Modeling of Multiphase Chemistry in Clouds under Marine Boundary Layer Conditions

A contribution to the sub-project CMD-MPM

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Introduction

The aim of this study is to investigate the contribution of clouds to halogen activation processes in the marine boundary layer. Halogens play an important role in chemical processes in the marine boundary layer. Halogen containing compounds are released by sea salt particles and then destroyed photochemically to form very reactive halogen atoms. These may have an impact comparable to that of the OH· radical on chemistry of the marine troposphere (Finlayson-Pitts, 1993). Sander and Crutzen (1996) proposed a mechanism to explain ozone destruction by halogens that are released from sea salt particles. Ayers et. al. (1999) analysed aerosol composition to validate this mechanism and they found in fact chlorine and bromine deficits in sea salt particles. Dickerson et al. (1999) partly explained the ozone depletion with halogen release in the marine boundary layer. However, still a large uncertainty in explaining the high amounts of halogen containing compounds in marine regions exist (Spicer et al., 1998).

In this study a complex mechanism for describing gas phase and aqueous phase chemistry is extended by a module which contains reactions of halogen containing species. This mechanism is applied to a 0-d box model for clean (marine scenario) and polluted (urban scenario) conditions.

Mechanisms and model parameters

The chemistry of clouds under marine conditions is described by a complex mechanism consisting of three parts. The gas phase reactions are described by RACM (Stockwell et al., 1997; regional atmospheric chemistry mechanism), the aqueous phase reactions are taken from CAPRAM 2.4 (MODAC mechanism, Ervens et al. 2000), which is a further development of CAPRAM 2.3 (chemical aqueous phase radical mechanism; Herrmann et al., 2000) and a special module developed to describe the reactions of halogen containing compounds. This module contains reactions of halogen species in both the gas and the aqueous phase and describes also phase transfer of the species. The phase transfer between aqueous phase and gas phase is treated as proposed by Schwartz (1986) considering Henrys Law, gas phase diffusion and mass accommodation.

A box model is applied to treat this complex multiphase chemistry system. Additional, to take the exchange of surrounding air into account, emissions and depositions are introduced to the box. The model runs were performed for a cloud (LWC = 0.3 g m^{-3}, r_{drop} = 10 µm, N_{dr} = 1·10^8 m^{-3} and RH = 100 %) under marine boundary layer conditions (T = 288 K, p = 1013 hPa). The two regimes for the input parameters, i. e. emission and deposition datasets were taken from the project MODAC (model development for tropospheric aerosol and cloud chemistry).

This leads to initial concentrations of $[Br^-] = 1.8 \cdot 10^{-6}$ M and $[Cl^-] = 5.6 \cdot 10^{-4}$ M for the clean (marine) case and of $[Br^-] = 3.0 \cdot 10^{-6}$ M and $[Cl^-] = 1.0 \cdot 10^{-4}$ M for the polluted (urban) case.
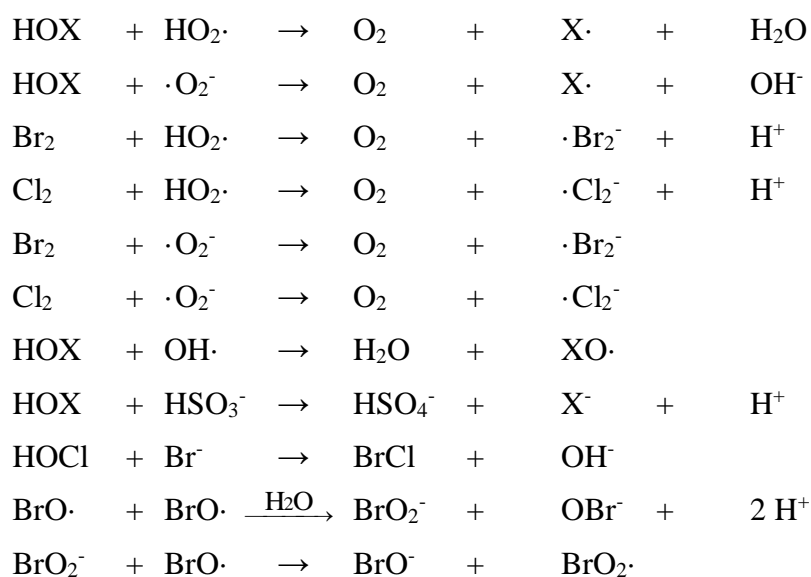
Halogen module

For the gas phase, there are no reactions of halogen containing compounds considered in RACM. For the aqueous phase, reactions of halogen radicals are already implemented in the mechanism CAPRAM 2.4 (MODAC mechanism).

The source of halogen atoms in the gas phase are the now appended photolysis reactions of X_2, HOX, and XNO_2 where X = Cl or Br. The generated radicals are able to react with ozone in a catalytic cycle. The result of this cycle is a depletion of ozone to O_2 and the recycled radical. The reaction of $XO\cdot + HO_2\cdot \rightarrow HOX + O_2$ leads to another, more important way of depletion of $XO\cdot$. This reaction is a pathway to form HOX which can be transfered into the aqueous phase.

The depletion of the halogen radicals in the gas phase is different for $Cl\cdot$ and $Br\cdot$. $Cl\cdot$ is depleted via the reaction with methane. The reaction of CH_4 with $Br\cdot$ is too slow to play an important role in the depletion of $Br\cdot$ so that the reactions of $HO_2\cdot$, HCHO, C_2H_4 and terminal alkenes with bromine radicals are added to the mechanism. Further gas phase reactions are $HX + OH\cdot \rightarrow X\cdot + H_2O$. A loss of gas phase hypohalogenic acids and halogenic acids is treated by dry deposition out of the box.

Phase transfer of the halogen containing compounds X_2, HX, HOX, XNO_2, $XO\cdot$ is implemented. HBr, HOCl, HOBr, $CLO\cdot$, and $BrO\cdot$ are added because the other species are already included in the basic mechanism.

For the aqueous phase the basic mechanism CAPRAM 2.4 (MODAC mechanism) already contains various reactions of the radicals $X_2^-\cdot$, and $X\cdot$. The irreversible aqueous phase reactions which are included in the additional halogen module are listed below:

HOX	+ $HO_2\cdot$	$\rightarrow$	O_2	+	$X\cdot$	+	H_2O	
HOX	+ $\cdot O_2^-$	$\rightarrow$	O_2	+	$X\cdot$	+	OH^-	
Br_2	+ $HO_2\cdot$	$\rightarrow$	O_2	+	$\cdot Br_2^-$	+	H^+	
Cl_2	+ $HO_2\cdot$	$\rightarrow$	O_2	+	$\cdot Cl_2^-$	+	H^+	
Br_2	+ $\cdot O_2^-$	$\rightarrow$	O_2	+	$\cdot Br_2^-$			
Cl_2	+ $\cdot O_2^-$	$\rightarrow$	O_2	+	$\cdot Cl_2^-$			
HOX	+ $OH\cdot$	$\rightarrow$	H_2O	+	$XO\cdot$			
HOX	+ HSO_3^-	$\rightarrow$	HSO_4^-	+	X^-	+	H^+	
HOCl	+ Br^-	$\rightarrow$	BrCl	+	OH^-			
$BrO\cdot$	+ $BrO\cdot$	$\xrightarrow{H_2O}$	BrO_2^-	+	OBr^-	+	$2 H^+$	
BrO_2^-	+ $BrO\cdot$	$\rightarrow$	BrO^-	+	$BrO_2\cdot$			

The equilibria of halogen compounds in the aqueous phase contain dissociation of HBr, HOX, $HBRO_2$ whereas the basic mechanism already includes the dissociation of HCl. The formation

of the trihalogenide anions Br_2Cl^- and $BrCl_2^-$ are as well a part of the halogen module as the hydrolysis of X_2.

Results

Fig 1 and 2 show time series of the concentrations of the halogen radicals Br· and Cl· in the gas phase. For the clean (marine) case daytime maximum at noon of Br· is in the order of magnitude of 10^2 molecules cm^{-3}, whereas Cl· reaches only 5 molecules cm^{-3}.
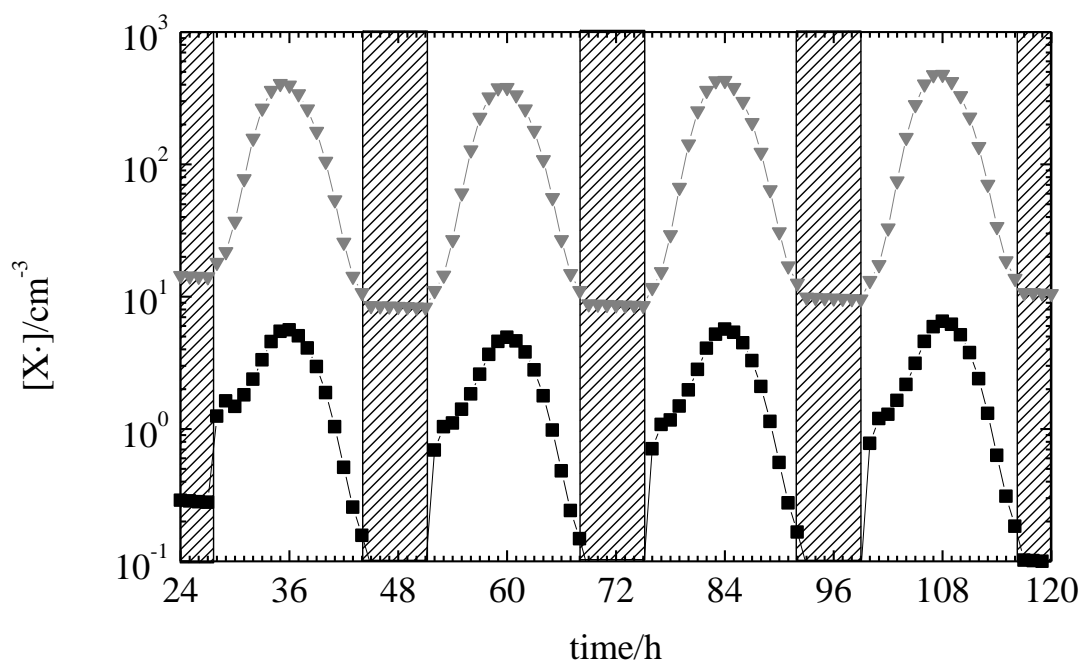

Fig. 1: Time series of activated halogen atoms in the gas phase for clean (marine) conditions; ■: Cl·, ▽: Br·
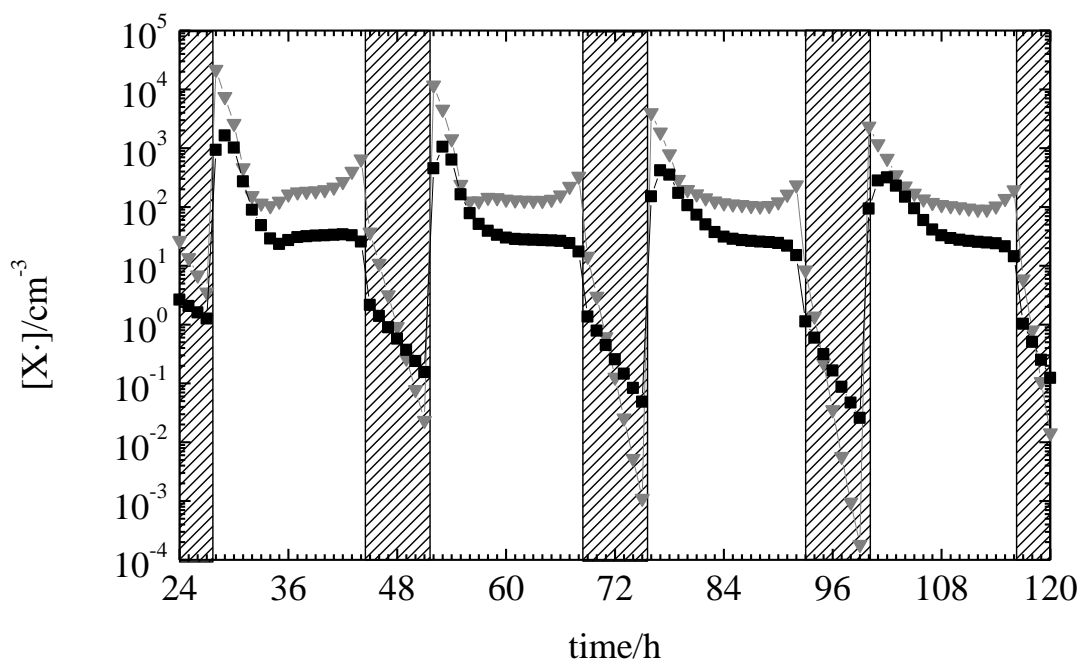
Fig. 2: Time series of activated halogen atoms in the gas phase for polluted (urban) conditions; ■: Cl; ▽: Br·

For the polluted (urban) case daytime maxima of the halogen atoms appear shortly after sunrise. The amount of Br· is at this time in the order of magnitude of 10^4 molecules cm^{-3} and the concentration of Cl· in the range of 10^3 molecules cm^{-3}.

Two orders of magnitude more halogen atoms are formed in the gas phase under polluted (urban) conditions. These are formed from the released halogen molecules. The formation of $Cl_{2\ (aq)}$ is mainly due to the formation and decay of $BrCl_2^-$, whereas the $Br_{2\ (aq)}$ is mainly formed by $\cdot Br_2^-$ - recombination, thus indicating coupling between halogen release to the gas phase and aqueous phase radical chemistry.

Conclusion

A module including reactions of halogen containing species is coupled with the complex mechanism RACM/CAPRAM 2.4 (MODAC mechanism). The release of halogen containing species from cloud droplets into the gas phase is very small under clean conditions. Under polluted conditions the amount of activated halogens is about 2 orders of magnitude higher and the diurnal cycle is different compared to their cycle in the clean case. In the time period shortly after sunrise these activated halogens are able to influence ozone depletion. Clearly, halogen activation from clouds deserves further detailed study.

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