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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. There is a continuing research made in field measurements (e.g. [1]), laboratory experiments (e.g. [2]) or modelling studies (e.g. [3]).

Despite the large number of modelling studies still several restrictions exist in either of the chemistry mechanisms. The current study aims at a comprehensive chemical multiphase mechanism that generally describes the complex halogen chemistry in distinct environments ranging from the pristine open ocean to polluted coastal areas.

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 are 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 HM2 1707 processes and 699 species are included with the HM2 as in Fig. 1:

Halogen Modul 2.0		
597 Processes		
(Cl: 227 - Br: 198 - I: 172)		
Gas Phase	Phase Transfer	Aqueous Phase
362 Reactions	37 Species	193 Reactions
(Cl: 157 - Br: 106 - I: 99)	(Cl: 11 - Br: 10 - I: 16)	(Cl: 59 - Br: 82 - I: 57)

Fig. 1. Overview over the number reactions in the HM2.

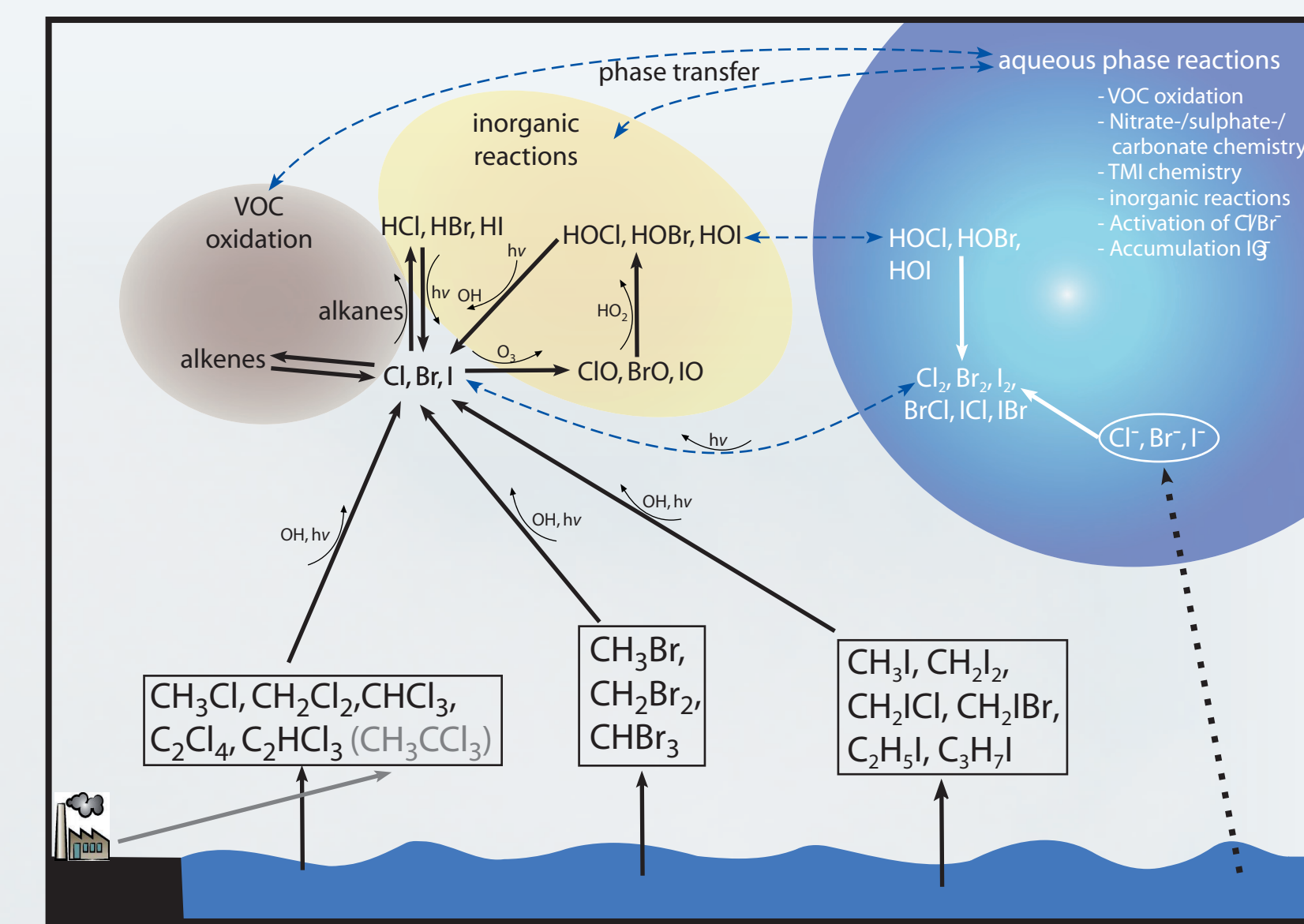


Fig. 2. Simplified scheme of the processes implemented in the halogen module 2.0.

Results and Discussion

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 with the 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 (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).

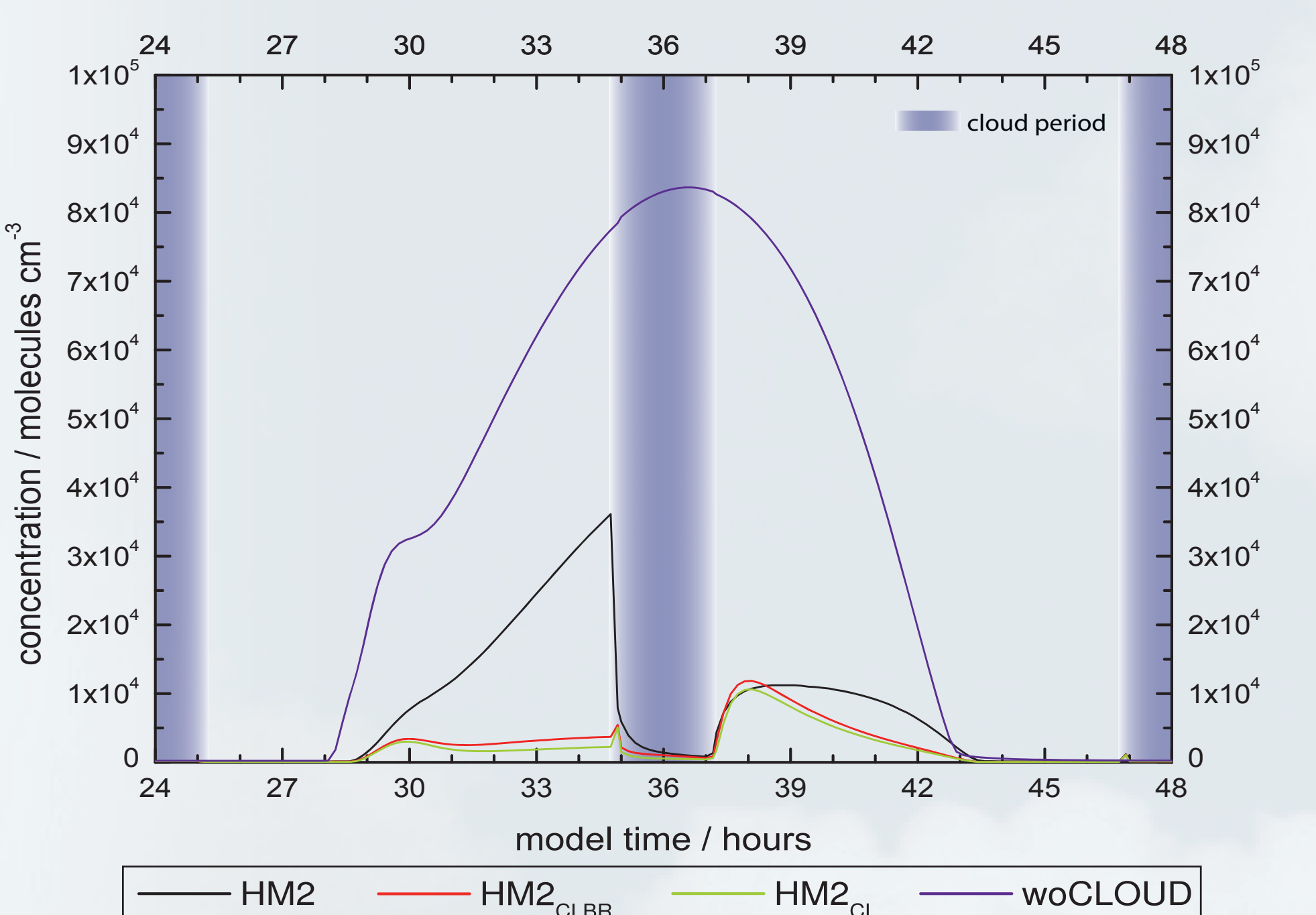
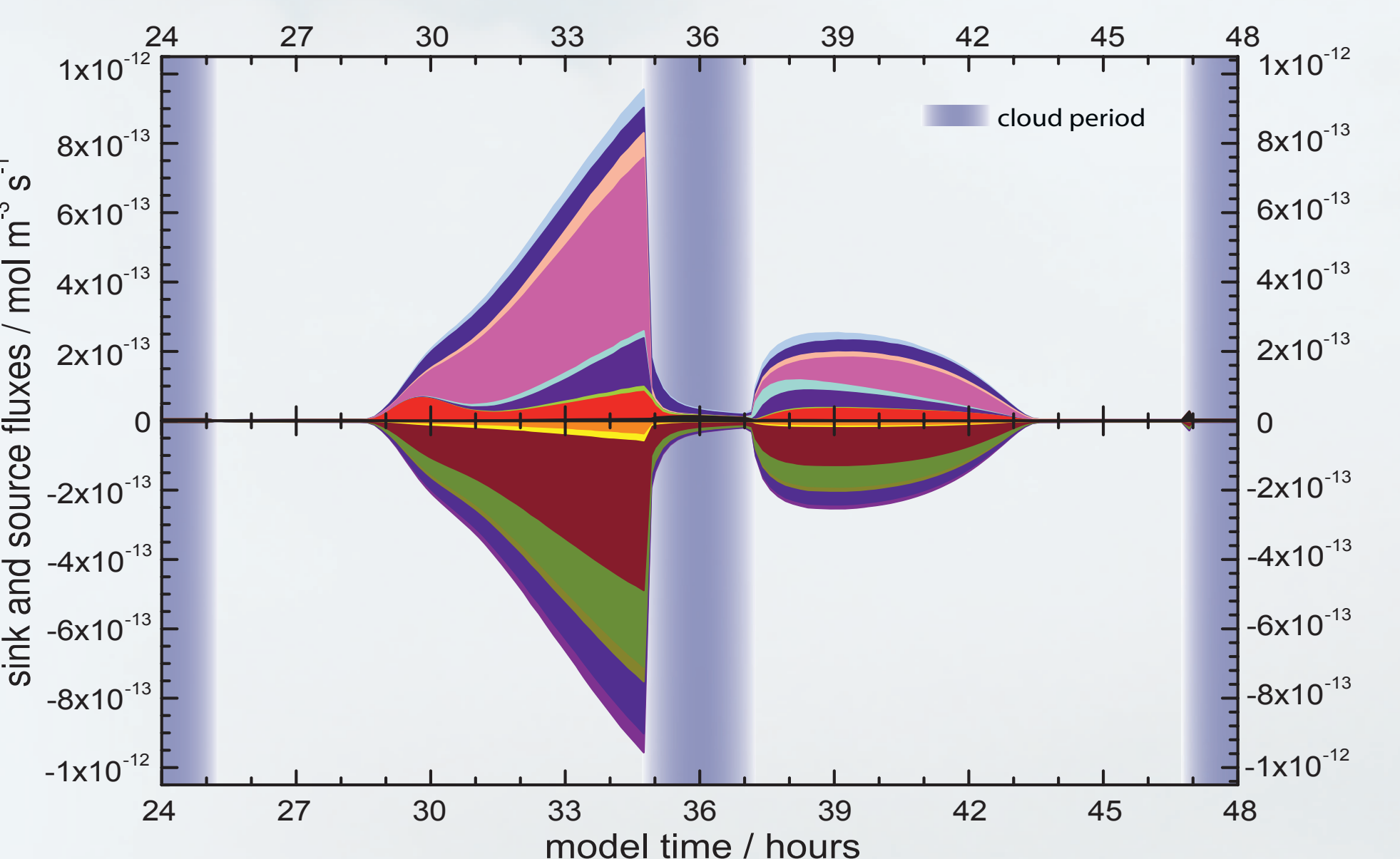


Fig. 3. Modelled concentrations of chlorine atoms in the gas phase for the second model day for the different scenarios.



Cl \rightleftharpoons Cl _(aq)	ClO + NO \rightarrow Cl + NO ₂
Cl ₂ $\xrightarrow{h\nu}$ 2 Cl	Cl + CH ₃ OOH \rightarrow HCl + CH ₃ OO
ClO $\xrightarrow{h\nu}$ Cl + O(¹ P)	Cl + CH ₃ CHO \rightarrow HCl + CH ₃ CO ₂
HOCl $\xrightarrow{h\nu}$ Cl + OH	Cl + CH ₄ $\xrightarrow{O(^1D)}$ Cl + CH ₃ OO
BrCl $\xrightarrow{h\nu}$ Br + Cl	Cl + C ₂ H ₆ $\xrightarrow{O(^1D)}$ HCl + C ₂ H ₅ OO
ICl $\xrightarrow{h\nu}$ I + Cl	Cl + higher alkanes \rightarrow products
Cl + O ₃ \rightarrow ClO + O ₂	further sources
ClO ₂ $\xrightarrow{h\nu}$ Cl + O ₂	further sinks

Fig. 4. Time resolved sink and source fluxes to the budget of Cl atoms in the gas phase 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 modelling period of 108h.

➤ Major ozone loss is caused as a consequence of the reaction O(¹D) + H₂O_(g) \rightarrow 2 OH (60%), HOx chemistry accounts for 13%, chlorine chemistry for 8%, bromine chemistry for 2%, and iodine chemistry for 13% (Fig. 9).

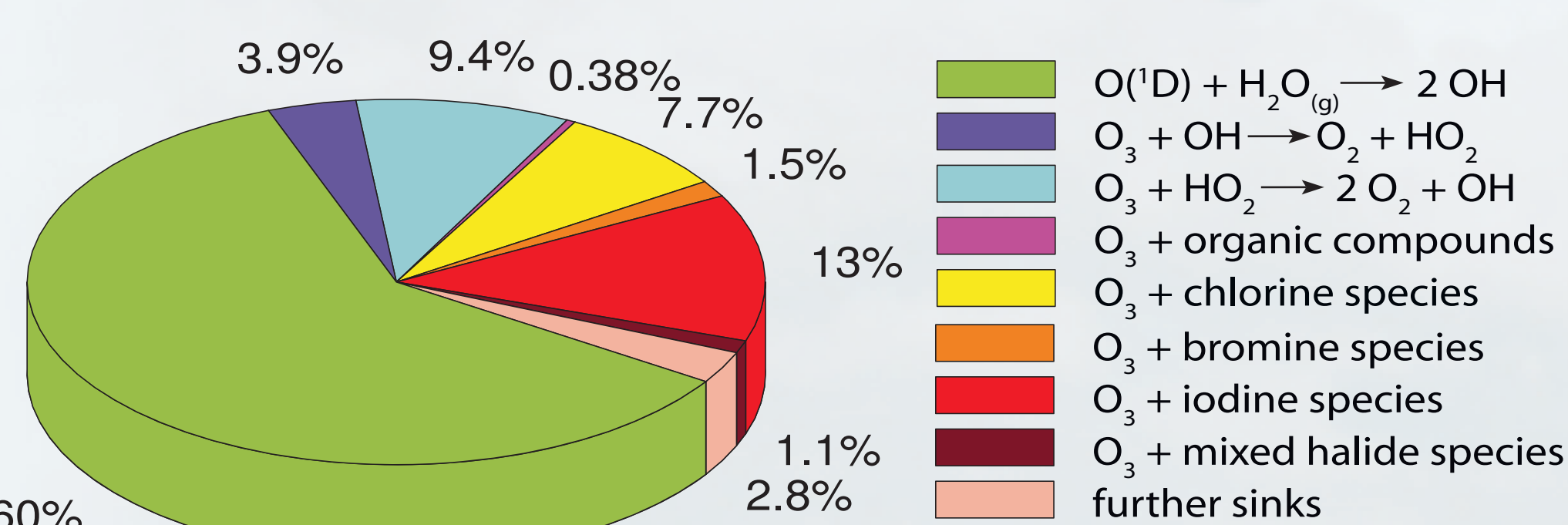


Fig. 9. Calculated relative contributions of different reactions to the destructions of Ox species.

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).

➤ Upon 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 $2.5 \cdot 10^7$ molecules cm^{-3}) only for the first model day due to the chosen scenario.

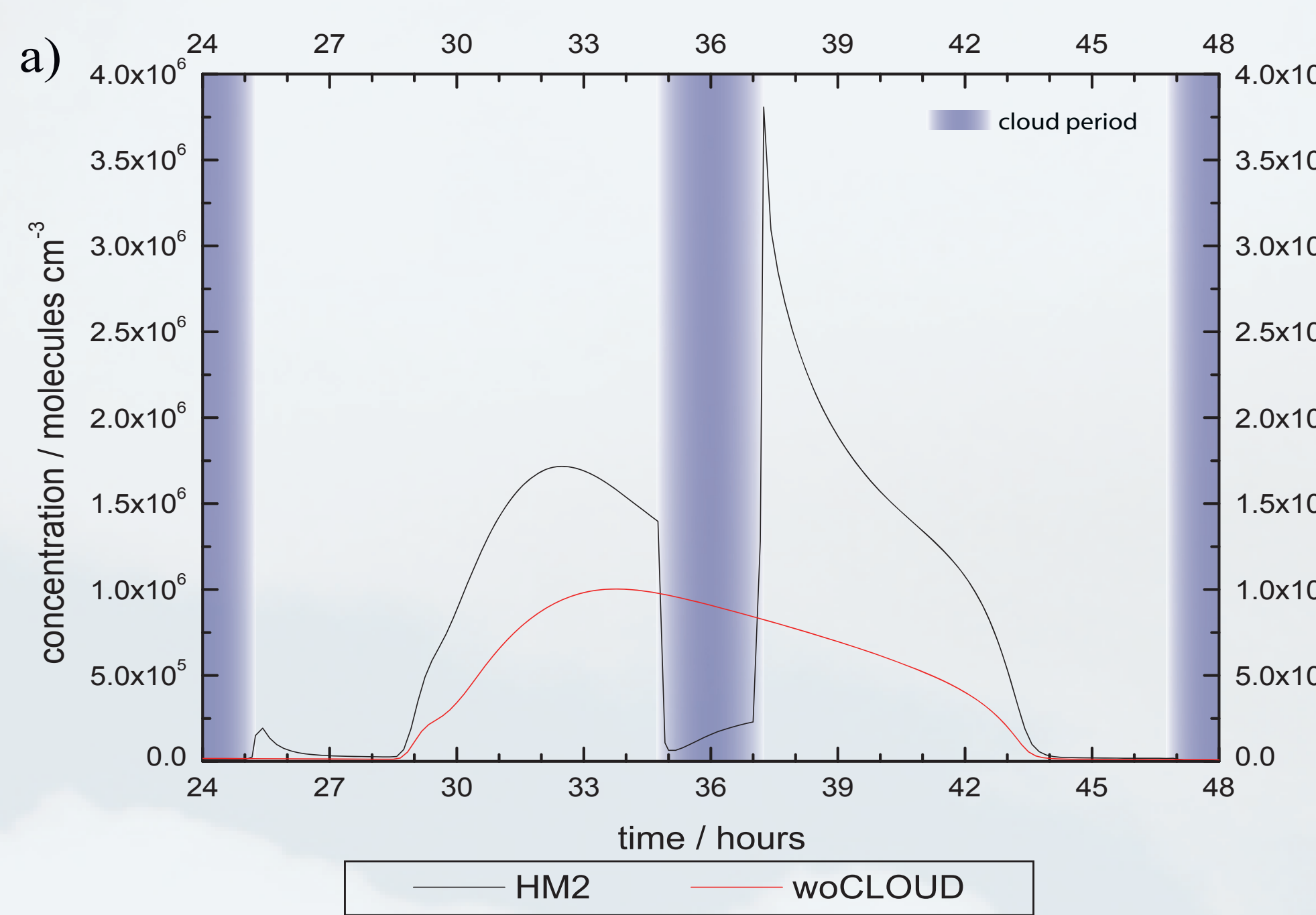


Fig. 5. Modelled concentrations of BrO radicals in the gas phase for the second model day with (HM2) and without clouds (woCLOUD) (a) and schematic of the different cycles in the presence and absence of clouds (b).

Interactions with organic compounds

➤ Halogens influence the atmosphere's oxidation capacity towards organic compounds.

➤ Increased oxidation is seen for most VOCs, including

- Alkanes (~50% contribution of chlorine, with up to 80% for ethane)
- Alkenes (9% contribution of chlorine and 2% of bromine for ethylene; 13% contribution of chlorine and 1% of bromine for propylene)

➤ Contribution of halogens to VOC production either directly, e.g. 16% of acetone production by photolysis of iso-propyl iodide or indirectly, e.g. acetaldehyde in the course of propylene oxidation.

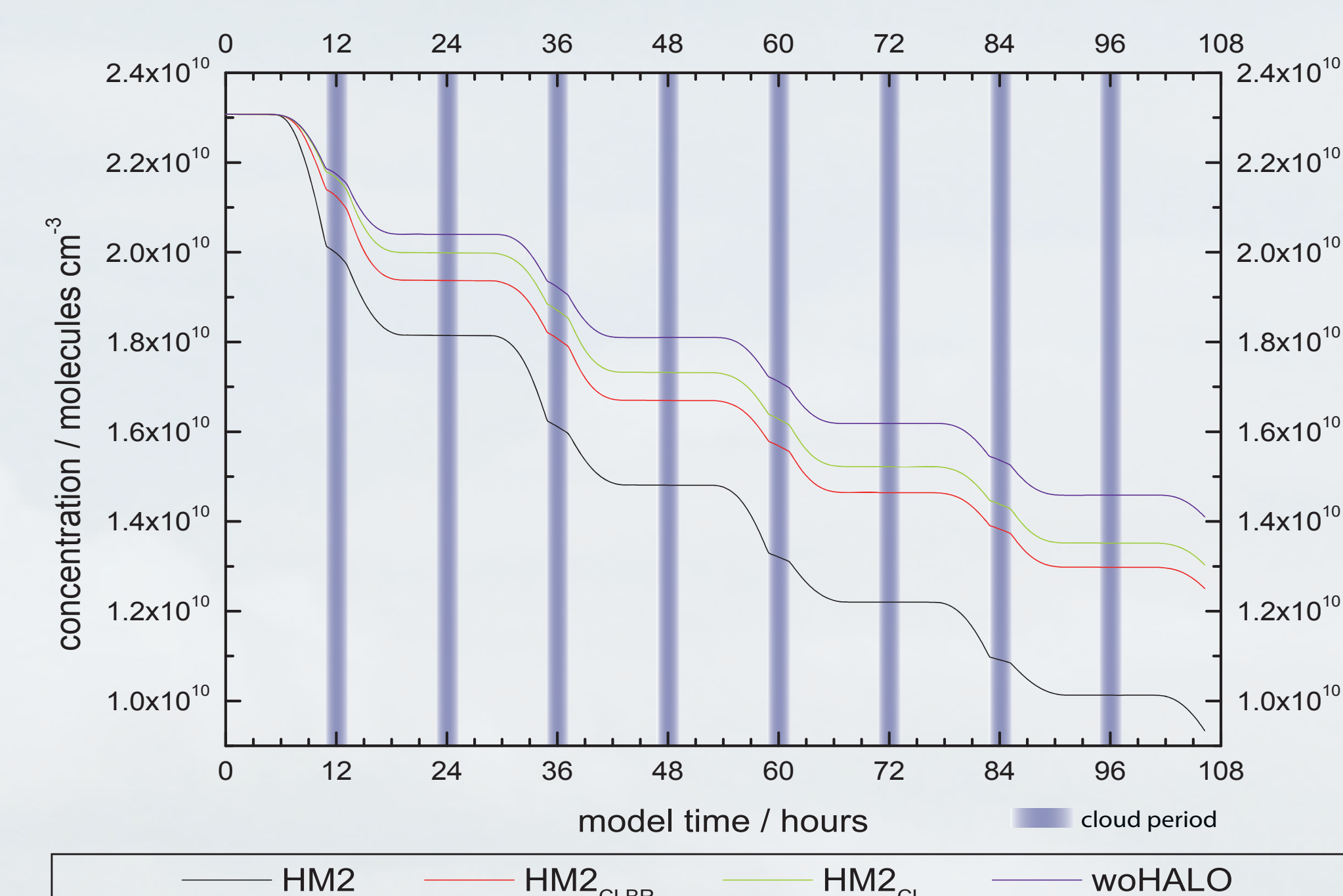


Fig. 10. Modelled concentrations of alkanes in the gas phase for the whole simulation time of 108h for the different scenarios as an example for the influence of halogens on the oxidation of VOCs.

Iodine chemistry

➤ Clouds lower concentrations of gaseous iodine species and accumulate iodate.

➤ Iodine chemistry is triggered mainly by the emission of CH₂I₂, CH₂I₂Br, and CH₂ClI from the ocean (Fig. 6).

➤ Photolysis is the predominant degradation pathway of alkyl iodides producing iodine atoms while OH oxidation is of minor importance (0% - 18%) and Cl oxidation is negligible

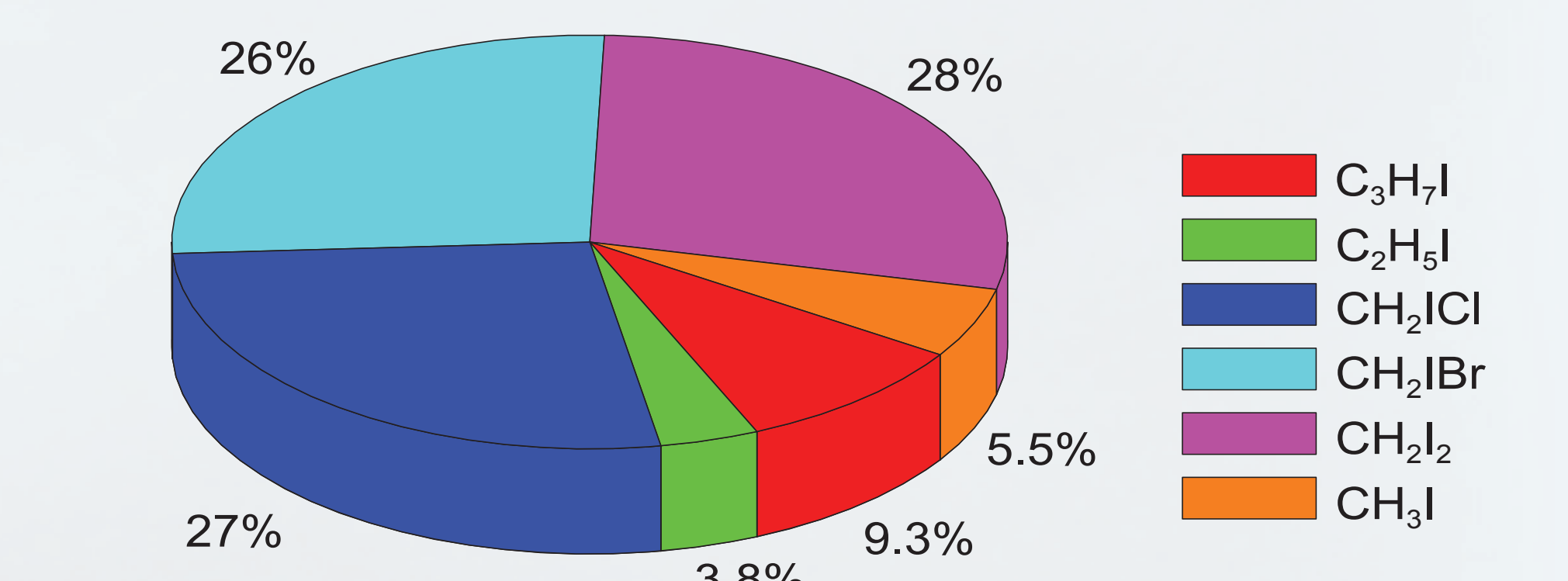


Fig. 6. Calculated relative contributions of alkyl iodides to the budget of tropospheric iodine atoms averaged for the whole simulation time of 108h.

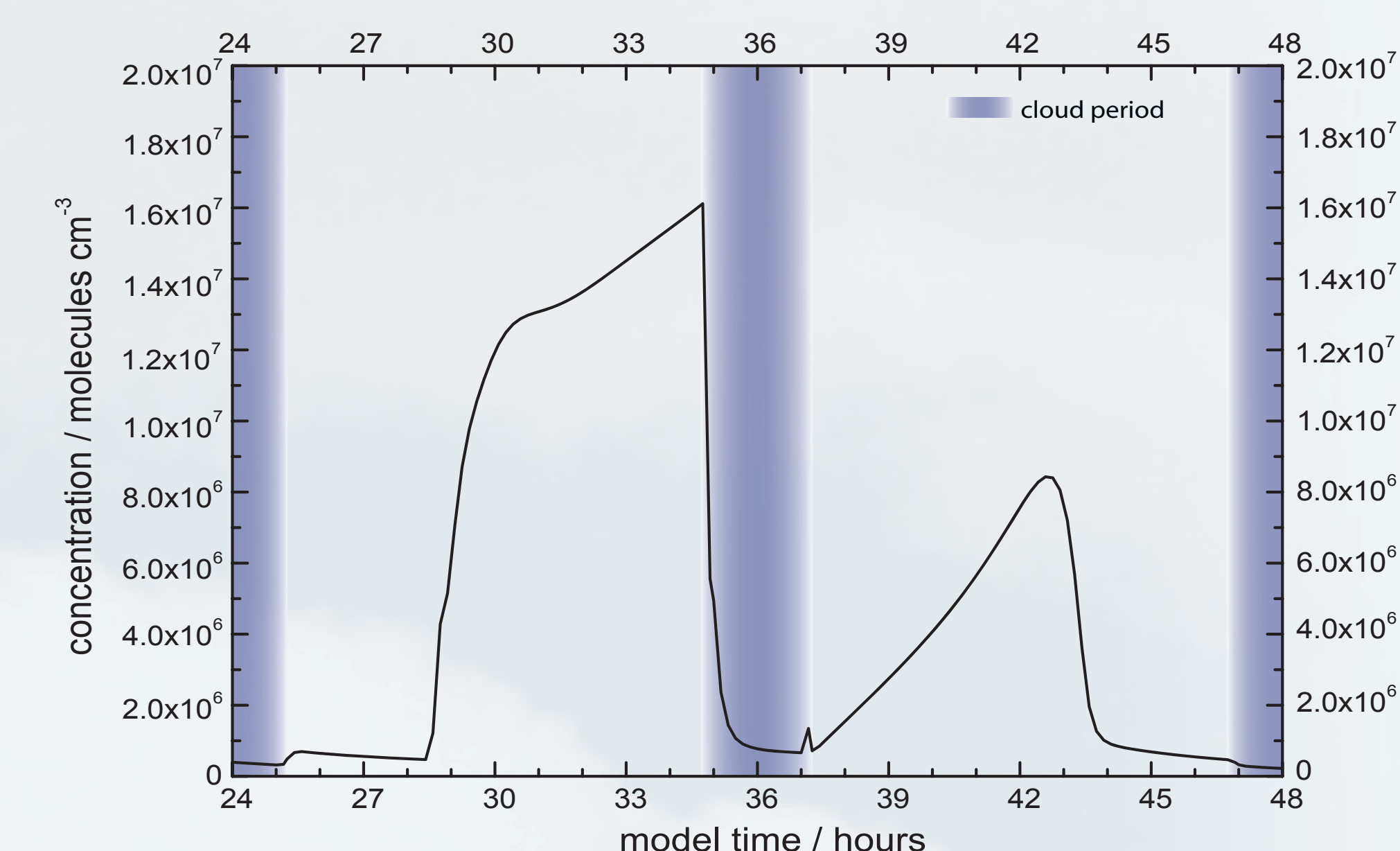


Fig. 7. Modelled concentrations of IO_{3(aq)} radicals for the second model day (scenario HM2).

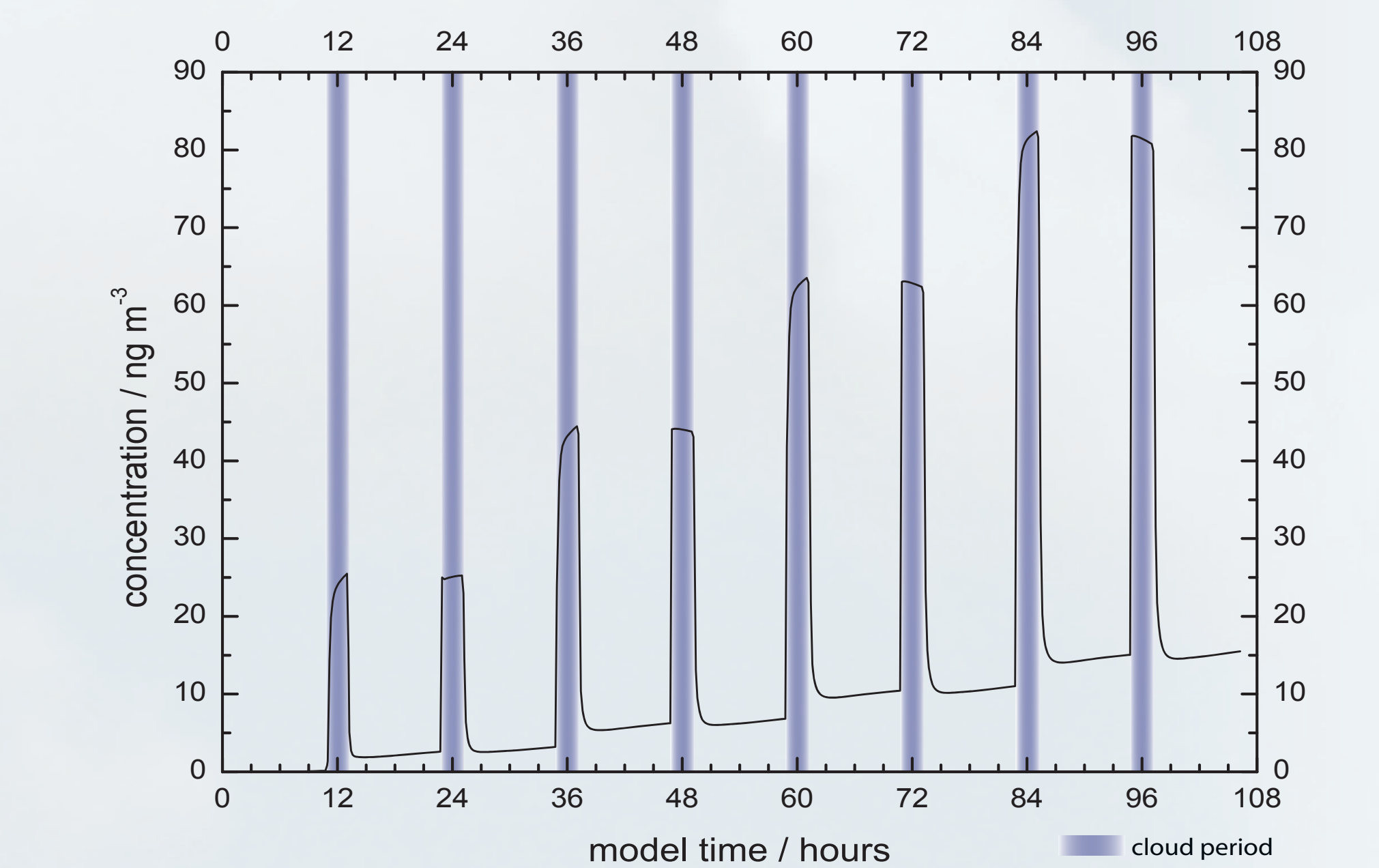


Fig. 8. Modelled concentrations of IO_{3(aq)} radicals for the whole simulation time of 108h (scenario HM2).

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 H₂O₂ 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. Furthermore the oxidation capacity of the atmosphere is influenced by halogens as shown for several VOCs and ozone.

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 CH₂I₂, CH₂ClI, and CH₂I₂Br 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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