Application of the CAPRAM Halogen Module 2.0 in mixed urban and maritime coastal areas

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Introduction and Motivation

It is well known that halogen multiphase chemistry plays an essential role in the marine boundary layer. In coastal regions, which cover ~20% of the earth's surface, they directly influence mankind as about one half of the world's population lives in these regions and 75% of the megacities are located here alongside with important transits and industrial locations[1].

In contrast to the marine chemistry, which is a low NO_x regime with short-chain organic compounds, the urban area is a high NO_x regime with high emissions of various organics. Halogens have a high reactivity towards NO_x and organic compounds, which can even exceed the OH reactivity. A mixing of maritime and urban air masses leads to different reaction pathways, which influence, for example, the air quality, cloud condensation nuclei radii and thus the global radiation budget, the chemical composition of aerosols and the ozone concentration levels. Therefore, it is of great interest to understand the interactions of maritime and continental urban influenced air masses in coastal regions.

Model Description

➢ Application of the CAPRAM Halogen Module 2.0 together with the multiphase chemical mechanism RACM-MIM2ext/CAPRAM 3.0n [2].

➢ Two different scenarios modelled for summer conditions with the box model SPACCIM [3]:
1. Maritime air mass moves over urban area: scenario Coastal → Urban (C_U)
2. Urban air mass moves over coastal ocean area: scenario Urban → Coastal (U_C)

➢ Different initial aerosols and concentrations and emissions of trace gases
➢ Both scenarios include non-permanent clouds with 8 cloud passages of the air parcel (see Fig. 1)
➢ Constant relative humidity of 90% between the cloud periods
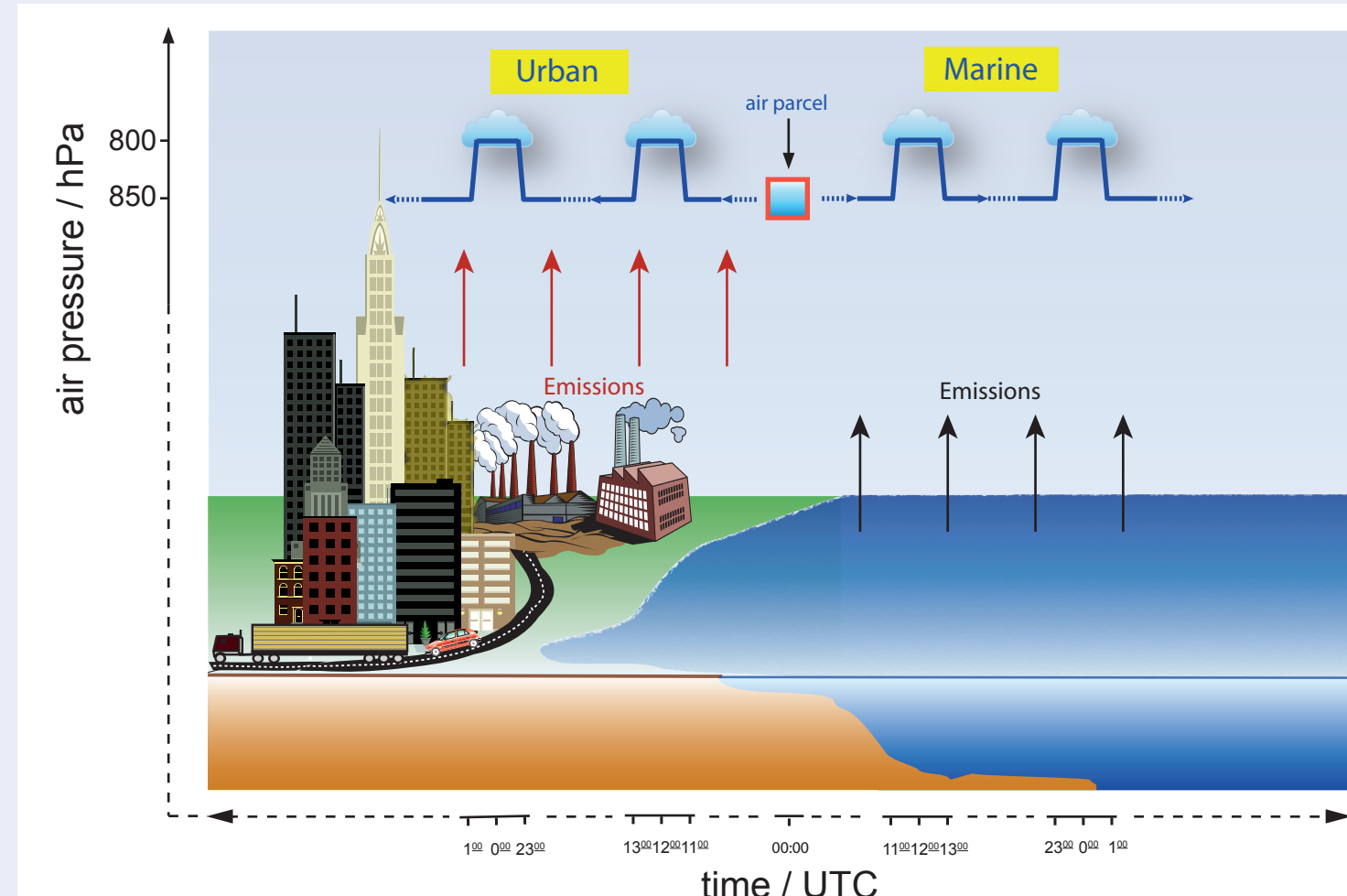➢ Performance of sensitivity runs to investigate estimated iodine emissions in the sc. U_C

Fig. 1: Scheme of the modelled scenarios C_U and U_C.

Results and Discussion

■ Chlorine chemistry

The scenario Coastal → Urban

➢ Modelled concentrations for $ClNO_2$ over the urban area show a good agreement with measurements, e.g. of Phillips et al. [4], with maximum concentrations of $2 \cdot 10^{10}$ molecules cm^{-3}.
➢ Over the urban area photolysis of $ClNO_2$ is the main source for reactive chlorine (see Fig. 2).
➢ Cl concentrations are not significantly decreased during the cloud period in contrast to the scenario U_C.
➢ Increased production of Cl atoms during night-time clouds due to NO_3 chemistry in clouds.

The scenario Urban → Coastal

➢ Modelled Cl concentrations in both sensitivity studies (withI_2 and withoutI_2) show a good agreement with inferred measurements from Pzenny et al. [5], who measured 2.2 – $5.6 \cdot 10^4$ molecules cm^{-3} (see Fig. 3).
➢ Main source for Cl is the photolysis of ICl, which is produced in the particle phase. Clouds suppress chlorine atom formation due to different cycles.
➢ The influence of the urban air mass is identified on the first model day.

■ Iodine chemistry

The scenario Coastal → Urban

➢ The reactions of IO with NO_x species form the largest sources for gaseous I atoms.
➢ Cloud periods suppress the iodine production.

The scenario Urban → Coastal

➢ Modelled concentrations of IO are in better agreement with measurements in scenario without I_2 emission than with I_2 emissions (see Fig. 4), but concentrations of OIO coincide better with the scenario with I_2 emission.
➢ The influence of the urban air mass is identified on the first model day.
➢ After the first day, clouds decrease the concentration of gaseous iodine and accumulate iodate in the aqueous phase.
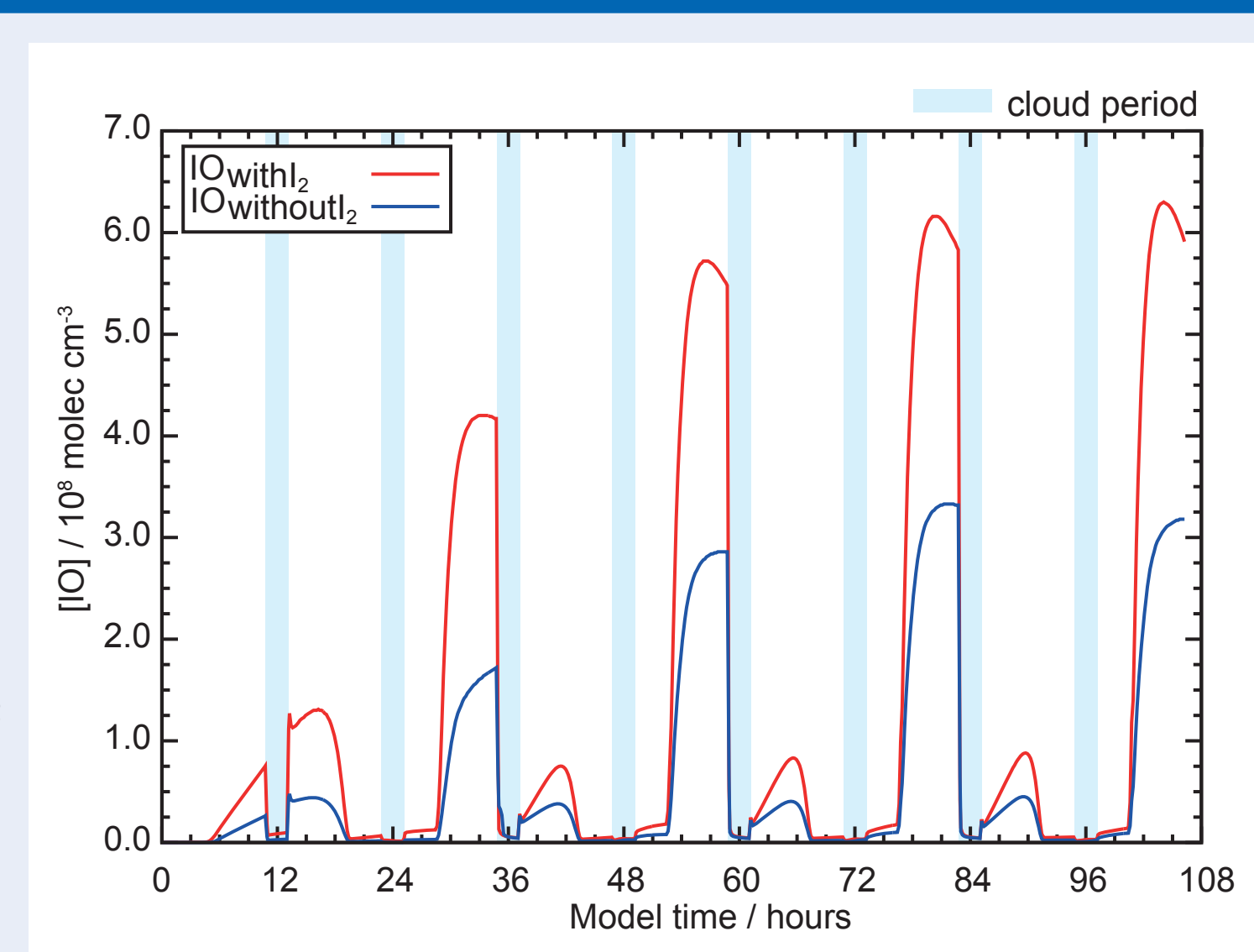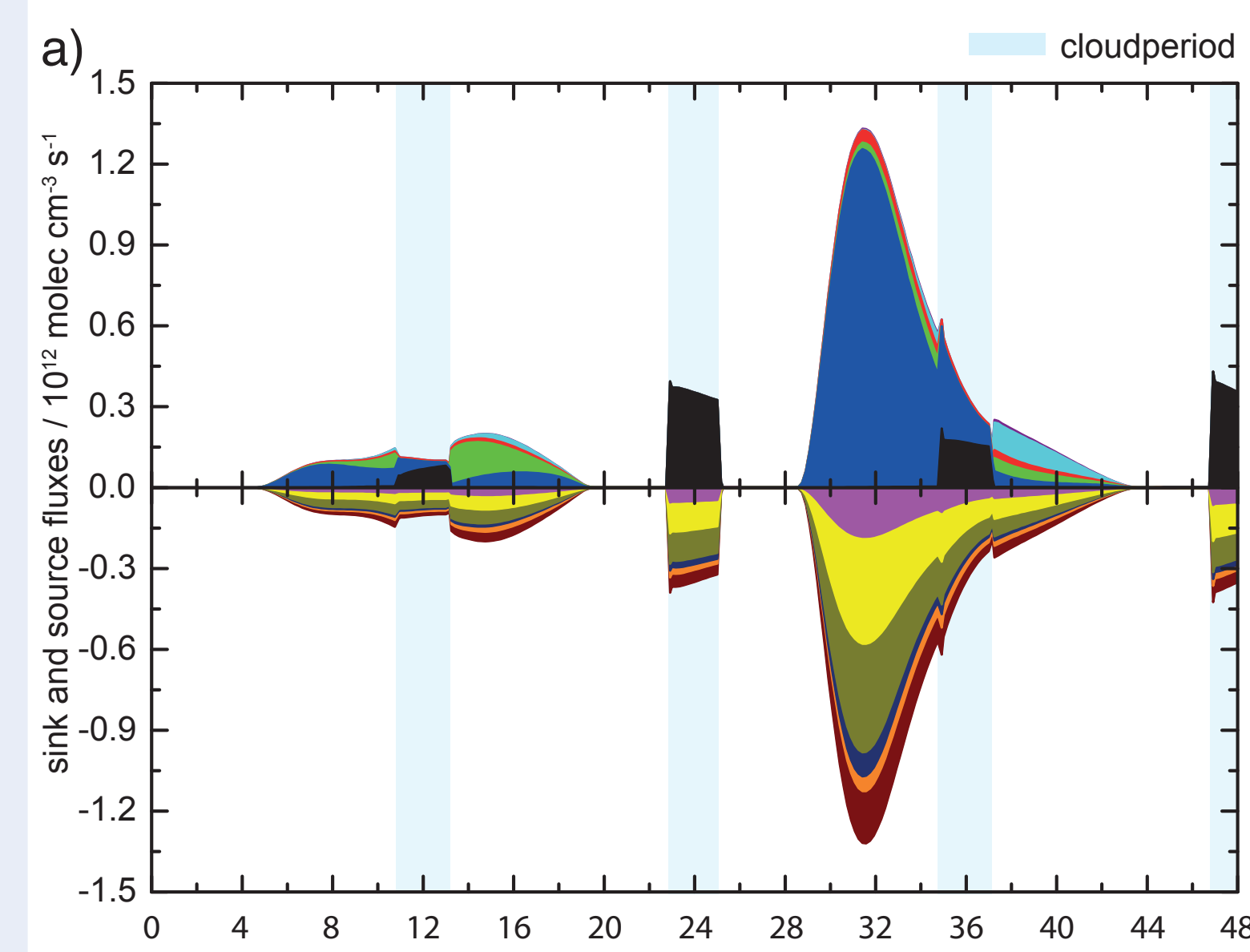
■ Interactions with organics

➢ In urban areas, VOC degradation by OH is dominat; degradation by NO_3 and halogens is mostly unimportant (see Tab. 1).
➢ Over the coastal ocean, the importance of Cl atoms in the VOC oxidation process rises and can even exceed the oxidation by OH. I_2 emissions increase the chlorine reaction channel (see Tab. 2).
➢ Bromine shows slightly higher turnovers in the VOC oxidation process in the scenario U_C than NO_3.

Fig. 5: Modelled concentrations of gaseous IO radicals over the whole simulation time for the scenario U_C with (withI_2) and without (withoutI_2) iodine emissions.

Tab. 1: Relative contributions of important oxidants (listed in the headline) to the gas phase oxidation of selected organic compounds averaged over the whole simulation time of the scenario C_U.

	OH	NO_3	Cl	Br	Further sinks
Methane	99.0%	-	1.0%	-	-
Ethane	87.9%	-	12.1%	-	-
$C_{3/4}$ alkanes	96.6%	-	3.4%	-	-
C_{5-7} alkanes	97.7%	-	2.3%	-	-
$C_{>8}$ alkanes	97.7%	-	2.3%	-	-
Ethylene	76.7%	0.0%	0.5%	0.0%	22.8% (O_3)
Acetylene	99.8%	-	0.2%	0.0%	-
Formaldehyde	20.0%	0.0%	0.1%	0.0%	79.9% (upt.)
Acetaldehyde	91.7%	0.2%	0.2%	0.1%	7.8% (hv)
Higher Aldehydes	91.9%	0.2%	0.2%	0.1%	7.6% (hv)
Methylglyoxal	25.9%	0.1%	0.0%	-	74.0% (hv)
Toluene	99.6%	-	0.4%	-	-

Tab. 2: Relative contributions of important oxidants (listed in the headline) to the gas phase oxidation of selected organic compounds averaged over the whole simulation time of the scenario U_C with (w I_2) and without (wo I_2) emissions.

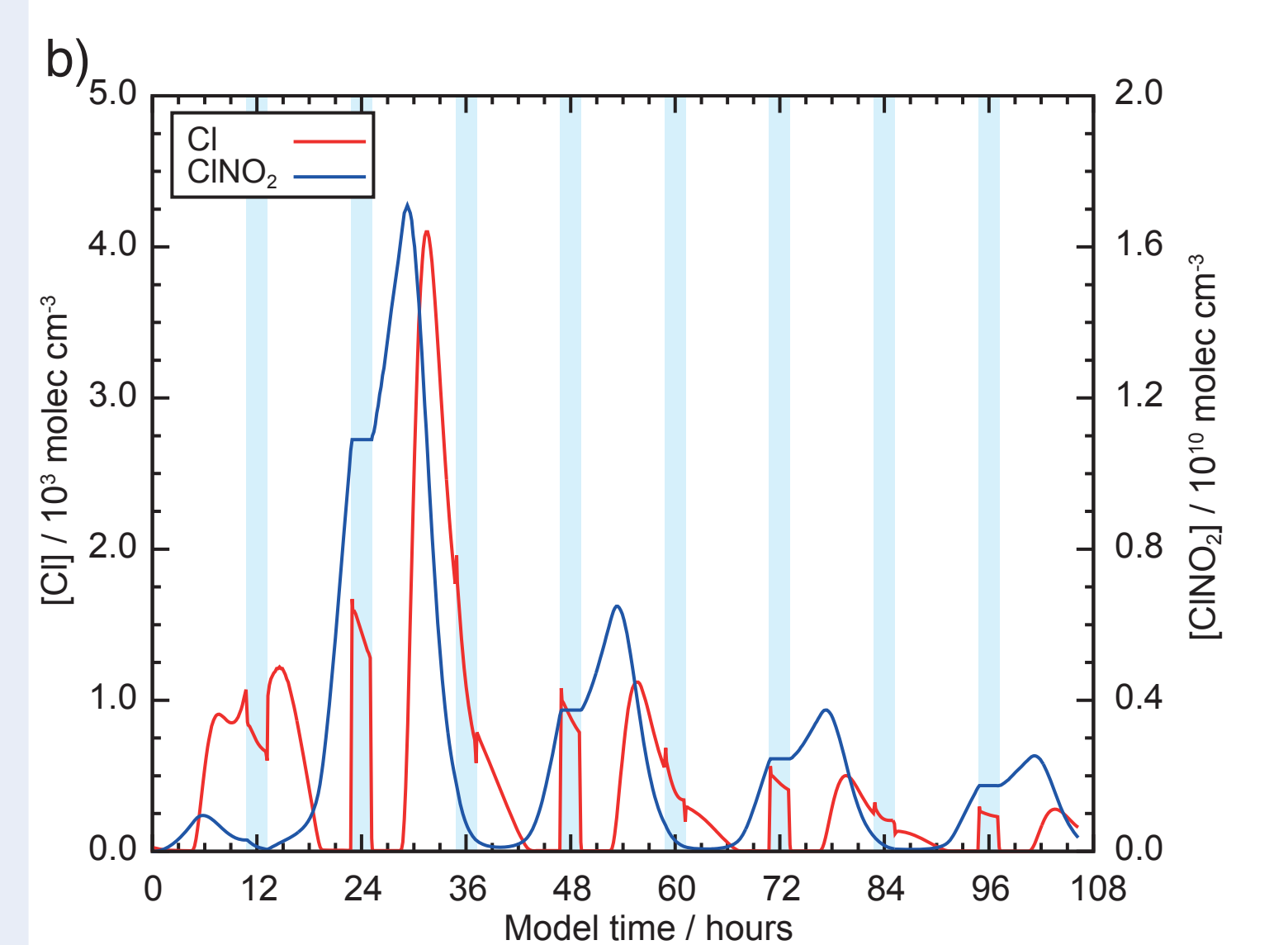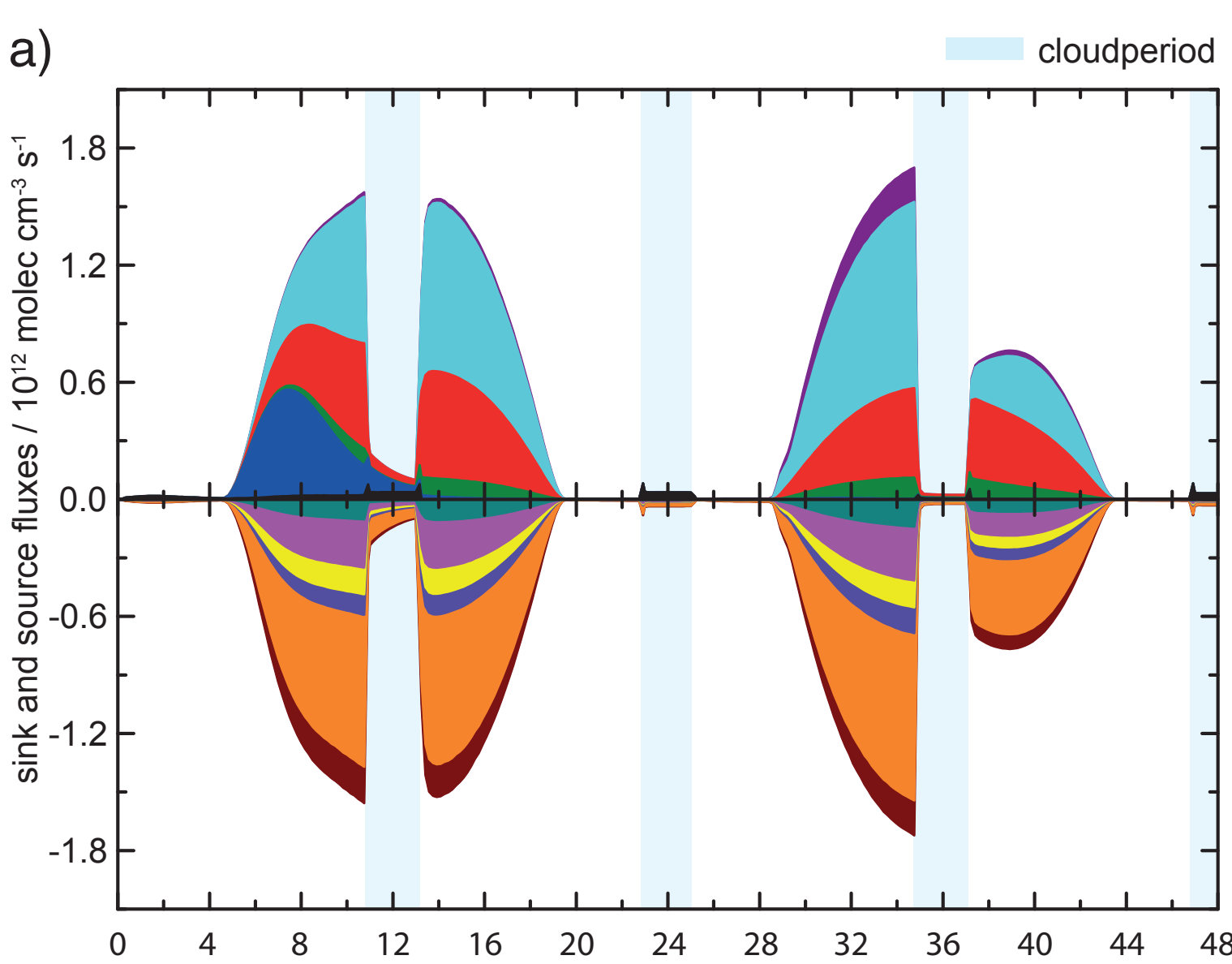|	OH		NO_3		Cl		Br		Further sinks	
	w I_2	wo I_2	w I_2	wo I_2	w I_2	wo I_2	w I_2	wo I_2	w I_2	wo I_2
Methane	44.3%	57.7%	-	-	55.7%	42.3%	-	-	-	-
Ethane	4.9%	8.0%	-	-	95.1%	92.0%	-	-	-	-
$C_{3/4}$ alkanes	18.7%	27.3%	-	-	81.3%	72.7%	-	-	-	-
C_{5-7} alkanes	27.8%	38.2%	-	-	72.2%	61.8%	-	-	-	-
$C_{>8}$ alkanes	35.5%	45.6%	-	-	64.5%	54.4%	-	-	-	-
Ethylene	42.0%	45.2%	0.1%	0.1%	25.9%	16.3%	0.6%	0.4%	31.4% (O_3)	38.0% (O_3)
Acetylene	77.2%	84.1%	-	-	22.7%	15.9%	0.1%	0.1%	-	-
Formaldehyde	7.6%	8.6%	0.1%	0.1%	2.8%	1.6%	0.2%	0.1%	89.3% (upt.)	89.6% (upt.)
Acetaldehyde	49.1%	53.1%	0.9%	1.2%	22.2%	14.9%	6.2%	4.4%	21.6% (hv)	26.4% (hv)
Higher Aldehydes	52.8%	58.7%	1.0%	1.2%	20.4%	13.0%	5.3%	3.5%	20.5% (hv)	23.6% (hv)
Methylglyoxal	14.3%	16.3%	0.3%	0.4%	1.4%	0.9%	-	-	84.0% (hv)	82.4% (hv)
Toluene	66.4%	77.0%	-	-	33.6%	23.0%	-	-	-	-

Fig. 2: Time-resolved sink and source fluxes to the budget of Cl atoms in the gas phase on the first two model days (a) and modeled concentrations of chlorine atoms and $ClNO_2$ over the whole simulation time (b) for the scenario C_U.
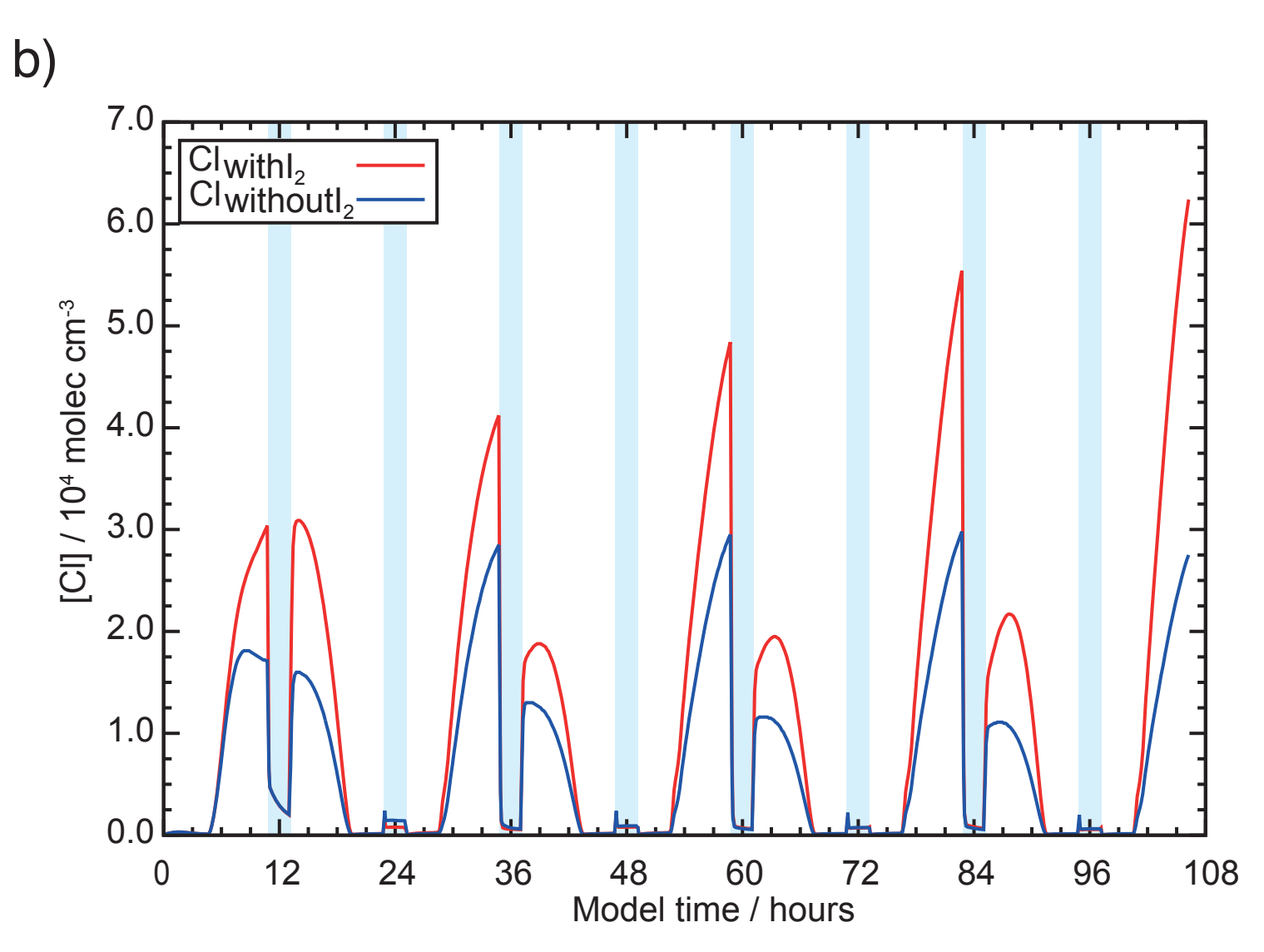

Fig. 3: Time resolved sink and source fluxes to the budget of Cl atoms in the gas phase on the first two model days of the scenario with I_2 emission (a) and modeled concentrations of chlorine atoms over the whole simulation time (b) for the scenario U_C.

■ Bromine chemistry

The scenario Coastal → Urban

➢ The reactions of Br and BrO with NO_x species form the largest sources for gaseous Br atoms.
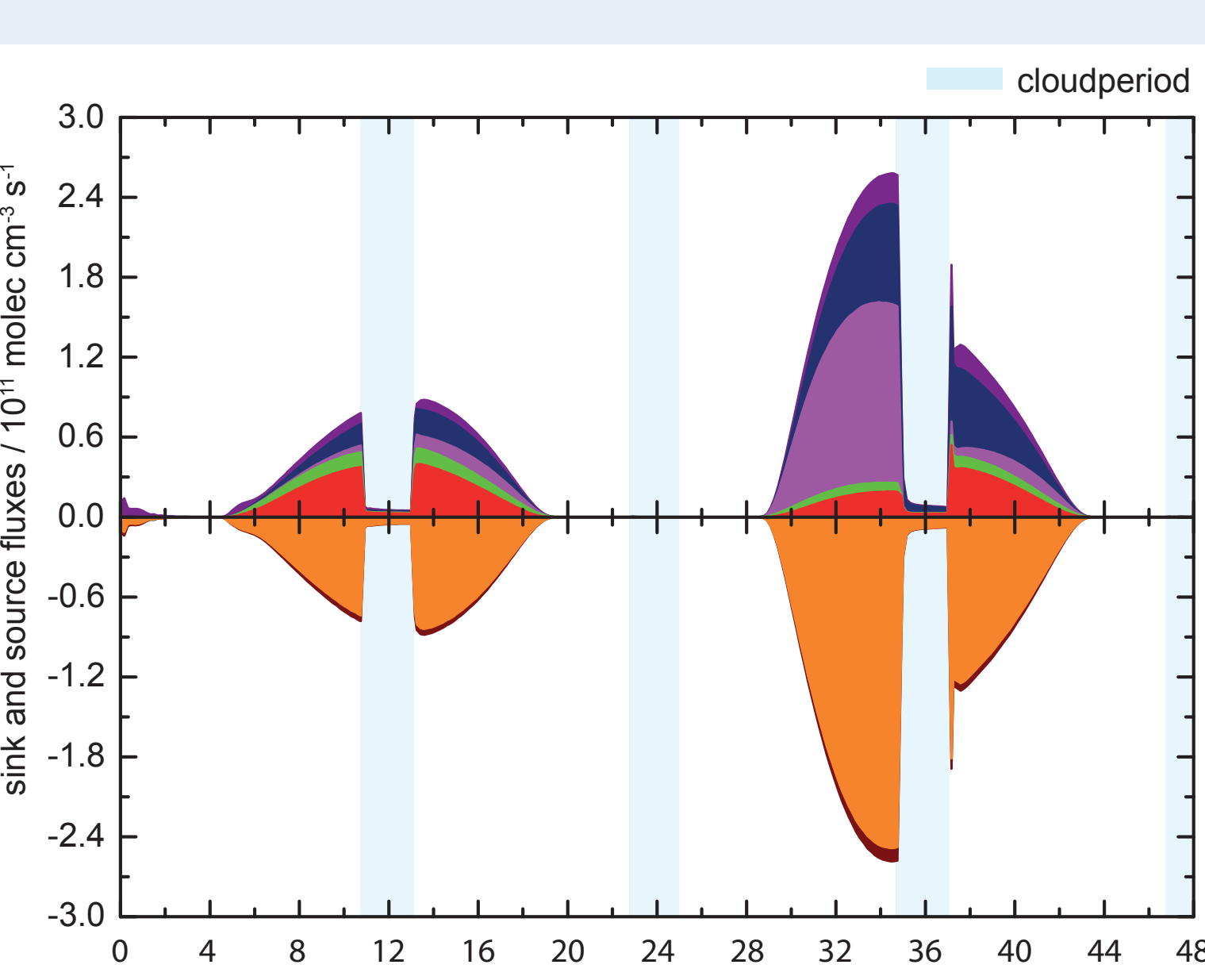➢ Cloud periods suppress the bromine production.

The scenario Urban → Coastal

➢ Modelled concentrations of bromine species do not agree very well with measurements.
➢ The influence of the urban air mass is identified on the first model day.
➢ Clouds decrease concentrations of bromine species significantly due to decreased IO concentration levels (see Fig. 4 and Fig. 5).
➢ A peak in several bromine species is caused by the photolysis of released IBr upon cloud evaporation. IBr is produced in the cloud via the reaction of HOI with Br^-.

Fig. 4: Time resolved sink and source fluxes to the budget of Br atoms in the gas phase on the first two model days of the scenario U_C with I_2 emission.

Summary and Outlook

Box model studies with a detailed multiphase chemistry mechanism (RACM-MIN2ext/CAPRAM 3.0n + HM2) have been performed to investigate the complex chemistry of halogens in coastal areas. Two scenarios have been applied with an urban polluted air mass moving over the coastal ocean and a marine air mass moving over a coastal city. The simulations have shown that influence of the air mass origin is most important on the first day. Thereafter, the emissions of the new environment dictate the multiphase chemistry. The scenario C_U showed the influence of halogen multiphase chemistry on NO_x species. The production of Cl is mainly triggered by $ClNO_2$, which is formed during the night and acts as a temporary reservoir for gaseous Cl and NO_2. The production of iodine and bromine is mainly triggered by the reactions of IO/BrO with NO_x. Because of the highly polluted air, chlorine prefers VOCs as reaction partners over ozone.

The sensitivity study of the scenario U_C demonstrated the importance of the emission strength of I_2 for the tropospheric oxidation capacity. A higher emission leads to increased HOI concentration levels, which trigger both halogen activation and HO_x chemistry. The increased halogen levels lead to decreased ozone concentrations. The additional source of OH radicals by HOI photolysis superimposes the decreased OH production from ozone photolysis and leads to an overall increase of the tropospheric oxidation capacity, which can be seen by the decreased VOC concentrations. Cloud periods have a significant influence on the concentrations of halogen species in contrast to the scenario C_U. After cloud periods, halogens show decreased concentration levels due to IO scavenging by cloud droplets and subsequent iodate formation.

Besides further modelling studies comparing the HM2 to measurements from field campaigns, further mechanism development is planned. A module describing the multiphase chemistry of DMS and its oxidation products is currently under constuction. Mechanism reduction of the overall mechanism for 2D- and 3D-modelling is planned.

References

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