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Introduction and Motivation

Halogen multiphase chemistry plays an essential role in marine environments. The emission of sea salt particles from the ocean and the activation and release of reactive halogen species as well as the direct emission of halogenated alkanes triggers complex multiphase reaction cycles. Interactions with many important chemistry cycles such as the catalytic ozone depletion, interactions with organic compounds, sulfur, and nitrogen species could be proven. Research was carried out and is still going on in all fields either by field measurements (e.g. [1]), laboratory experiments (e.g. [2]) or modeling studies (e.g. [3]).

Despite the large number of modeling studies still several restrictions exist in either of the chemistry mechanisms. In the current study a comprehensive chemistry mechanism is presented, which aims to generally describe the complex halogen multiphase chemistry in different distinct environments, e.g. pristine regions of the open oceans, coastal areas, or the chemistry of mixed urban and marine air masses. The halogen module 2.0 was developed as an update of the halogen module 1.0 [4] for the use together with the multiphase mechanism RACM-MIM2ext/CAPRAM 3.0i [5]. Simulations were carried out for an open ocean scenario with non-permanent clouds [5] with the model SPACCIM [6]. Besides this base run (HM2) several sensitivity studies have been performed omitting iodine chemistry (HM2_{CLBR}), both iodine and bromine chemistry (HM2_{CL}), and all halogen chemistry (woHALO). Cloud formation was suppressed in the run woCLOUD.

Mechanism development

- Kinetic data is based on the latest IUPAC or JPL recommendations [7, 8] and the most recent literature data.
- A near explicit oxidation scheme of alkyl halides is based on MCMv3.1 [9].
- 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. 2).

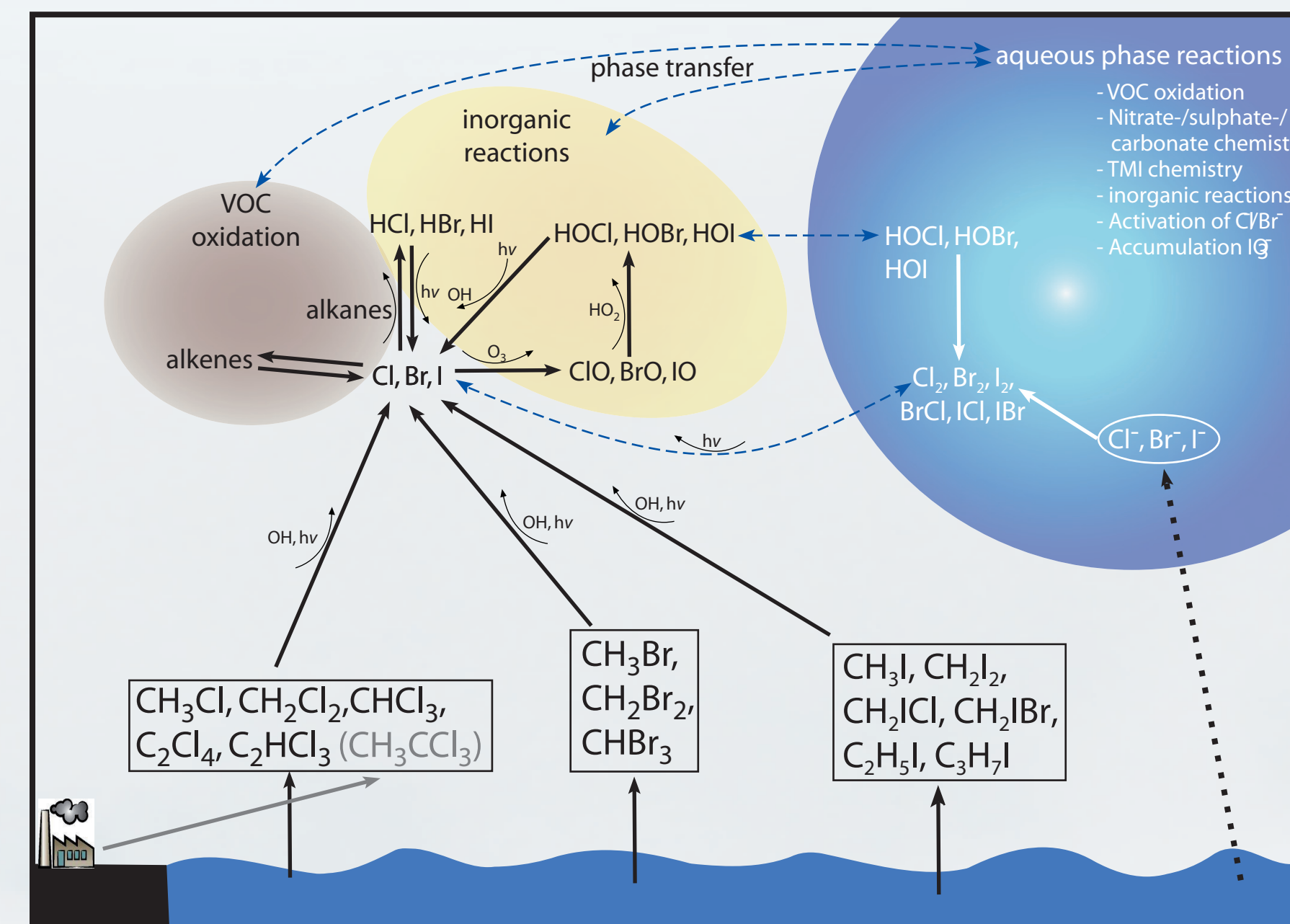


Fig. 1. Simplified scheme of the processes implemented in the halogen module 2.0.

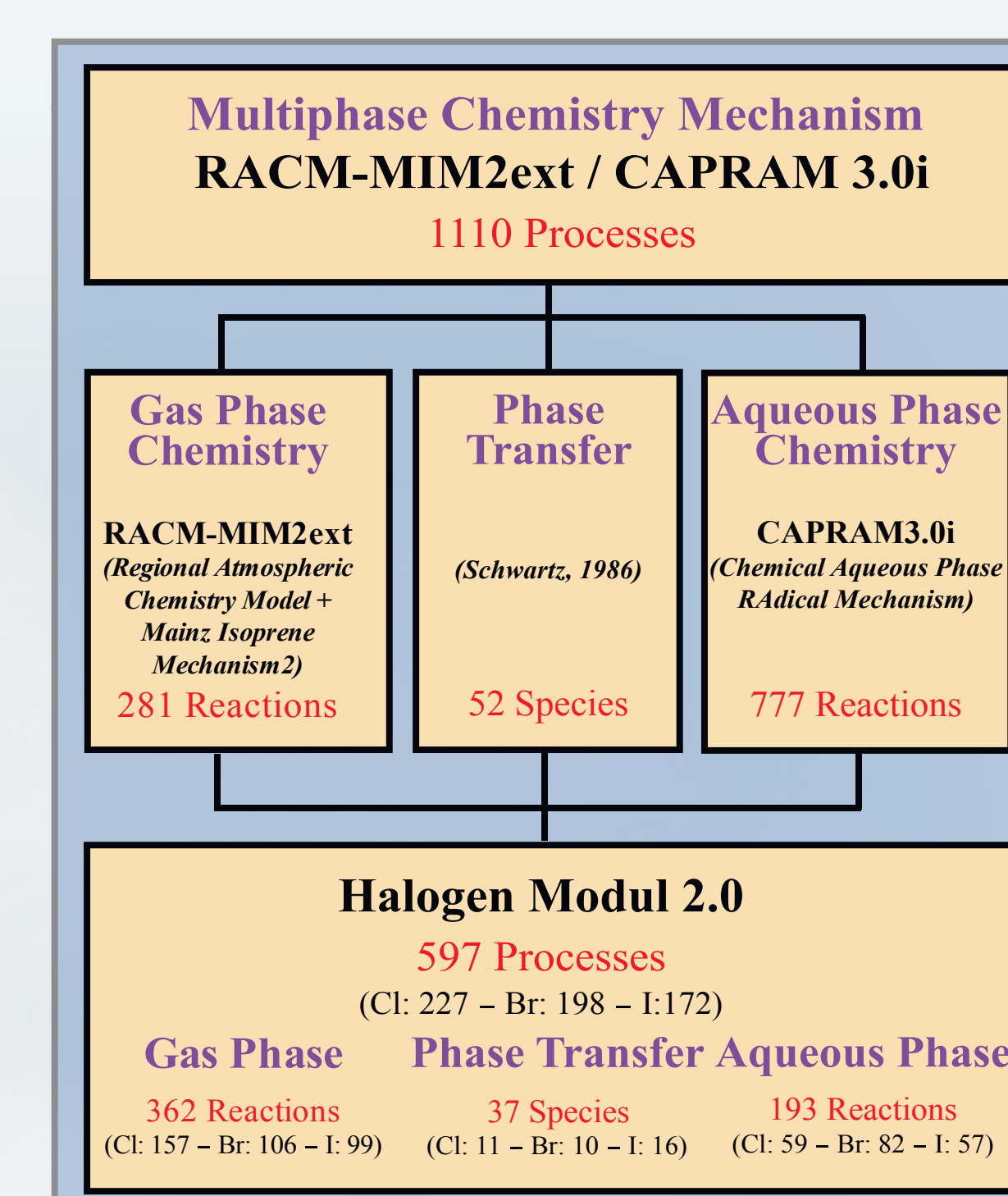


Fig. 2. Schematic representation of the multiphase mechanism.

Chlorine chemistry

- Inferred Cl concentrations of measurements by Pszenny et al. [1] of $2.2 - 5.6 \cdot 10^4$ 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 $5.2 \cdot 10^4$ molecules cm^{-3} before and $1.5 \cdot 10^4$ molecules cm^{-3} after the cloud phase for the scenario HM2 and $8.4 \cdot 10^4$ molecules cm^{-3} calculating no cloud chemistry in the sensitivity run woCLOUD).

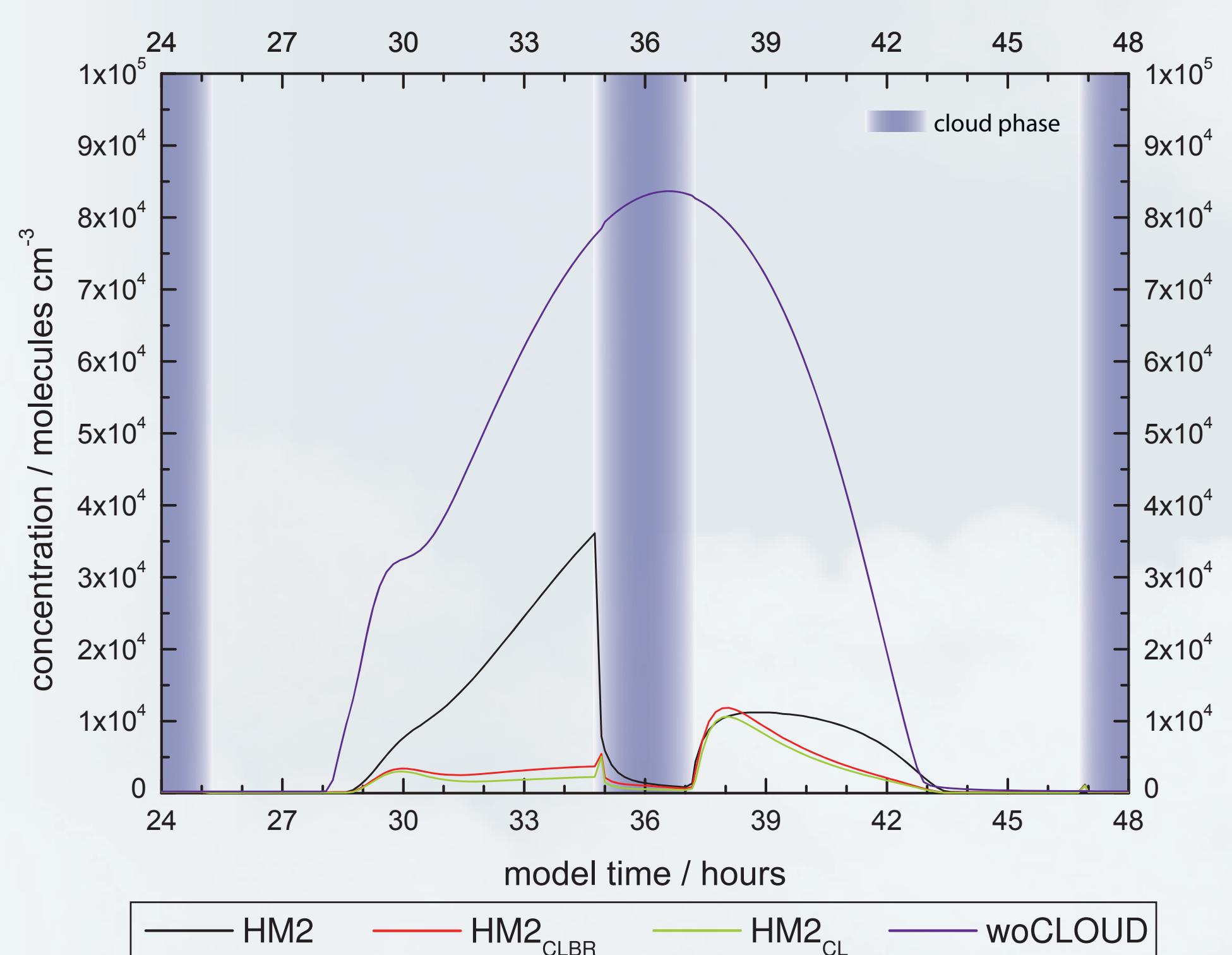


Fig. 3. Modeled concentrations of chlorine atoms for the second model day for the different scenarios.

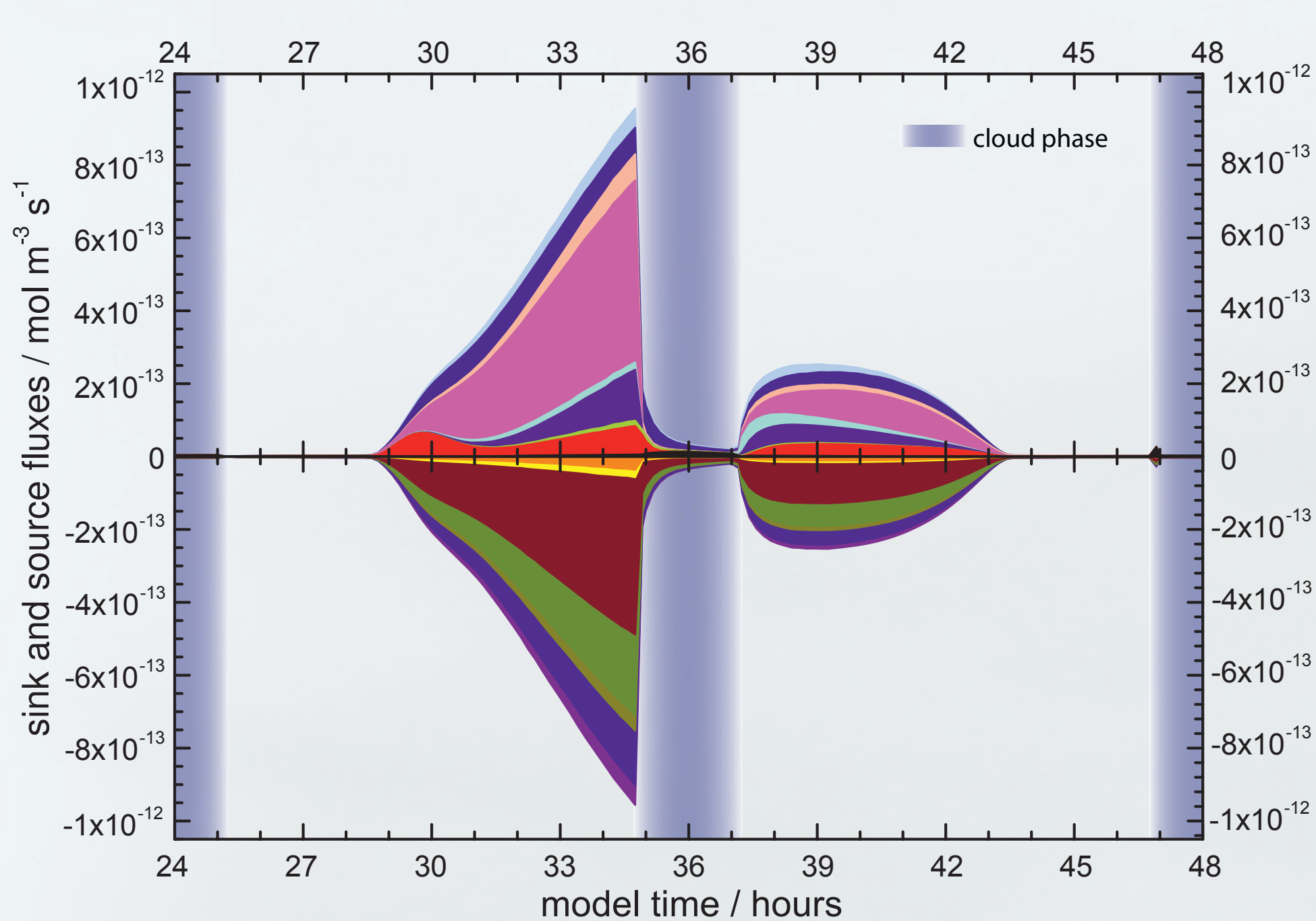


Fig. 4. Time resolved sink and source fluxes to the budget of Cl atoms for the second model day (scenario HM2).

Interactions with ozone

- The influence of halogens on ozone can be seen from the sensitivity studies omitting the respective halogen subsets (not shown).
- Calculations have been performed to determine the influence of halogens to the odd oxygen family Ox (based on [3]) averaged over the whole modeling period of 108h.
- Major ozone loss is caused as a consequence of the reaction $\text{O}(\text{D}) + \text{H}_2\text{O}_{(\text{g})} \rightarrow 2 \text{OH}$ (60%), HOx chemistry accounts for 13%, chlorine chemistry for 8%, bromine chemistry for 2%, and iodine chemistry for 13% (Fig. 9).

Results and Discussion

Iodine chemistry

- Typical concentrations of iodine species for open ocean conditions are reflected by the model (as shown for IO in Fig. 5).
- Clouds lower concentrations of gaseous iodine species and accumulate iodate.
- Iodine chemistry is triggered mainly by the emission of CH_2I_2 , CH_2IBr , and CH_2I_2 from the ocean (Fig. 6).
- Photolysis is the predominant degradation pathway of alkyl iodides producing iodine atoms.
- OH oxidation of alkyl iodides is of minor importance (between 0% and 18%), Cl oxidation is negligible for the fate of alkyl iodides.

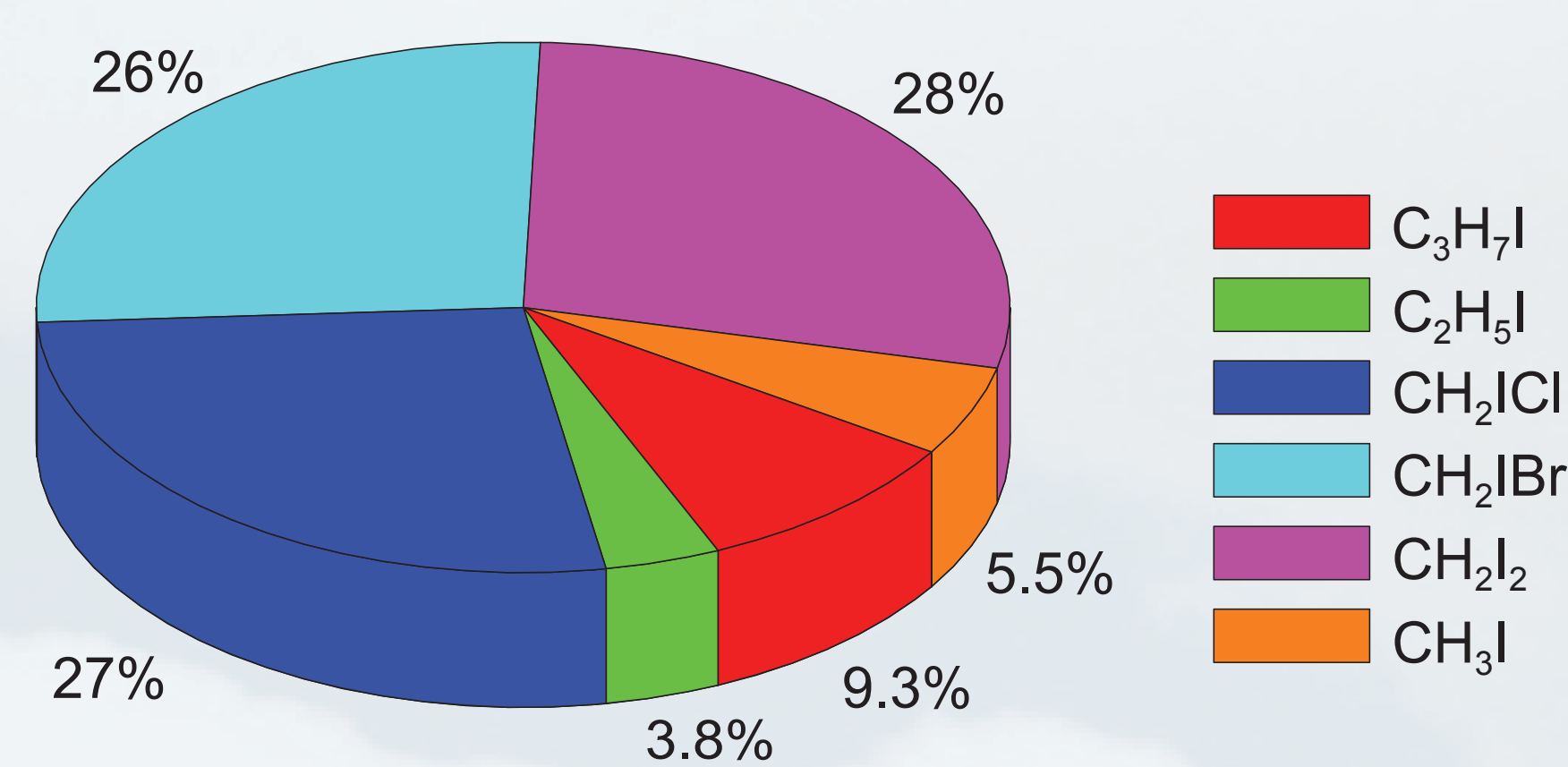


Fig. 5. Calculated relative contributions of alkyl iodides to the budget of tropospheric iodine atoms averaged over the modeling period of 108h.

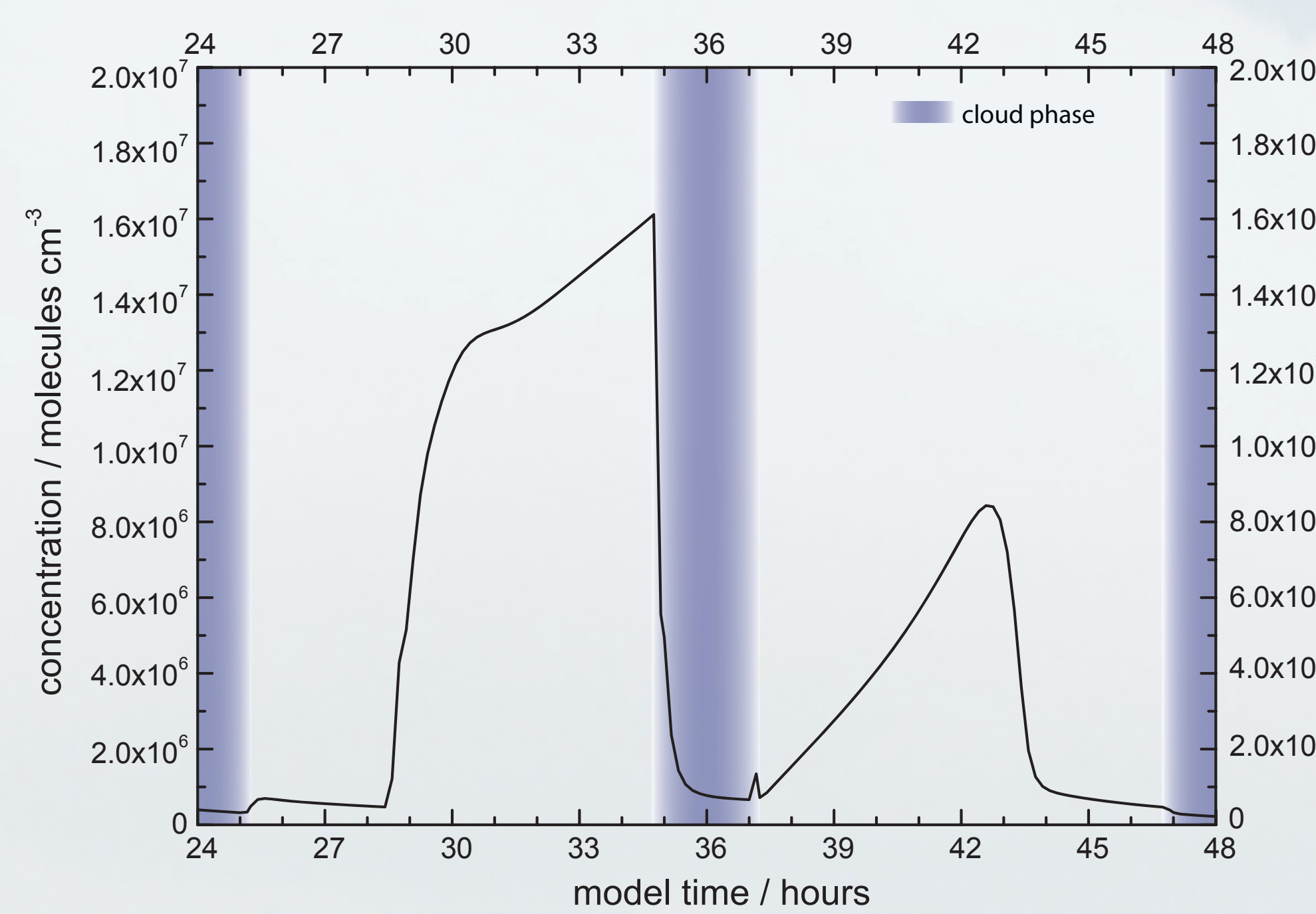


Fig. 6. Modeled concentrations of IO radicals for the second model day (scenario HM2).

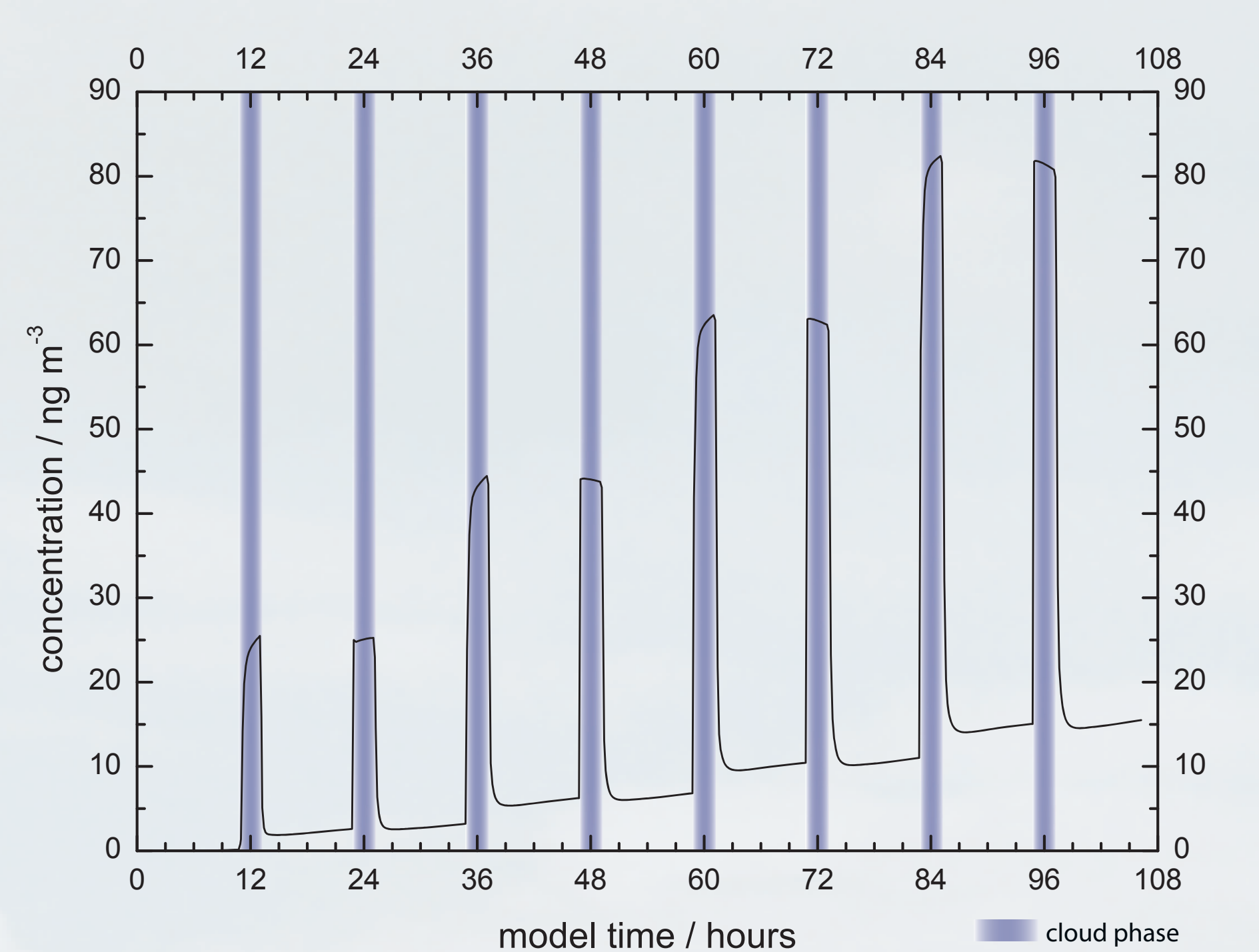


Fig. 7. Modeled concentrations of iodate over the whole period of 108h (scenario HM2).

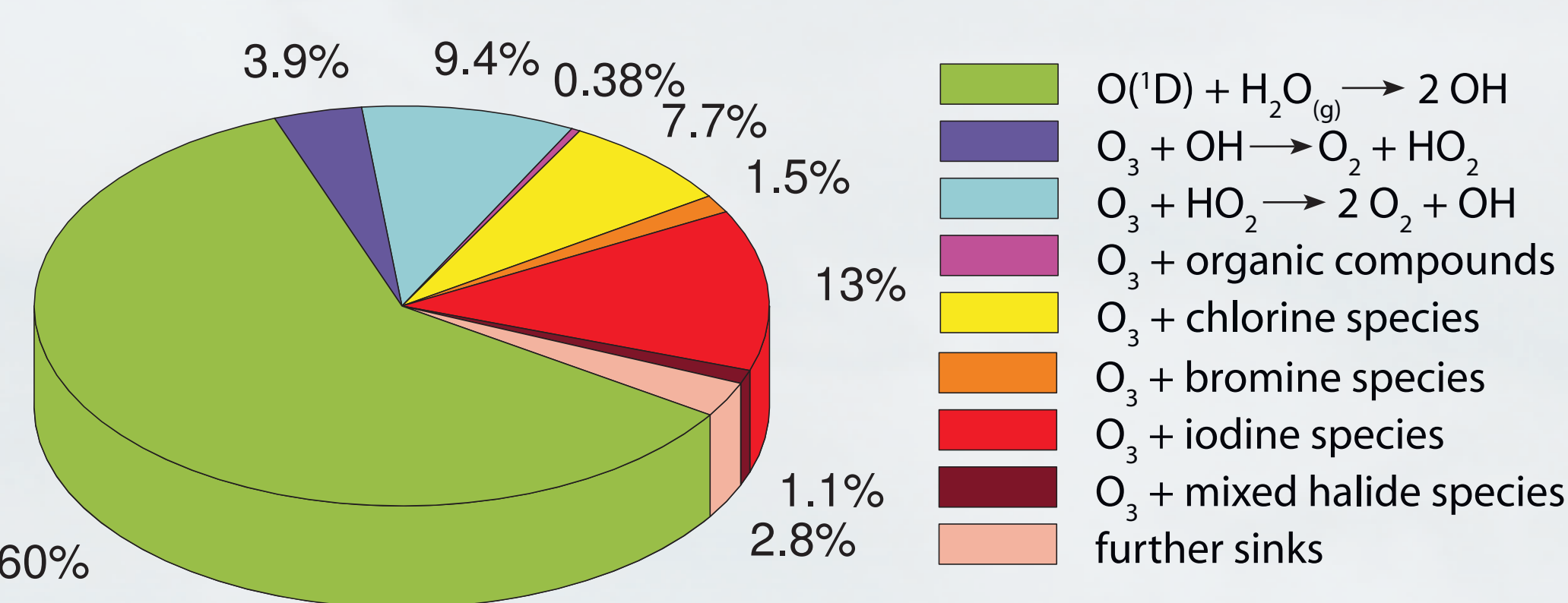


Fig. 9. Calculated relative contributions of different reactions to the destructions of Ox species.

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 (Fig 8).
- With cloud evaporation the produced Br is released causing a peak in several bromine species including BrO.
- Modeled BrO concentrations agree with measurements (several DOAS measurements inferred BrO concentrations around $2.5 \cdot 10^7$ molecules cm^{-3}) only for the first model day due to the chosen scenario.

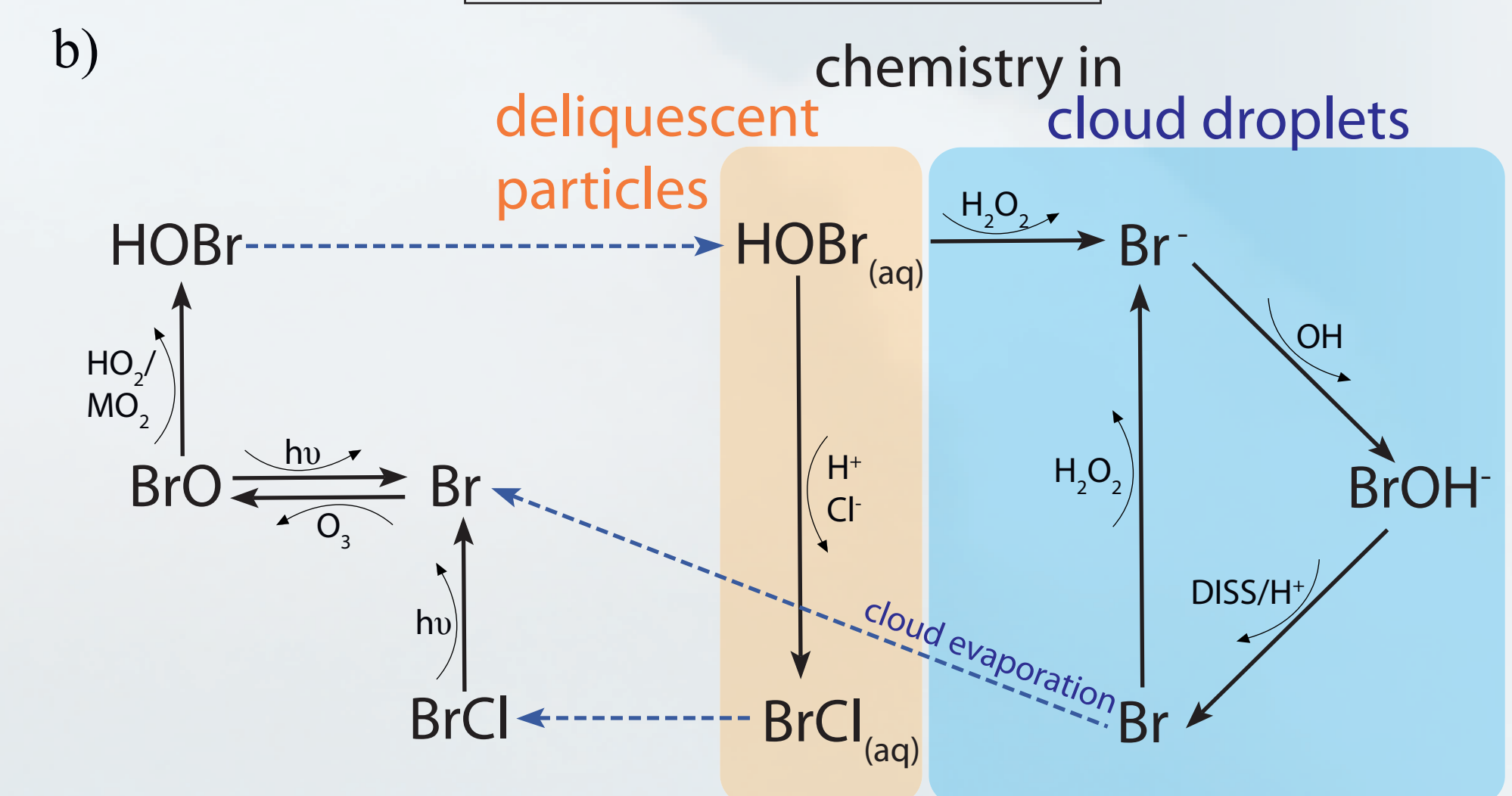
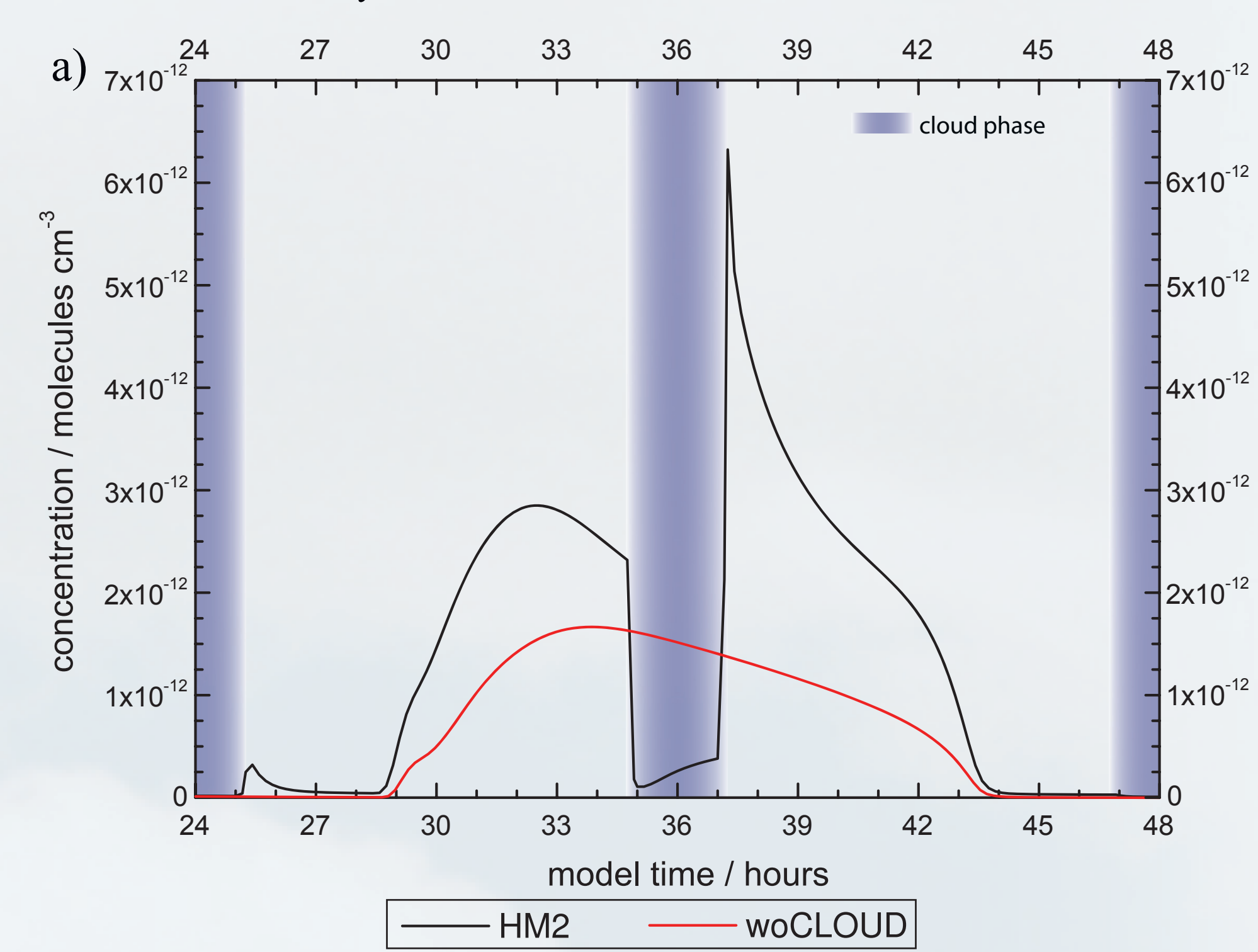


Fig. 8. Modeled concentrations of BrO radicals for the second model day with (HM2) and without clouds (woCLOUD) (a) and schematic of the different cycles in the presence and absence of clouds (b).

Summary

A halogen module with 597 processes has been developed and tested. Source and sink flux analyses can explain the halogen chemistry in more detail than before. Clouds alter the multiphase halogen chemistry significantly due to different reaction cycles. For example, IO radicals are scavenged from the gas phase and transformed into iodate, which accumulates in the condensed phase. The current study revealed the importance of H_2O_2 during cloud phases, which predominantly reacts with aqueous HOBr and causes an accumulation of bromine species in cloud droplets. Upon cloud evaporation Br is released to the gas phase causing a peak in the concentrations of several bromine species. The activation of chloride and bromide as a major source for reactive halogen species could be confirmed. The photolysis of alkyl iodides as major source for reactive iodine species was refined in the current study identifying CH_2I_2 , CH_2I_2 , and CH_2IBr as the main source with a contribution of about 80%. Further modeling studies are planned introducing new scenarios for polluted air masses in marine environments and the comparison of model results with specific case studies.

References

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