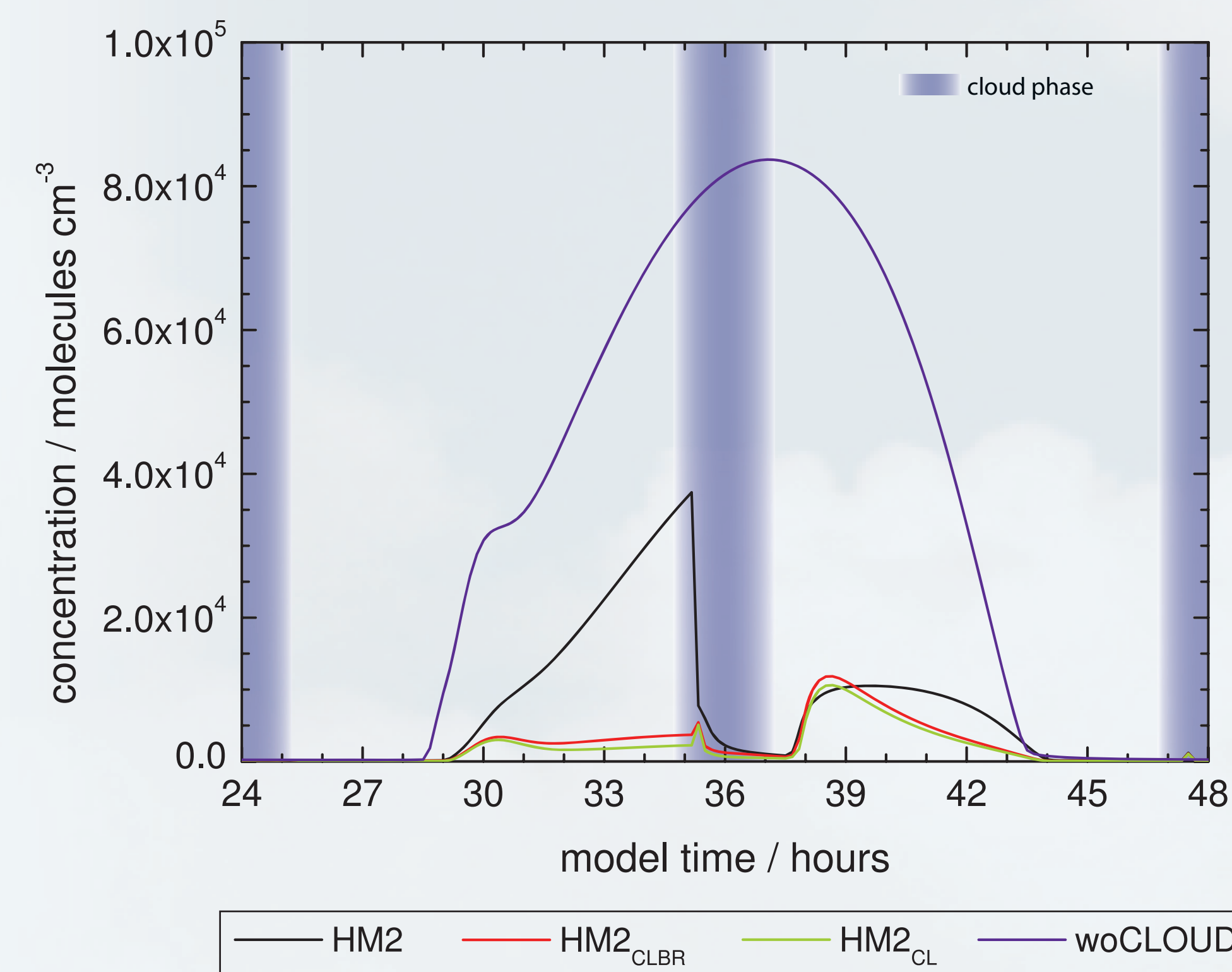
Figure 3. Modelled concentrations of chlorine atoms for the second model day for the different scenarios.

Bromine chemistry

➤ BrO concentrations are doubled after cloud phases due to different chemical reaction cycles including HOBr and BrCl under cloud free conditions and Br and Br under cloudy conditions.

➤ With cloud evaporation the produced Br is released causing a peak in several bromine species including BrO.

➤ Modelled BrO concentrations agree with measurements (several DOAS measurements inferred BrO concentrations around 2.5·10⁷ molecules cm⁻³) only for the first model day due to the chosen scenario.

Iodine chemistry

➤ Typical concentrations of iodine species for open ocean conditions are reflected by the model (as shown for IO in Fig. 6).

➤ Clouds supress iodine processing and budgets.

➤ Iodine chemistry is triggert mainly by the emission of CH$_2$I$_2$, CH$_2$IBr, and CH$_2$ICl from the ocean (Fig. 7).

➤ Photolysis is the predominant pathway of the oxidation of alkyl iodides producing iodine atoms.

➤ OH oxidation of alkyl iodides is of minor improtance (between 0% and 18%), Cl oxidation is neclegatble for the fate of alkyl iodides.
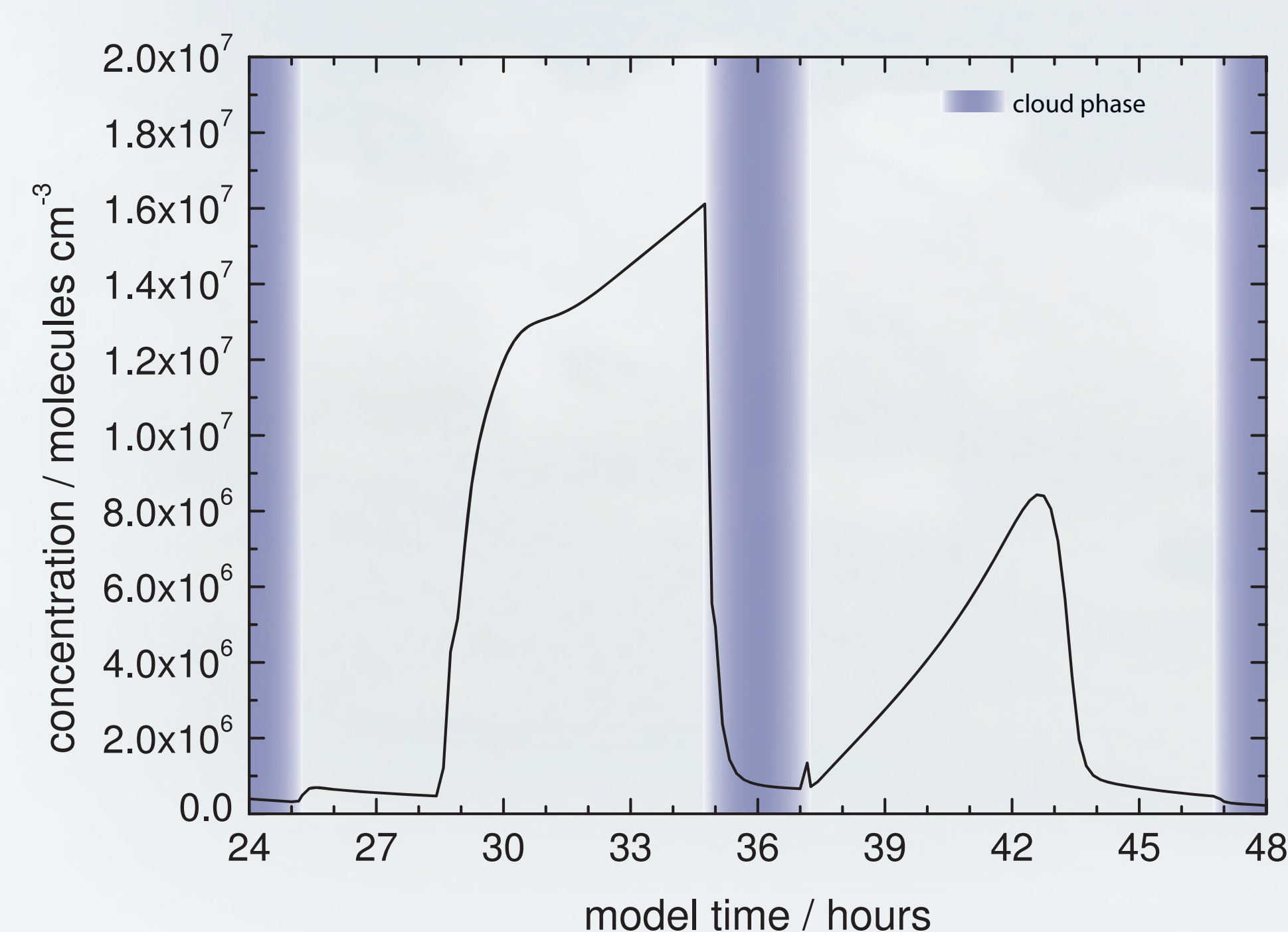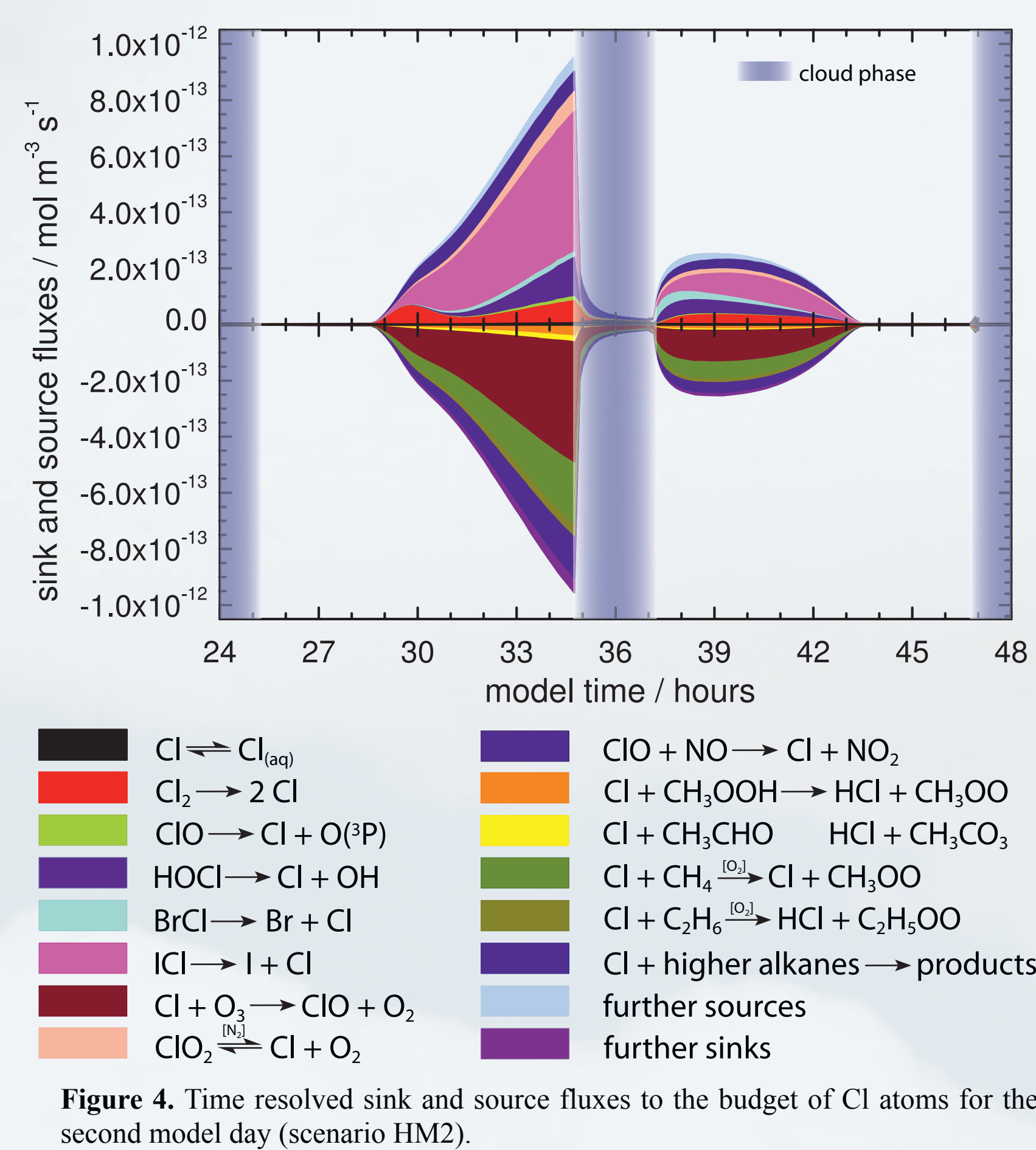
Figure 4. Time resolved sink and source fluxes to the budget of Cl atoms for the second model day (scenario HM2).

Cl ⇌ Cl$_{(aq)}$
Cl$_2$ → 2 Cl
ClO → Cl + O(^{3}P)
HOCl → Cl + OH
BrCl → Br + Cl
ICl → I + Cl
Cl + O$_3$ → ClO + O$_2$
ClO$_2$ $\xrightarrow{(N)}$ Cl + O$_2$
ClO + NO → Cl + NO$_2$
Cl + CH$_3$OOH → HCl + CH$_3$OO
Cl + CH$_3$CHO → HCl + CH$_3$CO$_3$
Cl + CH$_4$ $\xrightarrow{(O_2)}$ HCl + CH$_3$OO
Cl + C$_2$H$_6$ $\xrightarrow{(O_2)}$ HCl + C$_2$H$_5$OO
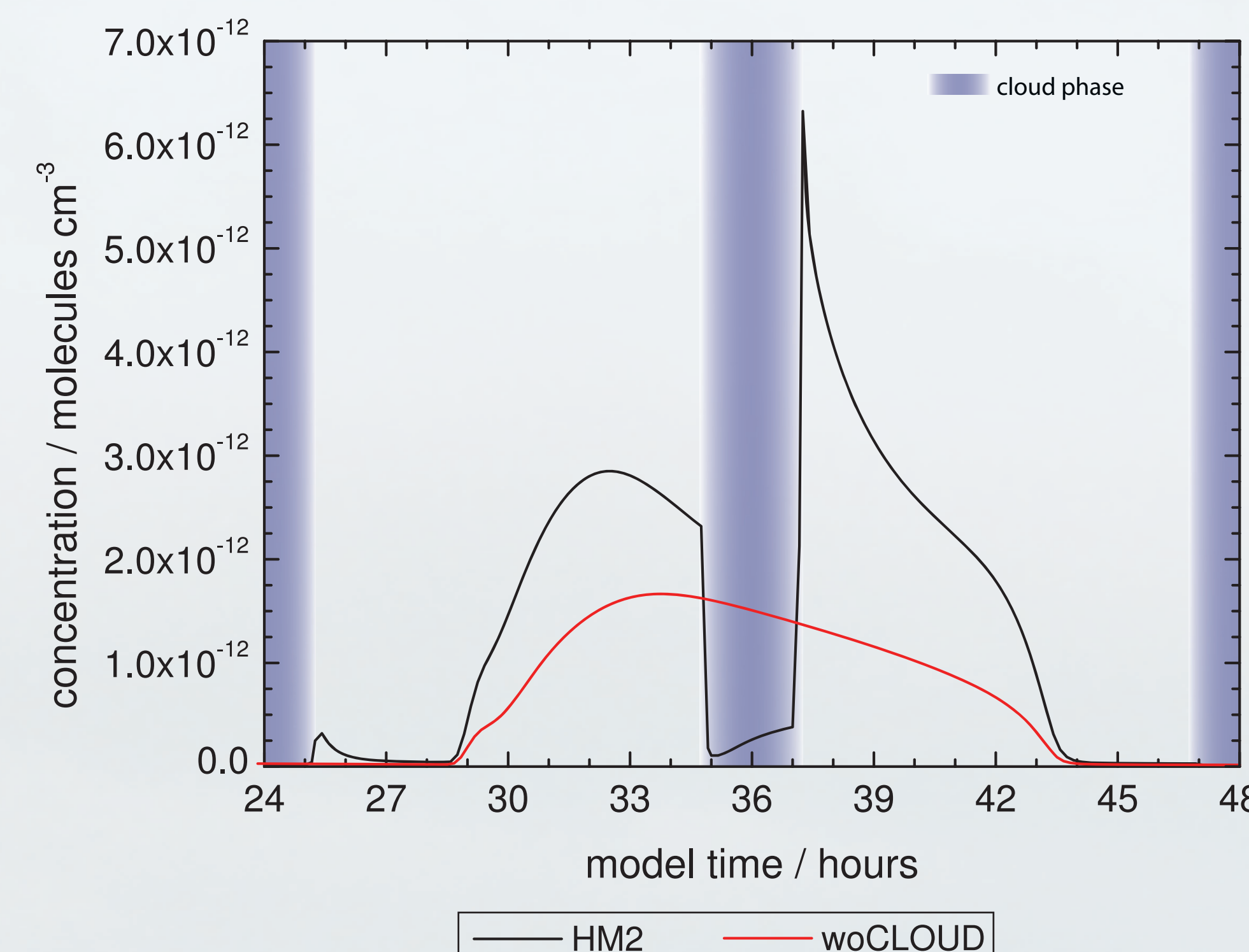Cl + higher alkanes → products
further sources
further sinks

Figure 5. Modelled concentrations of BrO radicals for the second model day with (HM2) and without clouds (woCLOUD).

Figure 6. Modelled concentrations of IO radicals for the second model day (scenario HM2).

Interactions with ozone

➤ The influence of halogens on ozone can be seen from the sensitivity studies omitting the respective halogen subsets (Fig. 8).

➤ Calculations have been performed to determine the influence of halogens to the odd oxygen family Ox (based on von Glasow et al., 2002) averaged over the whole modelling period of 108h.

➤ Major ozone loss is caused as a consequence of the reaction O(^{1}D) + H$_2$O$_{(g)}$ → 2 OH (60%), HOx chemistry accounts for 13%, chlorine chemistry for 8%, bromine chemistry for 1%, and iodine chemistry for 13% (Fig. 9).

Figure 8. Modelled concentrations of ozone over the whole period of 108h for the different scenarios.
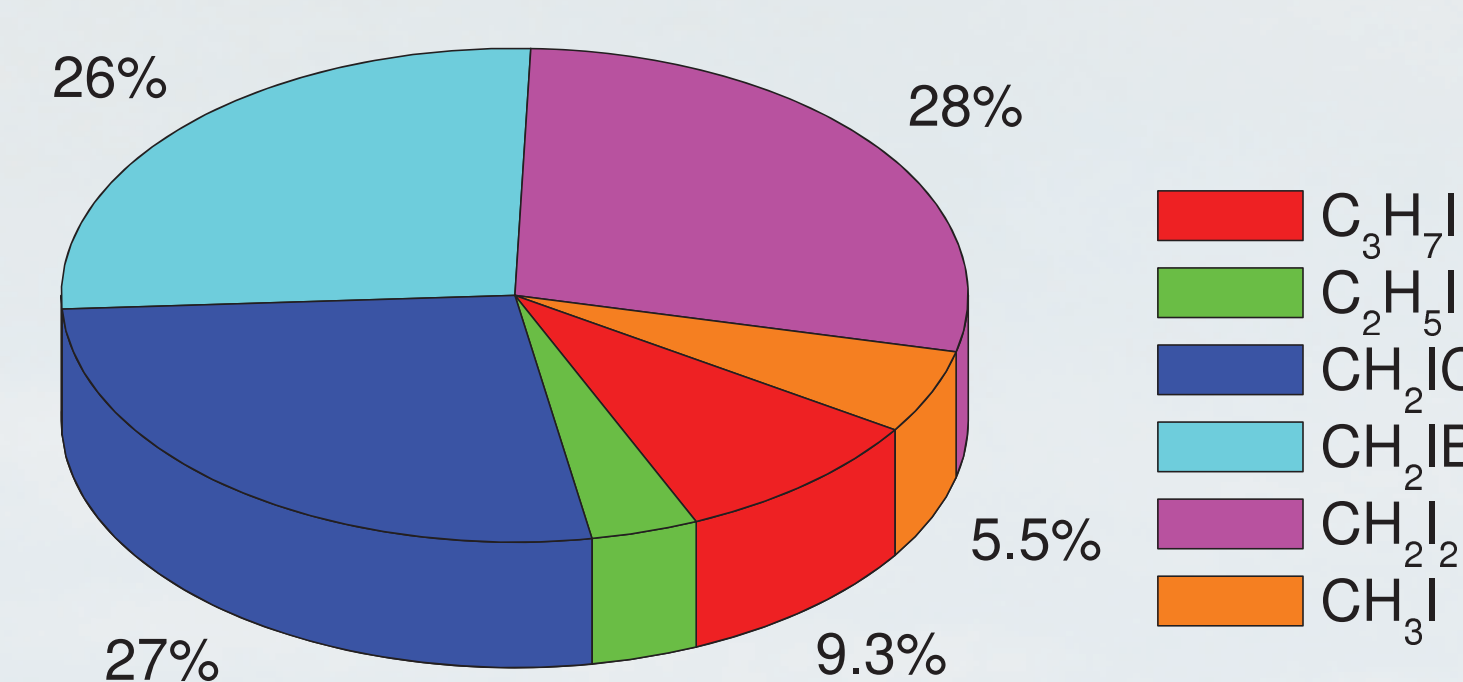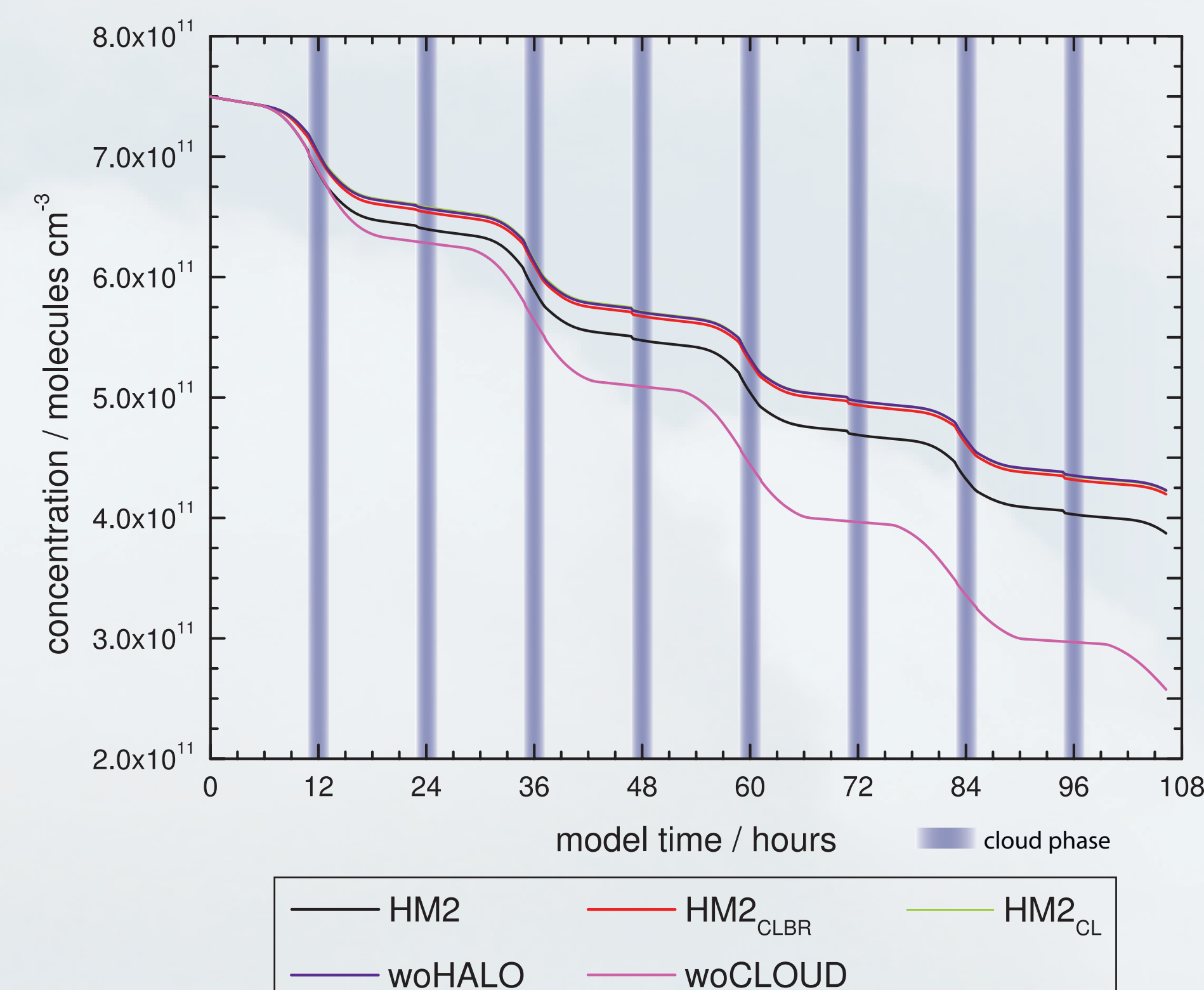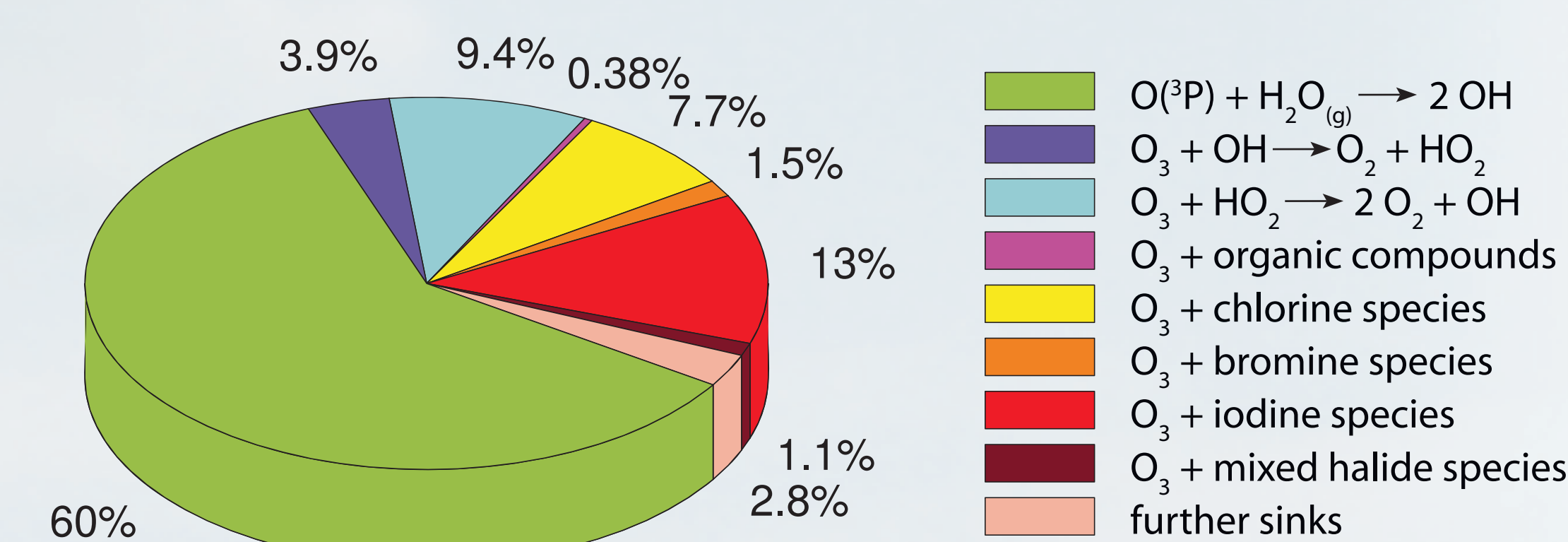
Figure 7. Calculated relative contributions of alkyl iodides to the budget of tropospheric iodine atoms averaged over the modelling period of 108h.

C$_3$H$_7$I
C$_2$H$_5$I
CH$_2$ICl
CH$_2$IBr
CH$_2$I$_2$
CH$_3$I

Figure 9. Calculated relative contributions of different reactions to the destructions of Ox species.

O(^{3}P) + H$_2$O$_{(g)}$ → 2 OH
O$_3$ + OH → O$_2$ + HO$_2$
O$_3$ + HO$_2$ → 2 O$_2$ + OH
O$_3$ + organic compounds
O$_3$ + chlorine species
O$_3$ + bromine species
O$_3$ + iodine species
O$_3$ + mixed halide species
further sinks

Summary

A chemistry mechanism with 597 processes has been developed and coupled to the multiphase mechanism RACM-MIM2ext/CAPRAM 3.0i. Calculations were performed with the model SPACCIM, which reflect measured concentration of halogen species in the troposphere. Source and sink flux analyses can explain the halogen chemistry in more detail than before.

Clouds have a profound influence on halogen chemistry. During cloud phases halogen chemistry is supressed in the gas phase, while different effects occur in the aqueous phase. Differences can also be seen in the diverse halogen species. Most gas phase concentrations of chlorine and iodine species are lowerd, but several bromine species show raised concentraion levels due to different reaction cycles under cloudy and cloud free conditions. Photolysis of alkyl iodides, especially CH$_2$I$_2$, CH$_2$ICl, and CH$_2$IBr, is the major source of iodine species in the troposphere. Due to missing products studies and relevance for tropospheric processes an OH or Cl induced oxidation of the mixed alkyl halides CH$_2$ICl and CH$_2$IBr has been omitted. Further modelling studies are planned, comparing field measurements with modelling results for specific case studies.

References

Atkinson, R. et al. (2007) Atmospheric Chemistry and Physics 7(4), 981 - 1191..
Burkholder, J. B. et al. (2004) Atmospheric Chemistry and Physics 4(1), 19 - 34.
Herrmann, H. et al. (2003) Chemsphere 52(2), 485 - 502.
Pilling, M et al. (AUG 2008) website: http://mcm.leeds.ac.uk/MCM.
Pszenny, A. A. P. et al.. (2007) Journal of Geophysical Research – Atmospheres 112(D10).
Sander, S. P. et al. (2006) JPL evaluation No. 15. website: http://jpldataeval.jpl.nasa.gov/
Tilgner, A. and H. Herrmann (2009) submitted to Atmospheric Environment.
von Glasow, R. et al. (2002) Journal of Geophysical Research – Atmospheres 107(D17).
Wolke R. et al. (2005) Athmospheric Environment 39(23-24), 4375 - 4388.

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