Sensitivity of tropospheric ozone to halogen chemistry in the chemistry-climate model LMDZ-INCA vNMHC

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Abstract. The atmospheric chemistry of halogenated species (Cl, Br, I) participates in the global chemical sink of tropospheric ozone and perturbs the oxidizing capacity of the troposphere, notably influencing the atmospheric lifetime of methane. Global chemistry-climate models are commonly used to assess the global budget of ozone, its sensitivity to emissions of its precursors, and to project its long-term evolution. Here, we report on the implementation of tropospheric halogens chemistry in the chemistry-climate model LMDZ-INCA and its effects on the tropospheric ozone budget. Overall, the results show that the model simulates satisfactorily the impact of halogens on the photooxidizing system in the troposphere, in particular in the marine boundary layer. To elucidate the mechanisms and quantify the effects, standard metrics representative of the behavior of the tropospheric chemical system (O_x, HO_x, NO_x, CH_4, and NMVOCs) are computed with and without halogen chemistry. Tropospheric halogens in the LMDZ-INCA model lead to a decrease of 22% in the ozone burden, 8% in OH, and 33% in NOx. Additional sensitivity simulations show that the inclusion of halogens chemistry makes ozone more sensitive to perturbations in CH_4, NO_x, and NMVOCs. Consistent with other global model studies, the sensitivity of the tropospheric ozone burden to changes from pre-industrial to present-day emissions is found to be ~20% lower when tropospheric halogens are taken into account.

1 Introduction

The atmospheric chemistry of halogenated species has been the focus of multiple studies early on because of its importance for the composition of the stratosphere and in particular the ozone layer (Molina and Rowland, 1974; Stolarski and Cicerone, 1974). The role of halogens in tropospheric chemistry has also been investigated but to a lesser extent than for stratospheric chemistry. With the progress of measurement techniques, marine aerosols were suspected to harbor and release reactive halogens into the gas-phase (Cicerone, 1981). Later on, halogenated species were found to be responsible for ozone destruction in the Arctic troposphere (Bottenheim et al., 1990; Oltmans and Komhyr, 1986). Meanwhile, natural and anthropogenic sources of halogens have started to be identified and characterized (Graedel and Keene, 1995; Lobert et al., 1999; McCulloch et al., 1999; Carpenter, 2003; Platt and Hönninger, 2003). In recent years, the addition of halogenated species into atmospheric chemistry models have revealed their significant influence on the photo-oxidizing chemistry of the troposphere on a global scale (Saiz-Lopez et al., 2012a; Simpson et al., 2015). This influence arises from the high reactivity of atomic halogens (e.g., Cl, Br, I) and halogen oxides radicals (e.g., ClO, BrO, IO and higher oxides), which are produced in the atmosphere by the decomposition of very short-lived halogenated substances (VSLS). These reactive halogens do not only destroy ozone but are also powerful oxidants, thereby contributing to the oxidization of organic and inorganic compounds throughout the troposphere.

The most important families of halogenated compounds for tropospheric chemistry are chlorine, bromine, and iodine. Details on their respective tropospheric chemistry can be found in review articles (e.g. Saiz-Lopez and von Glasow, 2012; Simpson et

al., 2015). The main effects about reactive halogen species is that they (1) modify the partitioning of HO_x (HO_2 + OH) and nitrogen oxides ($NO_x = NO_2$ + NO), (2) are involved in the oxidation of non-methane volatile organic compounds (NMVOCs) and mercury, (3) participate in the formation of new particles (Giorgi and Chameides, 1985; O'Dowd et al., 2002; von Glasow et al., 2004; Gómez Martín et al., 2020; Saiz-lopez et al., 2012), and (4) constitute a sink for tropospheric ozone at the global scale. Halogenated species play a role in the ozone and hydroxyl radical (OH) budgets and therefore influence the oxidative capacity of the troposphere (Iglesias-Suarez et al., 2020). In addition, by influencing the abundances of methane, ozone and particles, which all are radiative active agents, halogens can indirectly affect the climate (Saiz-Lopez et al., 2012b; Hossaini et al., 2015; Sherwen et al., 2017).

The loss of ozone by halogens can be induced by iodine, bromine and chlorine species (Sherwen et al., 2016a) and can be caused by direct catalytic ozone destruction and reduction in ozone production through the removal of NO_2 by halogen radicals. Halogen chemistry is thought to be especially active in pristine atmospheres that host 60 to 70% of the global burden of tropospheric ozone (Holmes et al., 2013). Based on model calculations, the halogen-driven ozone loss is estimated to be around 30% in the marine boundary layer (von Glasow et al., 2002, 2004; Saiz-Lopez et al., 2014; Sherwen et al., 2016a) and 5% to 20% globally (Yang et al., 2005; Saiz-Lopez et al., 2012b, 2014; Sherwen et al., 2016a), going up to 25 to 30% in Badia et al., 2019. Consequently, it might be important to consider halogens in chemistry-climate models. It could also help to reconstruct more reliably past atmospheric compositions (Saiz-Lopez et al., 2014; Young et al., 2013).

Chemistry-climate models are often used to assess the importance of specific chemical species on large scales and how changes in anthropogenic and natural emissions of gases and aerosols since the preindustrial period may have affected the atmospheric composition and the global climate. Such global models are also used to evaluate the effects of international policies (e.g. air pollution abatement strategies) through model intercomparison projects (e.g. HTAP, ACCMIP, AerChemMIP) (Fiore et al., 2009; Young et al., 2013; Stevenson et al., 2020). To this day, chemistry-climate models participating in ACCMIP exercises (Naik et al., 2013; Young et al., 2013), AerChemMIP (Collins et al., 2017; Stevenson et al., 2020) or CMIP6 (Griffiths et al., 2021) do not account for halogen chemistry.

The purpose of this work is to assess the potential importance of iodine, bromine and chlorine chemistry for global tropospheric ozone budget using such a global chemistry-climate model, the LMDZ-INCA model (Laboratoire de Météorologie Dynamique (LMD) General Circulation Model, LMDZ; Interactions with Chemistry and Aerosols, INCA). This work first focuses on the integration of tropospheric halogens chemistry in the LMDZ-INCA model. First, we evaluate the performances of the model by comparing our simulations to results of the few equivalent models with halogen chemistry (concentrations and fluxes through reactions and mechanisms of sources and sinks) and to compilations of in-situ observations of halogenated species. The representation of this chemistry in our model is shown to be sufficiently satisfactory to simulate the impact of halogens on the tropospheric photooxidizing system. Second, we investigate the sensitivity of ozone, methane and hydroxyl radical to perturbations in emissions of photooxidant precursors and explore changes in ozone burden and net destruction in simulations considering present-day (PD) and pre-industrial (PI) emissions. Finally, the last section recall key findings and we conclude with implications for chemistry-climate simulations of tropospheric ozone evolution.

2 Methodology

2.1 Model description

2.1.1 LMDZ-INCA

LMDZ is an atmospheric general circulation model developed by Sadourny and Laval (1984). The primitive equations of the GCM are solved with a time step of 3 minutes, a large-scale transport of tracers is carried out every 15 minutes and the physical processes are calculated at a time interval of 30 minutes. The LMDZ model provides at each time step the physical quantities

80   (temperature, pressure, water vapor, turbulence, boundary layer, etc.) needed for the calculation of the reaction and transport constants in INCA.

INCA is an atmospheric chemistry model developed at LSCE (Laboratoire des Sciences du Climat et de l'Environnement). The model takes into account the primary emissions from natural sources or by anthropogenic activities. It computes physical processes such as dry and wet deposition and photochemical reactions (Hauglustaine et al., 2004). The atmospheric

85   concentration fields are computed by solving differential equations with a time step of 30 minutes.

The gaseous species included in the NMHC version v_5.2.1 of the INCA chemistry model are in particular the inorganic species O_x, NO_x and HO_x system as well as CH_4, CO, non-methane hydrocarbons (NMHC), volatile organic compounds (NMVOCs) and their photooxidized products (Folberth et al., 2006). Biogenic emissions like those of isoprene are provided by the global vegetation model ORCHIDEE (Folberth et al., 2006). Anthropogenic emissions are based on the CEDS v2016-

90   07-2 emission inventory for the year 2010 (Hoesly et al., 2018).

The LMDZ-INCA model has been used and assessed in numerous model intercomparison exercises aimed at simulating the preindustrial, present and future tropospheric composition (e.g. Szopa et al., 2013), the Hemispheric Transport of Air Pollution (HTAP) or chemistry/climate interactions such as ACCMIP (Naik et al., 2013).

2.1.2 Halogen chemistry

95   The chemistry of halogenated compounds implemented in LMDZ-INCA is essentially based on the scheme developed for CAM-Chem (Fernandez et al., 2014b; Ordóñez et al., 2012; Prados-Roman et al., 2015a; Saiz-Lopez et al., 2012b, 2014, 2015) and GEOS-Chem described in Sherwen et al. (2016b). In total, 42 halogenated species and 160 chemical reactions were added to the INCA chemical scheme. A complete list of the halogen chemistry implemented in LMDZ-INCA can be found in Tables S1, S2, S3, S4 and S5 provided in the supplement. This includes photolysis, gas-phase and heterogeneous reactions occurring

100   on sea salt and sulfate aerosols.
The heterogeneous chemistry on sea salt and sulfate aerosols is included while the heterogeneous bromine reactions on water droplets and ice crystals are not. A study by Badia et al. (2019) using WRF-Chem suggested that including heterogeneous halogen chemistry results in better Br_y partitioning vertically, but contributes little (~6%) to ozone loss compared to gas-phase halogen chemistry (25%) on a global scale. The first aim of this work being to investigate the effect of halogenated chemistry

105   on ozone budgets, we decided to discard ice chemistry as a relevant compromise to ensure bromine recycling in the MBL. This choice allows to reproduce bromine-mediated ozone loss in the marine boundary layer and halogen-mediated ozone loss in the global troposphere. Photolysis reactions of halogens as well as relative quantum yields and absorption cross-sections are listed in Table S2. Uptake coefficients for heterogeneous reactions are reported in Table S5 and are based on literature values (Jacob, 2000; Sander et al., 2006; Ordóñez et al., 2012). Dry deposition is calculated with the Wesely scheme (Wesely, 1989)

110   while washout of gases by precipitation is simulated by using Henry's law constants detailed in Table S6.
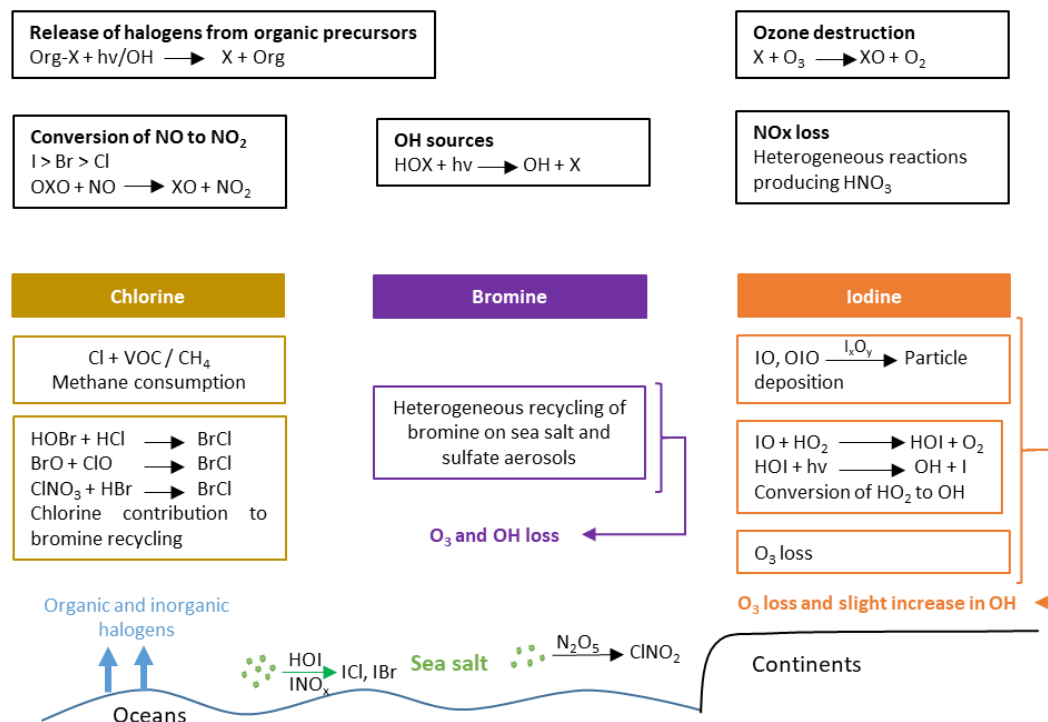
Figure 1: Schematic of the most important tropospheric chemical processes involving halogenated compounds (containing Cl, Br, I) as represented in LMDZ-INCA.

2.2 Simulations

For these developments, LMDZ-INCA is used with a $3.75° \times 1.9°$ resolution over 39 vertical layers. This resolution is lower than the resolution now commonly used in the CMIP6 model exercise, but it was the standard LMDZ resolution for CMIP5 and allows faster simulations necessary in model development phase. The LMDZ wind fields and sea surface temperature are nudged on ECMWF reanalysis for the year 2010 (climate is thus representative of PD in all simulations). The aerosol distribution and monthly variations considered for heterogeneous reactions comes from climatologies precomputed with the same model and a consistent framework. All simulations cover 1 year (2010), and follow a spin-up period of one year. Three types of simulations have been performed to simulate (i) PD conditions, (ii) preindustrial conditions, and (iii) sensitivity to ozone precursors. For sensitivity tests, simulations with individual emission perturbations of photooxidant precursors (-20%) of NO_x, CO and NMVOCs and concentration reduction (-20%) of CH_4, were performed. For each type of simulation, two versions of the model are applied: one accounting for the halogen chemistry (called Halo simulations hereafter) and a reference simulation without halogen chemistry called "NoHalo".

2.2.1 Present-day set-up

Primary halogenated compounds can originate from both inorganic and organic sources. Inorganic species are reactive species emitted by different sources, but also result from atmospheric reactions (Simpson et al., 2015). Organic species are only of primary origin and photolyze in the atmosphere to form halogen radicals (Simpson et al., 2015). Table 1 shows the emissions of halogenated compounds as considered in INCA. Organo-bromines ($CHBr_3$, CH_2Br_2), organo-iodines (CH_3I, CH_2I_2) and interhalogen species (CH_2IBr, CH_2ICl) are those used by the CAM-Chem model (Ordóñez et al., 2012).

Sources of organic chlorine are diverse, mainly originating from biological activity on the surface of the oceans and from forest fires. The emissions of these chlorocarbons are detailed in Table S7. In INCA, inorganic chlorine, HCl - the major reservoir of chlorine in the atmosphere - is considered as being emitted by sea salts (90 000 Gg Cl.yr^{-1}) and by forest fires (6400 Gg
135 Cl.yr^{-1}) (Lobert et al., 1999; Hossaini et al., 2016;). Note that more realistic but complex to implement approaches rely on pH dependent parameterization of the dechlorination of sea salts as considered in CAM-Chem and GEOS-Chem. HCl emissions from industrial sources (McCulloch et al., 1999) are neglected as recommended by Wang et al. (2019), to avoid overestimating HCl in urban areas. ClNO$_2$ is emitted by the heterogeneous reaction of N$_2$O$_5$ on sea salt and produces 2217 Gg Cl.yr^{-1}.
CH$_3$Br emissions are from oceanic origin (40%) and from agriculture (60%) (Barker et al., 2016) and represent 91 Gg of
140 Br.yr^{-1} (Schmidt et al. (2016). IBr and ICl originate from the heterogeneous reaction of HOI, INO$_2$ and INO$_3$ on sea salt aerosols (Table S5) as recommended in other models (Saiz-Lopez et al., 2014; Sherwen et al., 2017), but without accounting for pH dependence (McFiggans et al., 2000).

The inorganic iodine distribution of emissions (HOI and I$_2$) are from (Prados-Roman et al., 2015a) and have been computed by the CAM-Chem model in which the sea-air fluxes depend on the oxidation of aqueous iodide by atmospheric ozone on the
145 ocean surface (Carpenter et al., 2013; MacDonald et al., 2014), the deposition of ozone to the ocean surface, the sea surface temperature and the wind speed (Prados-Roman et al., 2015b).

2.2.2 Preindustrial set-up

Only emissions from natural sources are considered to simulate the pre-industrial troposphere. Emissions of halogenated compounds from biomass burning are reduced to 10% of their current values (Wang and Jacob, 1998). The methane
150 concentration is set at 700 ppbv (IPCC, 2014).

Organo-iodine emissions are almost unchanged between the PI and PD. For organo-bromines, CHBr$_3$ and CH$_2$Br$_2$ preindustrial emissions are equivalent to the PD ones, following the methodology of Parrella et al. (2012). A concentration of ~ 5 ppbv of CH$_3$Br is considered to match the recordings from ice cores (Saltzman et al., 2004). Preindustrial emissions of CH$_3$Cl, CHCl$_3$ and CH$_2$Cl$_2$ (see table S7) are from (Carpenter et al., 2014; Carpenter, 2003; Hu, 2012; Montzka et al., 2011; Worton et al.,
155 2006). HOI and I$_2$ emissions are ~ 40% lower than today because they are sensitive to atmospheric ozone content which was lower in the pre-industrial era (Prados-Roman et al., 2015a; Sherwen et al., 2017). Global emissions for each primary halogenated compound are reported in Table 1.

Table 1 : Emission of halogen gases for preindutrial and present-day simulations. Sources of long-lived species (CH$_3$X, CH$_2$X$_2$, CHX$_3$) are shown in terms of emissions. I$_2$ and HOI are the inorganic oceanic source that depends on surface ozone (Carpenter et al., 2013).
160 **IBr and ICl is released following gaseous iodine uptake on sea salt. ClNO$_2$ is emitted by absorption of N$_2$O$_5$ on sea salt.**

Compounds	I (Tg I.an^{-1})		Br (Tg Br.an^{-1})		Cl (Tg Cl.an^{-1})	
	Preindustrial	Present	Preindustrial	Present	Preindustrial	Present
CH$_3$X	209	219	36	91	2081	2166
CH$_2$X$_2$	108	108	62	62	199	628
CHX$_3$	-	-	506	506	236	315
HOI	1361	2448	-	-	-	-
I$_2$	34	59	-	-	-	-
ClNO$_2$	-	-	-	-	169	2217
CH$_2$IBr	50	50	32	32	-	-
CH$_2$ICl	168	168	-	-	47	47
IBr, ICl	-	-	495	799	1244	2008
HCl	-	-	-	-	96429	96429
Total	**1930**	**3052**	**1131**	**1490**	**100406**	**103810**

3 Evaluation of model halogen simulations

Before assessing the sensitivity of the modelled ozone to halogen chemistry, we first evaluate the performances of the model regarding simulating halogen species. In order to do so, model outputs are compared to a range of halogen observations and previous simulations from other models which contain halogen chemistry. An analysis of the model tropospheric budgets of key halogen species is also performed.

3.1 Present-day budgets for halogenated species in LMDZ-INCA

In order to reflect the role played by the halogenated species in their respective cycle, inorganic halogens are presented hereafter under the name X_y which can be divided into HX and X*. HX in LMDZ-INCA takes part in heterogeneous bimolecular reactions. In CAM-Chem and GEOS-Chem, the representation of this chemistry is more detailed: HX can associate with droplets or particles and dissociate (Fernandez et al., 2014b; Ordóñez et al., 2012; Prados-Roman et al., 2015a; Saiz-Lopez et al., 2012b, 2014, 2015) and GEOS-Chem described in Sherwen et al. (2016b). X* is subdivided into two: the reservoir species X_2, HOX, XNO_2, XNO_3 and which have a relatively long lifetime. These species are formed mostly at night and serve as reservoirs of reactive halogens far from its primary sources. The term "reactive halogen" is used hereafter to describe the radical species $XO_x = X + XO*$.

In the following subsections, we present, for each halogen, the species considered in each reservoir, their respective tropospheric mass burden and the main fluxes between these reservoirs. The purpose is to evaluate the recycling of species and to compare the balances and cycles of chlorine, bromine and iodine with the outputs of other models available in the literature. Finally, subsection 2.4 reports the capacity of the model to reproduce the measurements of Cl*, $ClNO_2$ and HCl available and a compilation of surface measurements of BrO and IO.

3.1.1 Chlorine

The total tropospheric burden of Cl_y (inorganic chlorine) is 290 Gg of Cl, largely dominated by HCl. The total load of HCl is smaller than the one found using GEOS-Chem (Wang et al., 2019) essentially because of the difference in the representation of the emissions. However, the total burden of reservoir species has a similar magnitude (10.4 Gg Cl). The halogens' chemistry in INCA leads to a 25% higher quantity of available reactive compounds (ClO * and Cl).

Atomic chlorine evolves in two main ways: the first and most important in terms of reaction flux, is the transformation of atomic Cl into ClO*. This conversion takes place mainly by reaction with ozone (99.5%), while the conversion of ClO_x to Cl is dominated by reaction with NO (93.9%). The second path is represented by the chemical loss of reactive chlorine Cl to inactive chlorine HCl. As shown in Fig. 2, this pathway is linked to the reactions of Cl with methane and several NMVOCs. These ratios are very similar to those in Wang et al. (2019), especially considering that differences in NMVOC and CH_4 concentrations exist between the two models. The conversion of Cl to ClO* is in strong competition with the second route. By dividing the fluxes of the conversion Cl to ClO* by the flux of conversion of Cl to HCl, we find that the chain length is short and equal to 1.3 (4.8×10^4 / 3.6×10^4). This is close to the chain length of 1.6 calculated by Wang et al. (2019) and shows that the branching ratios are in the same order of magnitude in both models. Overall, we find that the partition between Cl and ClO* is correct in the model as well as the balance between radical and non-radical species although the latter is a little more shifted towards reactive species in INCA, compared to GEOS-Chem.
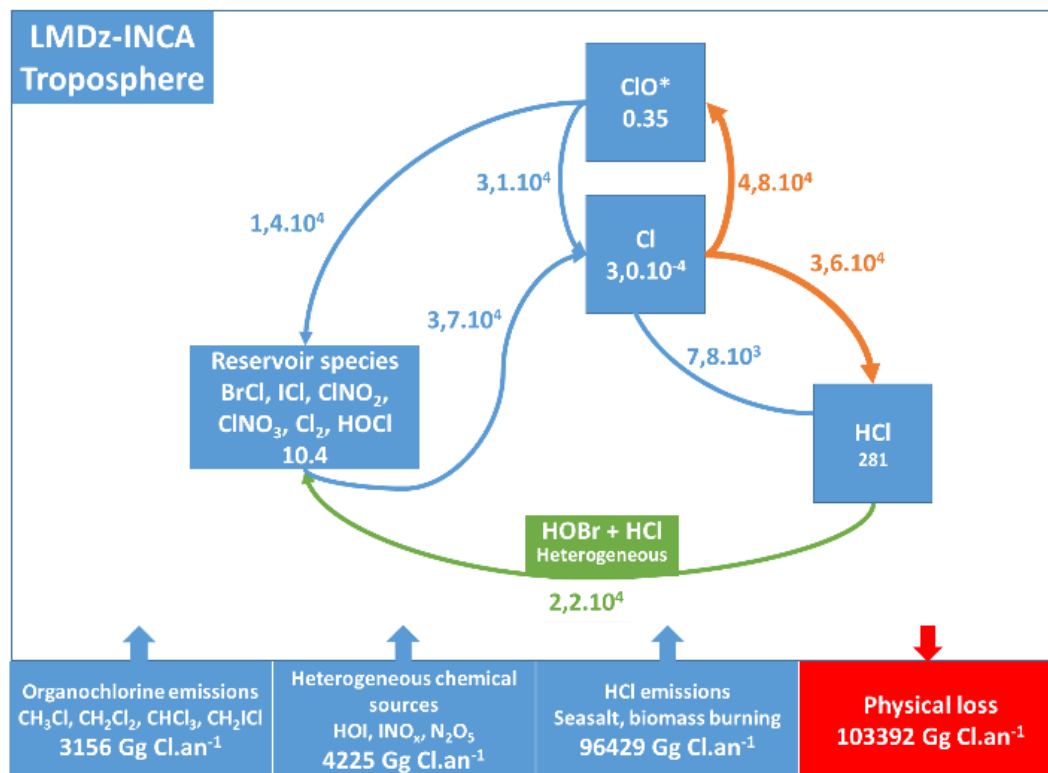
Figure 2: Simplified cycle of tropospheric Cl$_y$ species in the reference simulation. Fluxes through the reactions are in Gg Cl.yr^{-1}. Heterogeneous reactions are represented in green. The main loss pathways for atomic chlorine are in orange. The numbers in the boxes represent the mass balances of the species families in Gg Cl.

3.1.2 Bromine

The simplified tropospheric bromine cycle illustrated in Fig. 3 shows that the recycling of bromine is efficient in LMDZ-INCA, but within the lower limit of what is reported in older versions of GEOS-Chem (Parrella et al., 2012a; Schmidt et al., 2016; Sherwen et al., 2016a; Zhu et al., 2019) where heterogeneous phase processes were enhanced. The total inorganic bromine is ~ 27 Gg in the troposphere in LMDZ-INCA, close to the 28 Gg reported in the most recent version of GEOS-Chem (Wang et al., 2021). On an annual average, daytime BrO values in the FT are ~0.3 pptv within the tropics, close to what is suggested by CAM-Chem (~0.2 pptv) (Fernandez et al., 2014). At an altitude of 17km, the modeled tropical BrO concentrations in INCA are ~3 pptv, close to the CAM-Chem modelling result of 2.0±1.5 pptv at 17 km and the observed concentrations of 3.2±1.6 pptv at 18 km (Dorf et al., 2008; Fernandez et al., 2014a).

Since our goal is to simulate the impact on global and ground-level ozone, rather than simulating a state-of-the-art partition within inorganic bromine, we make sure that the bromine cycle is chemically active by investigating the fluxes through the main reactions. In terms of percentages, reaction pathway percentages are consistent with Schmidt et al., (2016) even though reaction fluxes are a factor of 1 to 2 smaller in INCA.
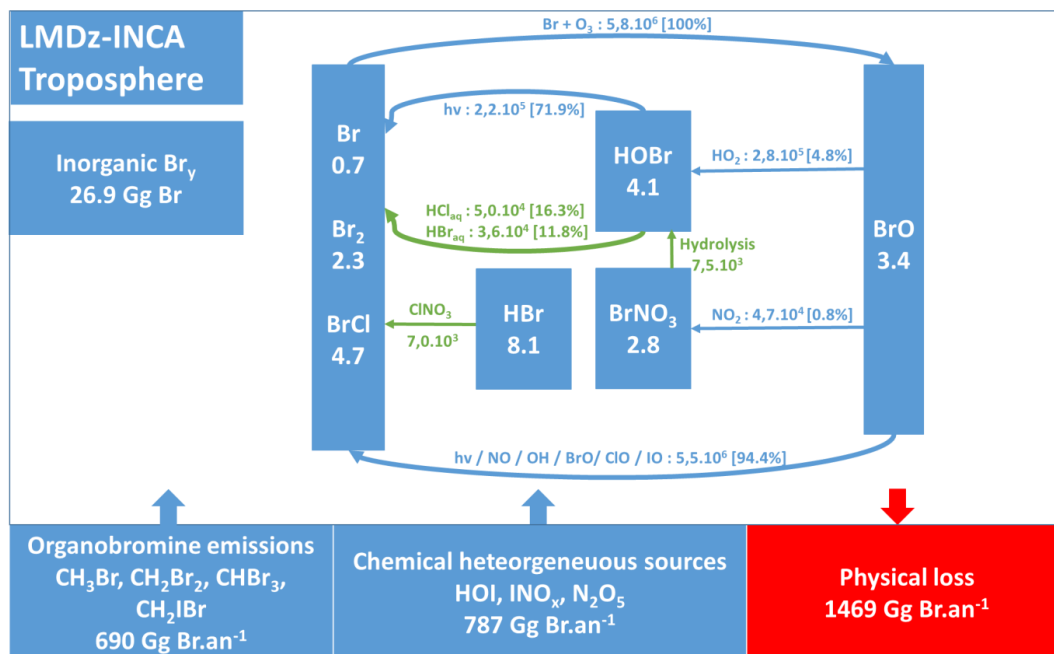
Figure 3: Simplified cycle of tropospheric Br_y species in the reference simulation. Fluxes through the reactions are in Gg Br.yr^{-1}. Heterogeneous reactions are represented in green. The numbers in the boxes represent the mass balances of the species families in Gg Br.

3.1.3 Iodine

The simplified iodine cycle is shown schematically in Fig. 4. The burden of inorganic iodine excluding IBr / ICl and iodine in aerosols is ~ 22.0 Gg in the troposphere in LMDZ-INCA, comparable to the value of ~ 27.9 Gg proposed by Sherwen et al., (2016a). HOI is the most abundant iodine species and its wet deposition controls the total atmospheric iodine burden. The concentrations of HI, INO_2, and I_2 are lower than what is reported in GEOS-Chem (Sherwen et al., 2016a). The difference in I_2 is explained by the assumptions made about the fate of INO_3, INO_2 and HOI, which here photodissociate to produce IBr and ICl. Other quantifications in the literature are lacking to explain the differences in INO_2 and HI, however, Saiz-Lopez et al. (2014) groups these species in CAM-Chem into a group defined as minor iodine species (I_{min} = HI + OIO + INO_2 + INO) that represent less than 5% of the mass in tropospheric inorganic iodine (2.3% in our case). Lastly, in the tropics (20° S – 20° N), IO in INCA (0.35 ppt) is in agreement at surface level with CAM-Chem (~0.4 ppt) (Saiz-Lopez et al., 2014). In the free troposphere IO levels reach 0.46 ppt (10km) in INCA while CAM-Chem in its most recent setup for the upper troposphere, recycling on sea ice crystals contributes to IO levels and suggests 0.16 ppt (Saiz-Lopez et al., 2015). Note also that there are differences in the geographical representation of organic / inorganic iodine sources between the models which can have considerable effects on the atmospheric iodine burden.

Iodine fluxes

The IO_x family influences the oxidative capacity of the troposphere through the catalytic cycles of ozone depletion (Brasseur, 2005), modifies the HO_x (HO_2 / OH) and NO_x (NO_2 / NO) ratios (Bloss et al., 2010) and produces photolabile higher order iodine oxides (I_xO_y) (Gómez Martín et al., 2020; Lewis et al., 2020) and generates different forms of inorganic iodine (Saiz-Lopez et al., 2012a). For that reason, we next study the branching ratios and the generation and loss of IO_x. Globally, IO_x production is dominated by inorganic photolysis of HOI (80.5%), OIO (10.2%), INO_3 (5.4%) and I_2O_x (3.9%). The main IO_x loss pathway is the production of HOI by IO reaction with HO_2 (78.5%), with additional loss pathways by self-reaction, reaction with NO_x and BrO contributing 11.3%, 5.7% and 4.5%, respectively.
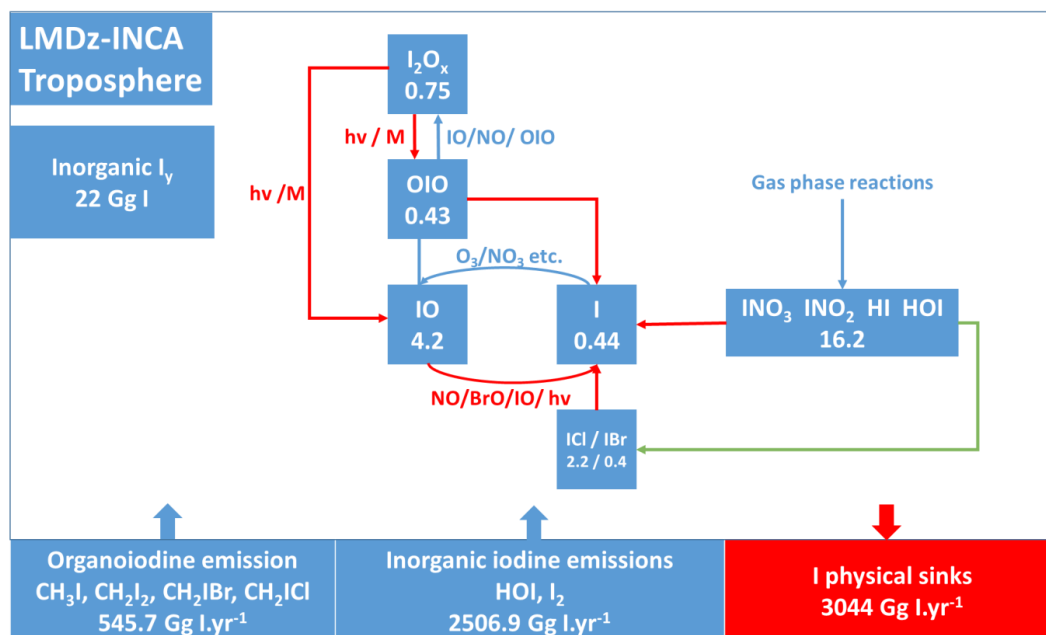
Figure 4: Simplified cycle of tropospheric I_y species in the reference simulation. Heterogeneous reactions are shown in green. Photolysis reactions are in red. The numbers in the boxes represent the mass balances of the species families in Gg I.

3.2 Evaluation of the reference simulation compared to inorganic halogen observations

The average simulated HCl surface mixing ratios are 193 pptv according to LMDZ-INCA, 246 pptv according to GEOS-Chem (Wang et al., 2019) and 196 pptv according to observations on coastal sites and over the oceans, the results are detailed in Fig. S1. However, for continental regions, LMDZ-INCA underestimates the HCl concentrations compared to observations due to the choice to neglect industrial emissions. LMDZ-INCA underestimates the continental ClNO$_2$ content for many sites. This could be due to the coarse resolution of the model with respect to the spatial inhomogeneity of these observations (Sherwen et al., 2016b) and the absence of ClNO$_2$ production in sulphate-nitrate-ammonium aerosols (Wang et al., 2019). The chlorine Cl* measurements to which we compare LMDZ-INCA results represent the sum of Cl$_2$, HOCl, ClNO$_2$, ClNO$_3$ and other minor components as explained in (Pszenny, 1993) and are in a satisfactory order of magnitude compared to the measurements (see table S9).

Overall, the diurnal tropospheric mean of BrO is 0.6 pptv (in agreement with what Parrella et al. (2012) also find) which is in the lower range of 0.5 to 2 pptv often cited in the literature (Stone et al., 2012). Comparisons with observations are detailed in the table 2 and show overall a good agreement at the surface and higher altitudes.

In the troposphere, the mean of I_y is 1.3 pptv, which is larger than what previous model studies suggest (~ 0.5-1 pptv) (Saiz-Lopez et al., 2014; Sherwen et al., 2016a, 2016b). Overall, the annual mean surface concentrations of IO over the oceans is approximately 0.2 pptv which approximates the range that Sherwen et al. (2016a) found (0.25 - 1 pptv). Mixing ratios range from 0.4 to 1 ppt during the Malaspina 2010 campaign in the marine boundary layer (Prados-Roman et al., 2015b), while LMDZ-INCA suggests values ranging from 0.3 to 0.7 ppt in different latitudes. Comparisons with observations are detailed in the table 2 and show overall a good agreement at the surface and but an overestimation of IO in the tropical FT.

Table 2: Comparison of BrO and IO measurements with LMDZ-INCA results. The symbol "<" indicates that mixing ratios are below detection limit. Measured concentrations in bold represent daily maxima while regular values are diurnal averages. LMDZ-INCA values are all diurnal averages calculated in accordance to measurement months, location and altitude, as reported in the references.

Species	Measurement	Location	Modelled (ppt)	Measured (ppt)	Reference
	Ground-based	Hawaii	0.6	< 2.0	Sander et al., 2003
	Ground-based	Crete	0.4	< 0.7	Sander et al., 2003
	Ground-based	Cabo Verde	0.9	2.5 ± 1.9	Mahajan et al., 2010; Read et al., 2008
	Ground-based	Tenerife island	0.2	3.0	Keene et al., 2007
	Ship-based	Atlantic Ocean	0.8	~ 1.0	Leser et al., 2003; Martin et al., 2009; Saiz-Lopez et al., 2012
BrO	Ship-based	Atlantic Ocean	0.7	<1.0 – 3.6	Leser et al., 2003
	Aircraft-based (FT)	Eastern tropical Pacific Ocean	0.4	0.26 ± 0.15	Dix et al., 2016; Volkamer et al., 2015; Wang et al, 2015
	Aircraft-based (FT)	Western tropical Pacific Ocean	0.9	0.63 ± 0.74	Chen et al., 2016
	Aircraft-based (FT)	Western tropical Pacific Ocean	0.3	0.28 ± 0.16	Le Breton et al., 2017
	Aircraft-based (FT)	Svalbard	2.0	**1.5**	Prados-Roman et al., 2011
	Ground-based	Cabo Verde	2	**2.0**	Read et al., 2008
	Ground-based	Tropical ocean	0.5	**0.6**	Dix et al., 2013
IO	Aircraft-based (surface)	Eastern Pacific	0.65	0.37	Volkamer et al., 2015; Wang et al., 2015
	Aircraft-based (FT)	North subtropical	0.2	**0.4**	Puentedura et al., 2012
	Aircraft-based (FT)	Tropics	0.6	**0.1**	Dix et al., 2013

4 Model ozone sensitivity to halogen chemistry

270 The focus of this section is mostly on the impact of halogen chemistry on the tropospheric ozone budget. The impact on OH radical concentrations and the subsequent effect on CH_4 are also discussed. The model ozone budget is compared whenever possible to results from the GEOS-Chem model with bromine and iodine chemistry (Sherwen et al., 2016a) and with chlorine, bromine, and iodine chemistry (Sherwen et al., 2016b) and to results from the CAM-Chem model (Saiz-Lopez et al., 2012; Saiz Lopez et al., 2014; Iglesias-Suarez et al., 2020). These comparisons with other models also allow us to complete the

275 evaluation of the model performances. The budget analysis is used to quantify the impact of halogen chemistry on the photo-oxidizing chemistry, notably the sensitivity of tropospheric ozone to halogens. The evolution of the model ozone sensitivity from the pre-industrial period to the present-day is also assessed.

4.1 Impact on ozone loss in present-day

Overall, the annual mean mixing ratio of ozone is reduced by 9.7 ppbv (compared to 9.4 ppbv in GEOS-Chem, Sherwen et al.,

280 2016b) with the inclusion of halogens. This corresponds to a 22% reduction in the tropospheric ozone burden and is in the 5-25% range reported by other models (Yang et al., 2005; Saiz-Lopez et al., 2012; Saiz-Lopez et al., 2015, 2012a; Sherwen et al., 2016b; Badia et al., 2019). The annually averaged tropical tropospheric ozone column decreases by 8 ppbv (21%) which is double the amount of the relative change reported in Saiz-Lopez et al. (2012b). Surface ozone in continental areas undergoes a decrease of 6 ppbv (23%) while surface ozone in oceanic areas, where the majority of primary halogenated compounds are

285 emitted, decreases by 7.7 ppbv (32%) (reported range in other studies is 20-33%; Saiz-Lopez et al., 2014; Long et al., 2014; Prados-Roman et al., 2015a; Sherwen et al., 2016b).

The tropospheric ozone burden is 250 Tg (against 339 Tg in GEOS-Chem) while the current value proposed by the AR5 is 370 Tg and that of the CMIP6 simulations (without halogen chemistry) is 356 ± 31 Tg (Griffiths et al., 2021). This difference in the ozone mass balance is due to the different assumptions considered in the models, in particular NMVOC emissions.

290 Figure 5 shows the absolute changes in surface ozone and relative change in zonal ozone between simulations with and without halogen chemistry. Significant relative losses are observed in the Southern Hemisphere, which testifies to the strong emissions of halogenated species between the ocean and the atmosphere in this region (Long et al., 2014; Saiz-lopez et al., 2012; Schmidt et al., 2016; Sherwen et al., 2016b, 2016a). Most of the change in total tropospheric ozone concentration occurs in the free troposphere between 350 hPa and 900 hPa (63%). This result is similar in magnitude to the relative change reports in GEOS-

295 Chem (65%; Sherwen et al., 2016b) and CAM-Chem (65%; Iglesias-Suarez et al., 2020).
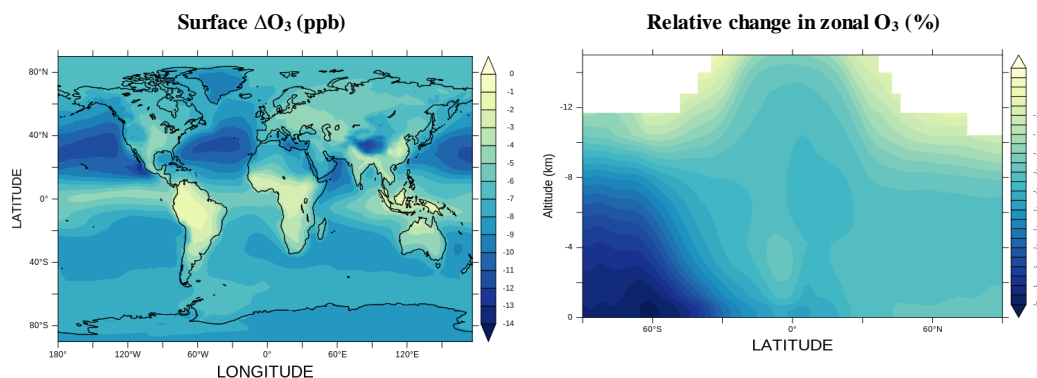
Figure 5: Absolute and zonal changes in surface and tropospheric ozone (ppbv) between simulations with and without halogen chemistry.

The annual production of ozone decreases by 4.7% when the chemistry of halogens is considered. This decrease is due to a

300 reduction in NO_x concentrations of 32.8% (Table 2) due to the hydrolysis of XNO_3 (X = Cl, Br, I) leading to deposition losses, in accordance with previous studies (Saiz-Lopez et al., 2012b; Long et al., 2014; von Glasow et al., 2004; Parrella et al., 2012; Schmidt et al., 2016, Sherwen et al., 2016b).

The ozone loss processes differ considerably between simulations with and without halogenated compounds (Table 2). The total ozone chemical annual loss decreases by 2.4%. The loss of ozone by chlorine, bromine and iodine represents 0.5%, 4.7%

305 and 18% of the total losses, respectively; thus, halogens represent 23.2% of the total loss of ozone. The sum of the ozone losses caused by the halogens is 984 Tg.yr^{-1}. Iodine is responsible for 78% of that halogen-mediated loss, while bromine accounts for 19%, which is within the range of reported values in Iglesias-Suarez et al., 2020 (80%, 16% respectively). Iodine is responsible for an overall tropospheric ozone loss of 762 Tg.yr^{-1} (compared to 748 Tg.yr^{-1} in Sherwen et al., 2016a). Much of this loss arises from the photolysis of HOI after its production from the reaction of IO with HO_2.

310 The difference between the terms of production and loss of ozone shows that the inclusion of halogens leads to an overall decrease in the net production of tropospheric ozone (PO_3-LO_3) of 20% (126 Tg.yr^{-1}). Consequently, the lifetime of ozone decreases by 3.2 days and reaches 17.9 days which is less important than what is reported in the IPCC AR5 report: 22.3 ± 2 days (Stevenson et al., 2006) and 23.4 ± 2.2 days (Young et al., 2013).

Table 3: Comparison of global tropospheric O_x budgets of "Halo" and "NoHalo" simulations in INCA for the PI and PD.

	Preindustrial Halo	Preindustrial NoHalo	Present day Halo	Present day NoHalo
Ozone burden (Tg)	170.7	218.9	249.9	317
Ozone chemical sources (Tg.yr^{-1})				
NO + HO$_2$	1459	1554	2954	3190

NO + CH₃O₂	474.9	477.2	1134	1159
NO + RO₂	380.7	355.5	625.8	596.7
Total chemical ozone sources (PO₃)	**2314**	**2387**	**4714**	**4946**
Ozone chemical sinks (Tg.yr⁻¹)				
O₃ + H₂O → 2 OH + O₂	1099	1497	1905	2460
O₃ + HO₂ → OH + O₂	431.5	648	917	1295
O₃ + OH → HO₂ + O₂	207.1	297.8	349.4	488.7
Bromine O₃ sinks	155.3	-	186.9	-
Iodine O₃ sinks	536.9	-	762.3	-
Chlorine O₃ sinks	23.51	-	22.16	-
Other O₃ sinks	78.06	85.11	88.5	92.87
Total chemical ozone sink (LO₃)	**2531**	**2528**	**4231**	**4337**
Ozone PO₃-LO₃ (Tg.yr⁻¹)	**-216.6**	**-141**	**483**	**609.1**
Ozone dry deposition (Tg.yr⁻¹)	**403.4**	**593.4**	**875.5**	**1139**
Ozone lifetime (days)	**21.2**	**25.6**	**17.9**	**21.1**
Ozone STE (PO₃-LO₃-Dry dep) (Tg.yr⁻¹)	**-620**	**-734.5**	**-392.4**	**-530.2**

315 **4.2 Sensitivity runs and metrics**
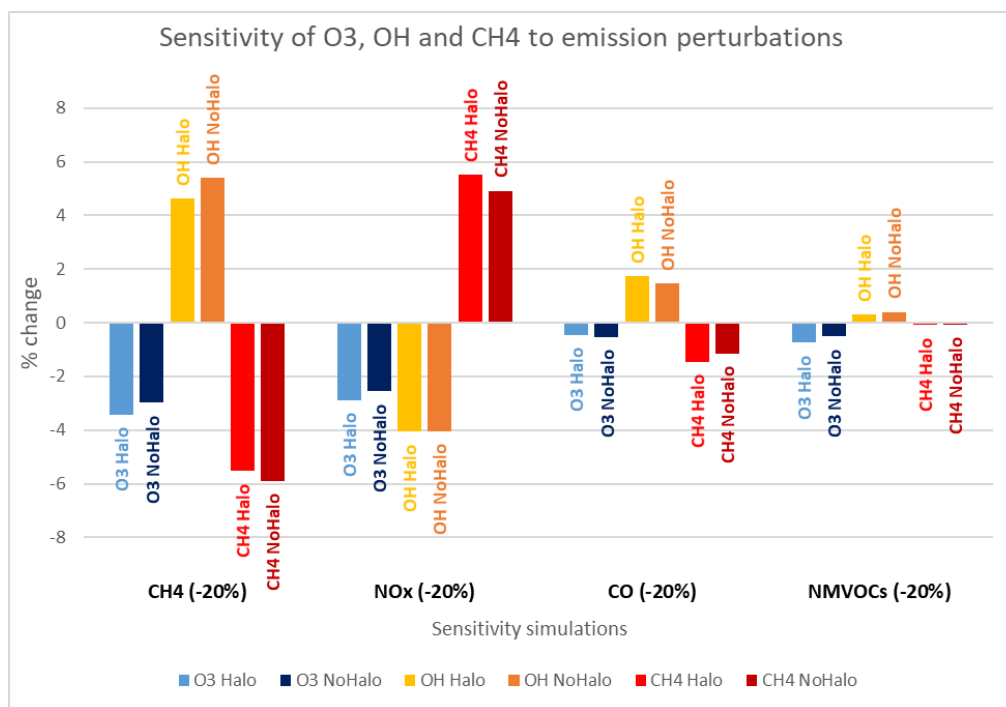
Figure 6: Tropospheric relative changes (%) in ozone mass budget, OH concentration and methane lifetime for different sensitivity tests (NOₓ, CH₄, CO, NMVOCs) with and without halogens chemistry.

In order to study the sensitivity of the tropospheric oxidative system following the inclusion of halogen chemistry, we explore,

320 in fig. 6, the relative changes (%) of ozone and OH regarding emission perturbations of photooxidant precursors (-20%) of CH₄, NOx, CO and NMVOCs. Our results show that the sensitivities of ozone and OH are important in the following increasing order: NMVOCs, CO, NOₓ and CH₄ (Fig. 6). It is also clear that the OH radical is more sensitive to perturbations in CH₄, NOₓ and CO than ozone. Notably, upon including halogens, ozone becomes more sensitive to changes in CH₄, NOₓ and to a lesser

extent disturbance in NMVOCs. On the other hand, under the sensitivity of CH_4, NO_x and NMVOCs perturbations, the OH

325   radical becomes more resilient in the presence of halogens. Traditionally, the chemical lifetime of CH_4 reflects the lifetime of CH_4 to removal by OH in the troposphere and provides a useful proxy for global tropospheric oxidizing capacity (Wild et al., 2020). The simulations examined here show, that the lifetime sensitivity of CH_4 changes according to the changes affecting the OH concertation in the troposphere and remains a useful proxy for global tropospheric oxidizing capacity for all perturbations. When NO_x emissions are reduced, atomic chlorine, a secondary oxidant of methane (see subsection 3.5),

330   becomes more relevant and influences the sensitivity of CH_4.

4.3 Pre-industrial to present-day changes

With and without halogenated chemistry, the model simulates significantly lower ozone concentrations in the pre-industrial compared to present due to the decrease in NO_x concentrations. Taking into account pre-industrial halogen chemistry reduces the average surface ozone concentrations by 5.0 ppbv (38%) (which would make the model more consistent with past

335   observations). This reduction is largest over the oceans (5.5 ppbv, or 42.4%).

Globally, halogens reduce the tropospheric load of ozone by 67.1 Tg today and 48.2 Tg in pre-industrial (Table 3). Between PI and PD, ozone increases by 98.1 Tg (113 Tg in Sherwen et al., 2017) without halogen chemistry and by 79.2 Tg (90 Tg in Sherwen et al., 2017) with halogen chemistry. Both in PD and PI, halogens are responsible for about 23-28% of ozone destruction. Tropospheric ozone lifetimes drop from 21.1 to 17.9 days in the present with the inclusion of halogens and from

340   25.6 to 21.2 days in the pre-industrial. The sensitivity of the burden of ground-level ozone to pre-industrial – present changes is ~ 20% lower when the chemistry of the halogens is considered. The changes observed in LMDZ-INCA and schematized in Fig. 7 are in agreement with the changes in Sherwen et al. (2017).
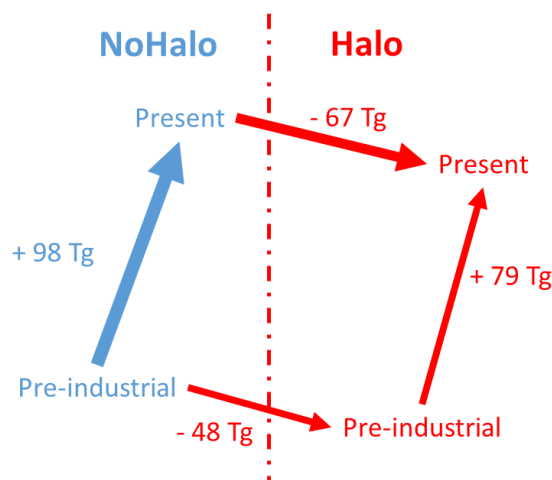
Figure 7: Rough schematic representation of the evolution of ozone mass budget changes between PI and PD, following the inclusion
345   **of halogen chemistry in LMDZ-INCA.**

4.4 Net ozone chemical loss

In the marine boundary layer, where primary halogens are in high quantity, NO_x concentrations are very low (around 10 pptv) due to the lack of primary sources. In these areas, with chemical regimes being NO_x-limited, net ozone production occurs only above a certain NO_x concentration threshold. The response of the chemical system to the change in emissions between PI and

350   PD is an increase in the amount of NO_x from ~ 24-27 pptv to ~ 39-41 pptv. This change is low and consistent with a previous result by Wild and Palmer, (2008). In PD, the extent of net ozone loss environments represents 46% of the Earth's surface in

"NoHalo". Due to the overall reduction in NOx concentrations in the "Halo" simulation, 53% of the Earth's surface is then affected by net ozone losses.

4.5 Impact on methane lifetime

355   The inclusion of tropospheric halogens affects the atmospheric concentrations of a large number of compounds in the model. A marked decrease in oxidants (O_3, OH, HO_2, H_2O_2) is then computed. This leads to an increase in the concentrations of CO (8.5%) and some NMVOCs, including isoprene (7.1%). The lifetime of methane with respect to chlorine and the OH radical as well as the share of chlorine in the losses of methane in the literature are shown in Table 3. The synthesis corresponds to the values reported in international modelling exercises (averages multi-model), models including halogen chemistry,

360   observation-based studies and the IPCC AR5 report. In the reference simulation, the tropospheric chemical lifetime of methane due to its consumption by OH is of 7.9 years. With the inclusion of halogen chemistry, the OH concentration decreases, increasing this chemical lifetime of methane to 9.3 years. The chemical lifetime of methane linked to oxidation by Cl is 333 years, less than the 384 years suggested by Hossaini et al. (2016) but closer to IPCC AR5 estimates. This oxidation by Cl represents 2.7% of the total loss (close to the values reported in the literature and in Table 3). Thus, in LMDZ-INCA,

365   accounting for both OH and the chlorinated radicals consumption, methane oxidation leads to a total chemical lifetime of CH_4 of 9.0 years.

The chemical lifetime of CH_4 in INCA is more in agreement with the estimate based on the observations of 9.1 ± 0.9 years by (Prather et al., 2012) and the value of 11.2 ± 1.3 years suggested by the IPCC AR5 - when the chemistry of halogen compounds is considered.

370   **Table 3: Methane lifetime with respect to chlorine and OH radical as well as the share of chlorine in methane losses in the literature.**

	Lifetime relative to		Total lifetime (years)	Observations (years)	Method	Share of chlorine in methane loss (%)
	Chlorine (years)	OH radical (years)				
Prather et al. (2012)	-	-		9.1 ± 0.9	Observations	-
Naik et al. (2013)		9.7 ± 1.5			Multimodels	-
Voulgarakis et al., 2013	-	9.3 ± 0.9		-	Multimodels	-
AR5 IPCC (2014)	200 ± 100	11.2 ± 1.3			Synthesis	-
Hossaini et al. (2015)	384.4	10			TOMCAT model	2.5
Schmidt et al. (2015)	-	9.5		-	GEOS-Chem model	-
Lelieveld et al. (2016)	-	8.5			MOM model	-
Sherwen et al. (2016b)	-	8.28	8.16	-	GEOS-Chem model	2.0
Maasakkers et al. (2019)	-	10.8 ± 0.4			Observations	-
This work	**-**	**7.9**	**7.9**	**-**	**LMDZ-INCA model (NoHalo)**	**-**
	332.5	**9.28**	**9.0**	**-**	**LMDZ-INCA model (Halo)**	**2.7**

5 Conclusion

Global chemistry climate models are our best tools for simulating and projecting the atmospheric chemical composition within the framework of international model intercomparisons such as AerChemMIP. Most of these models do not account for

halogen chemistry. We have used the three-dimensional climate-chemistry model LMDZ-INCA to understand and quantify the role of the chemistry of halogenated compounds on the tropospheric chemistry, notably ozone.

First, the halogenated species, their sources and sinks, their reactions in the gas and heterogeneous phase and their physicochemical characteristics have been integrated into INCA. In order to simplify the integration of this chemistry, a chemical scheme already tested and evaluated in the CAM-Chem model has been used as a basis for our developments. To avoid introducing new cumbersome and technical routines into INCA, heterogeneous reactions on water droplets and ice crystals were not taken into account in this work.

The representation of this chemistry has been shown to be sufficient to simulate properly the impact of halogens on the photooxidizing system in the troposphere and particularly in the atmospheric boundary layer. The response of the tropospheric chemical system O_x, HO_x, NO_x, CH_4 and NMVOCs to incorporation of halogen chemistry has been quantified. On a global tropospheric scale, this chemistry induces decreases of the ozone burden by 22%, of OH by 8% and of NO_x by 33%. An increase in CO, NMVOC concentrations are simulated and the lifetime of methane increases by one year. These changes are consistent with those reported in the literature.

Sensitivity tests, consisting on reducing in turn the emissions of ozone precursors, show that in the presence of halogen chemistry, ozone becomes more sensitive to NO_x, CH_4 and NMVOC perturbations. Comparison between simulations considering preindustrial and present-day emissions shows that the sensitivity of the ozone burden to changes in emissions is ~ 20% lower in the presence of halogen chemistry (mainly because of the chemistry of iodine). In present-day conditions, the surface area of net chemical destruction of ozone has increased from 46% to 53%.

Still rarely represented in chemistry climate models, our model results confirm that the chemistry of halogenated species (Cl, Br, I) plays a significant role in the global consumption of tropospheric ozone. Since halogen chemistry affects substantially the ozone burden, both in preindustrial and present-day chemical conditions, international exercises examining the evolution of ozone between preindustrial, present, and future should take into account halogen chemistry.

Data availability

The main model code and the chemical scheme with halogenated compounds as well as the data outputs are publicly accessible at https://drive.google.com/drive/folders/1qj8Qy9k6rPjLST0mXqc-mkiShN5viw5p?usp=sharing

Author contributions

The idea of the study, the implementation of the halogens chemical scheme, the design of numerical simulations come from Cyril Caram and Sophie Szopa. Anne Cozic acted as a data engineer for model developments and diagnostics. Slimane Bekki acted as a scientific advisor and an author. Cyril Caram and Sophie Szopa prepared the first draft of the paper. Carlos Cuevas provided emission data sets. Alfonso Saiz-Lopez acted as a scientific advisor. All authors contributed to its editing.

Competing interests

The authors declare that they have no conflict of interest.

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