

# *KEY ROLE OF SHORT-LIVED HALOGENS ON GLOBAL ATMOSPHERIC OXIDATION DURING HISTORICAL PERIODS*

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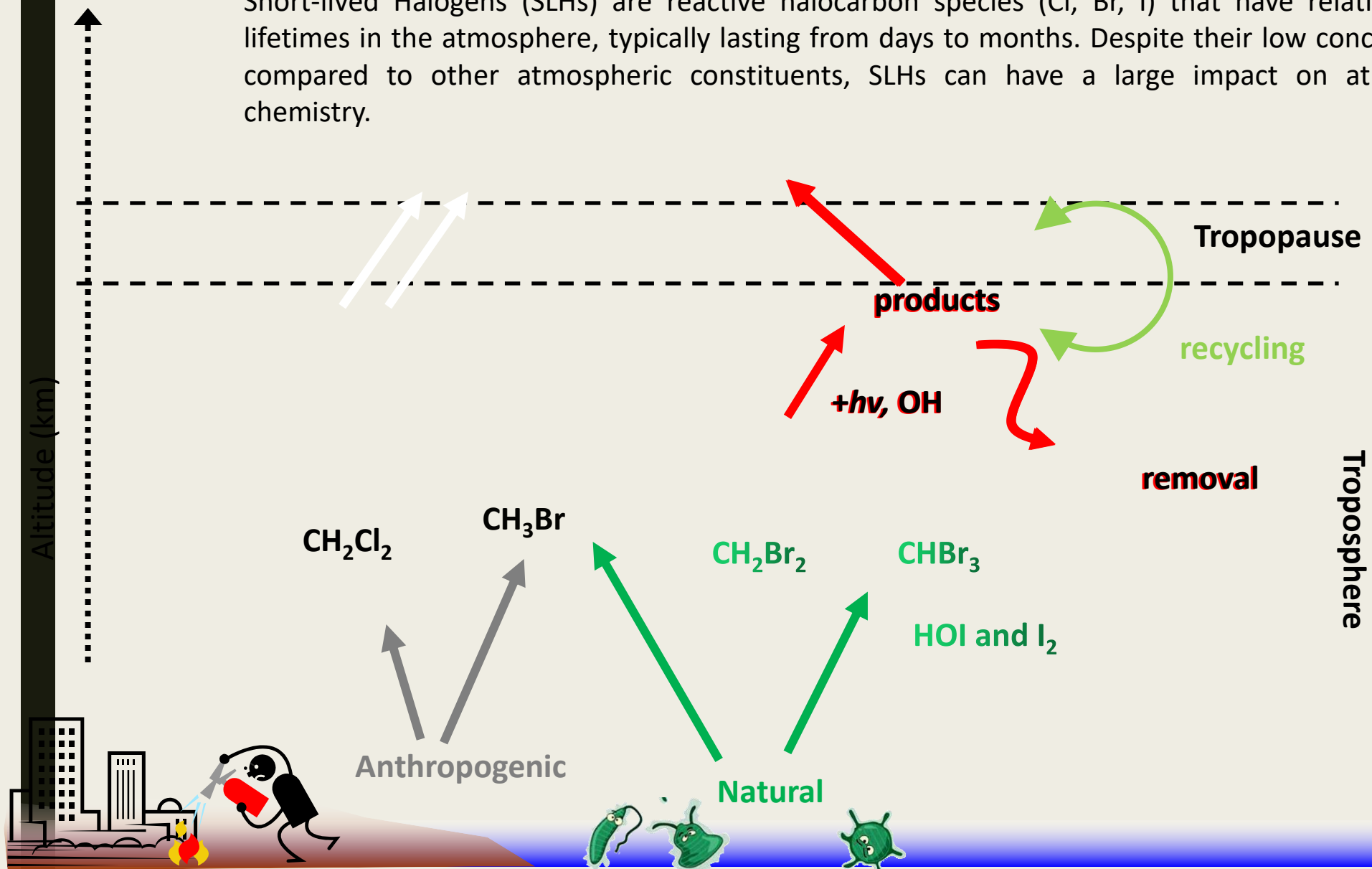
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# Introduction

Short-lived Halogens (SLHs) are reactive halocarbon species (Cl, Br, I) that have relatively short lifetimes in the atmosphere, typically lasting from days to months. Despite their low concentrations compared to other atmospheric constituents, SLHs can have a large impact on atmospheric chemistry.



# Motivation and Goals

Comprehensive global assessment of their impact on the abundance of atmospheric oxidants during historical periods.

Improve knowledge of Short Lived Halogens (SLH) on the atmospheric oxidation capacity.

Last advances in the SLH chemistry: Including natural and anthropogenic sources.

Implication in the principal oxidants (OH, O<sub>3</sub>, NO<sub>3</sub>, Cl)

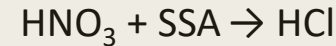
# Simulations Set-up

- Global Simulations using CESM1.2, with a state-of-the-art SLH chemistry mechanism in CAM-Chem

- For set of simulation (with and without SLH), running for a period of 5 years:
  - PI (1850-1854)
  - PD (2000-2004)

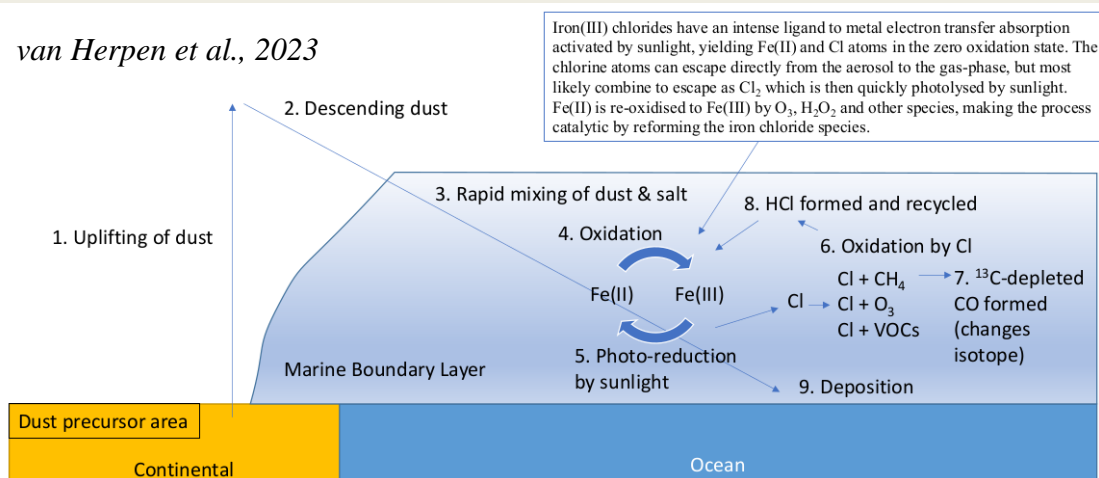
- Natural sources:  $\text{CHBr}_3$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CH}_2\text{BrCl}$ ,  $\text{CHBr}_2\text{Cl}$ ,  $\text{CHBrCl}_2$ ,  $\text{CH}_3\text{I}$ ,  $\text{CH}_2\text{I}_2$ ,  $\text{CH}_2\text{IBr}$  and  $\text{CH}_2\text{ICI}$
- Inorganic iodine ( $\text{HOI}$  and  $\text{I}_2$ ) emitted from the ocean
- Anthropogenic SLH sources ( $\text{CH}_2\text{Cl}_2$  and  $\text{C}_2\text{Cl}_4$ )

## Updates for chlorine chemistry:

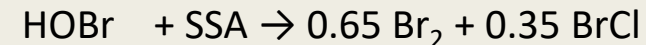
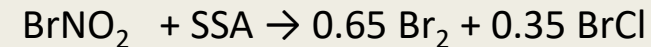
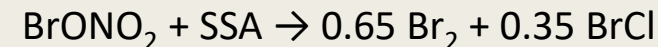


Enhanced Chlorine-uptake due to acidification  
(Hossaini et al., 2016; Li et al., 2022)

## MDSA-induced $\text{Cl}_2$ production



## SSA-dehalogenation:



Het-recycling of Halogen Reservoirs  
(Fernandez et al., 2014; 2021)

# Simulations Set-up

Cases	SLH emissions (Gg yr <sup>-1</sup> )							VOCs Emission Fluxes (Tg yr <sup>-1</sup> )			
	Surface Flux Halocarbons			Sea Salt Recycling Inorganic Halogens		Oceanic emissions	Acid-displacement	Cl from MDSA			
	SLH <sup>Cl</sup>	SLH <sup>Br</sup>	SLH <sup>I</sup>	SLH <sup>Cl</sup>	SLH <sup>Br</sup>	SF <sub>2</sub> /HOI	SLH <sup>Cl</sup>	Cl <sub>2</sub>	VOCs	CH <sub>4</sub>	CO
<i>noSLH_PI</i> <sup>1</sup>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	782	189	459.5
<i>wSLH_PI</i> <sup>2</sup>	60.9	595.7	586.4	2483	1578	898	2090	15079	782	189	459.5
<i>noSLH_PD</i> <sup>3</sup>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	828	499	1142
<i>wSLH_PD</i> <sup>4</sup>	849.7	616.9	591.7	2136	2750	1875	14214	15444	828	499	1142

<sup>1</sup>***noSLH PI***: standard chemical scheme without SLH sources

<sup>2</sup>***wSLH PI***: only natural SLH emissions for pre-industrial

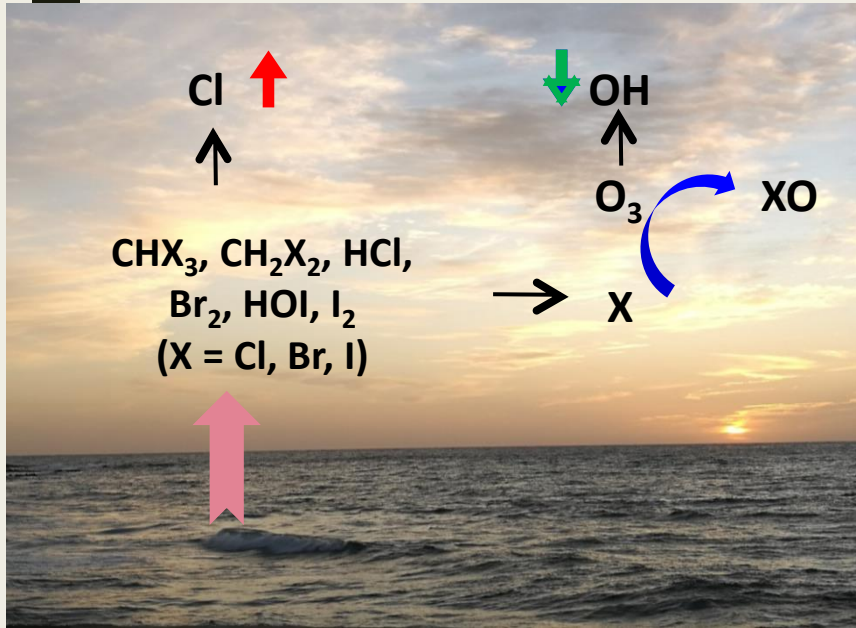
<sup>3</sup>***noSLH PD***: standard chemical scheme without SLH sources

<sup>4</sup>***wSLH PD***: natural and anthropogenic SLH sources from present-day conditions.

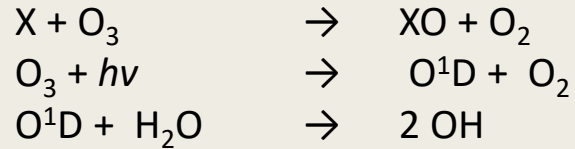
The percentage of changes of each scenario (*wSLH\_PI* or *wSLH\_PD*):

$$\% \Delta(wSLH-noSLH) = ((wSLH\_X - noSLH\_X) / noSLH\_X) \times 100\%$$

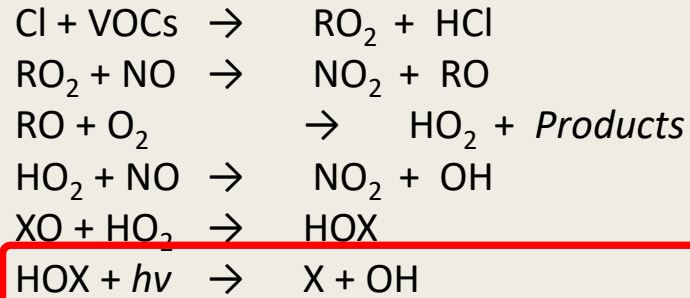
# Changes in global atmospheric oxidants PI and PD



## Halogen influence on Oxidation Capacity: (clean environments)

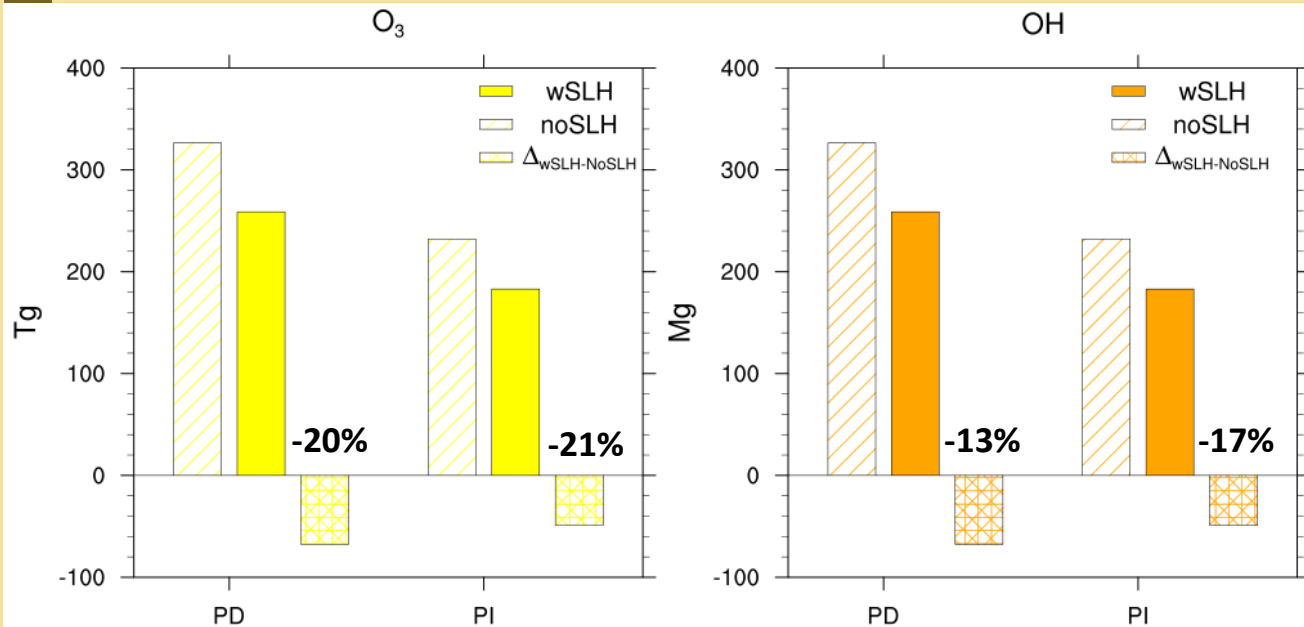


## (polluted environments)



SLH indirectly decrease OH

SLH Halogens indirectly increase OH



SLH reduce global tropospheric OH, principally due to reduction in O<sub>3</sub>

SLH reduce tropospheric O<sub>3</sub> by 20% in PD and 21% in PI.

Indirectly reduces the tropospheric OH burden by 13% in the PD and 17% during PI.

# Changes in global atmospheric oxidants PI and PD

$\text{NO}_3$  reduction more pronounced during the PI than in the PD primarily due to ozone depletion and lower  $\text{NO}_2$  abundance.

$\text{NO}_3$  levels much lower in the PI period, but the relative reduction due to SLH chemistry is larger.

Cl burden increases:

PD: 778%.

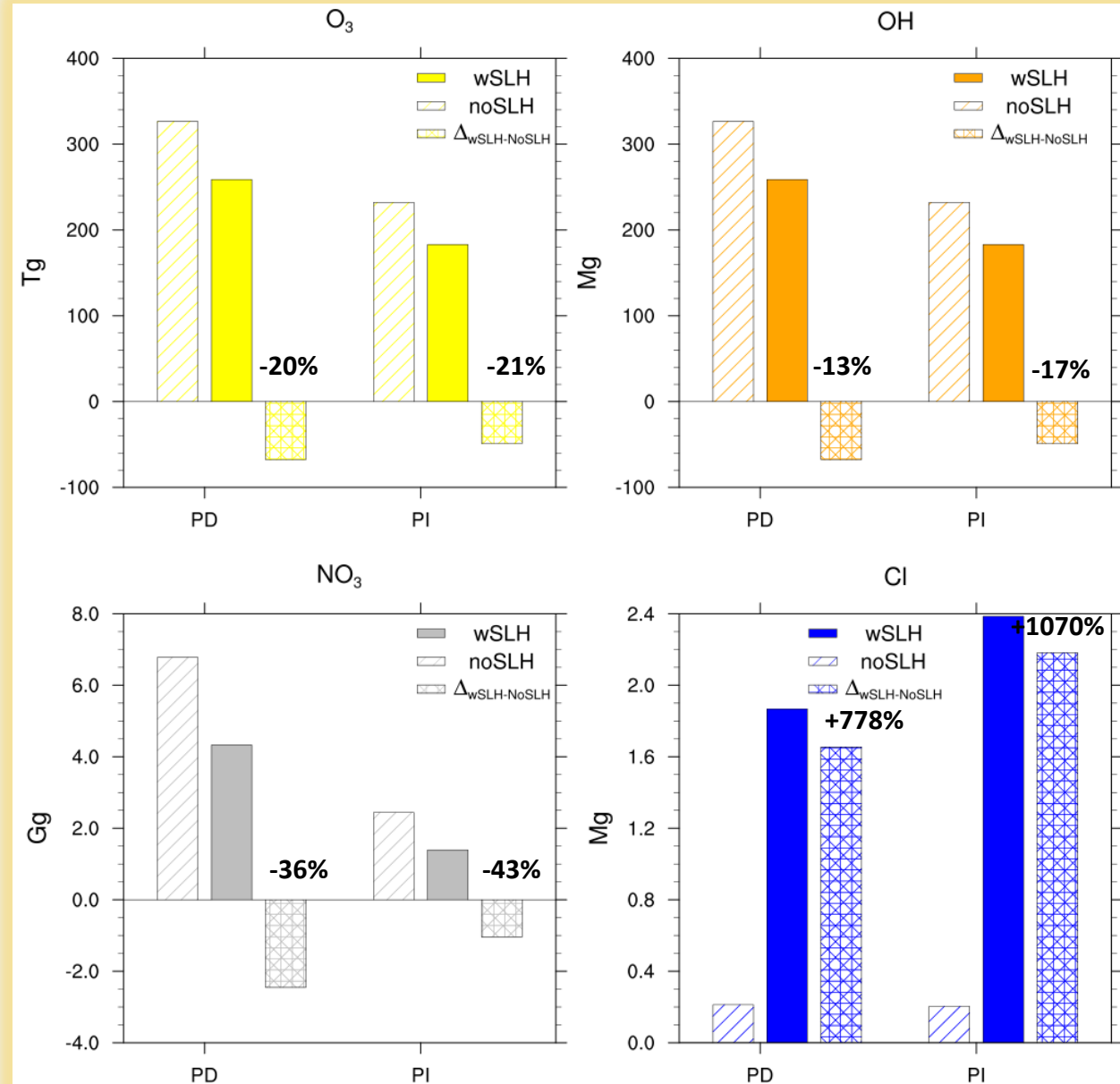
PI: 1070%.

The relative increase in Cl is larger in the PI.

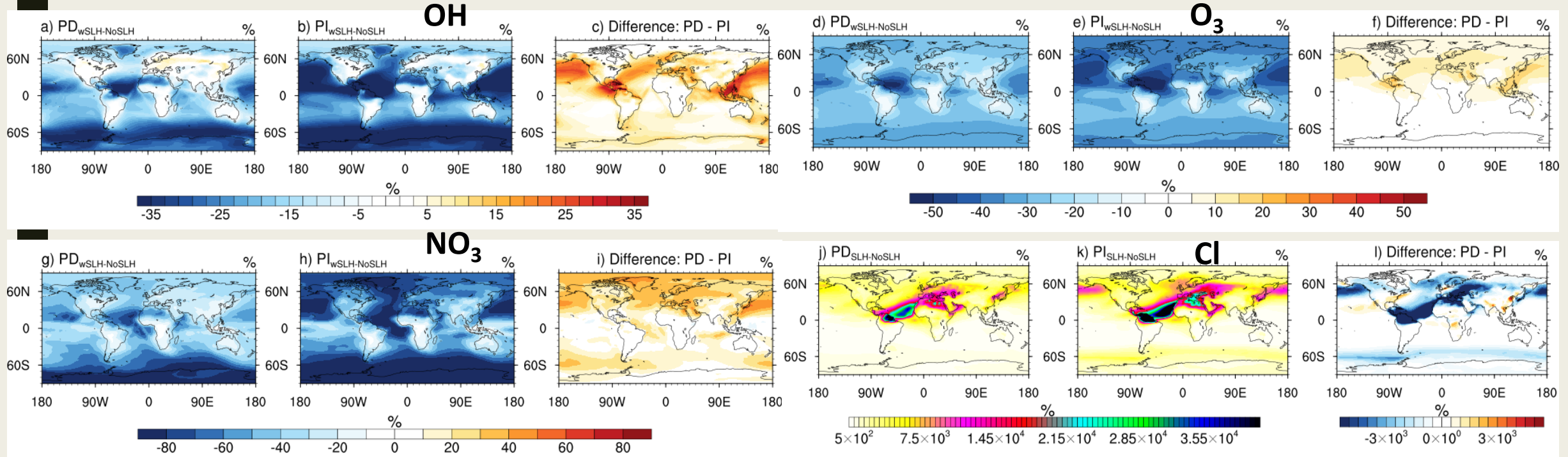
At PD greater fraction of chlorine being stored in reservoir species, reducing the available Cl atoms (higher  $\text{NO}_x$  and  $\text{HO}_x$  levels in the PD from anthropogenic emissions).



## Global integrated tropospheric burden of main oxidants



# Spatial heterogeneity in the influence of SLH on oxidants



- SLH lowering OH and O<sub>3</sub> in remote, clean environments (such as the open ocean)
- SLH increase OH production in polluted continental regions:
  - by increasing O<sub>3</sub> formation through the oxidation of VOCs and
  - by the photolysis of hypohalous acids (HOX; X = Cl, Br, I).

Cl increases in both the PI and PD, particularly in regions with abundant dust and sea salt aerosols, such as the Atlantic Ocean.

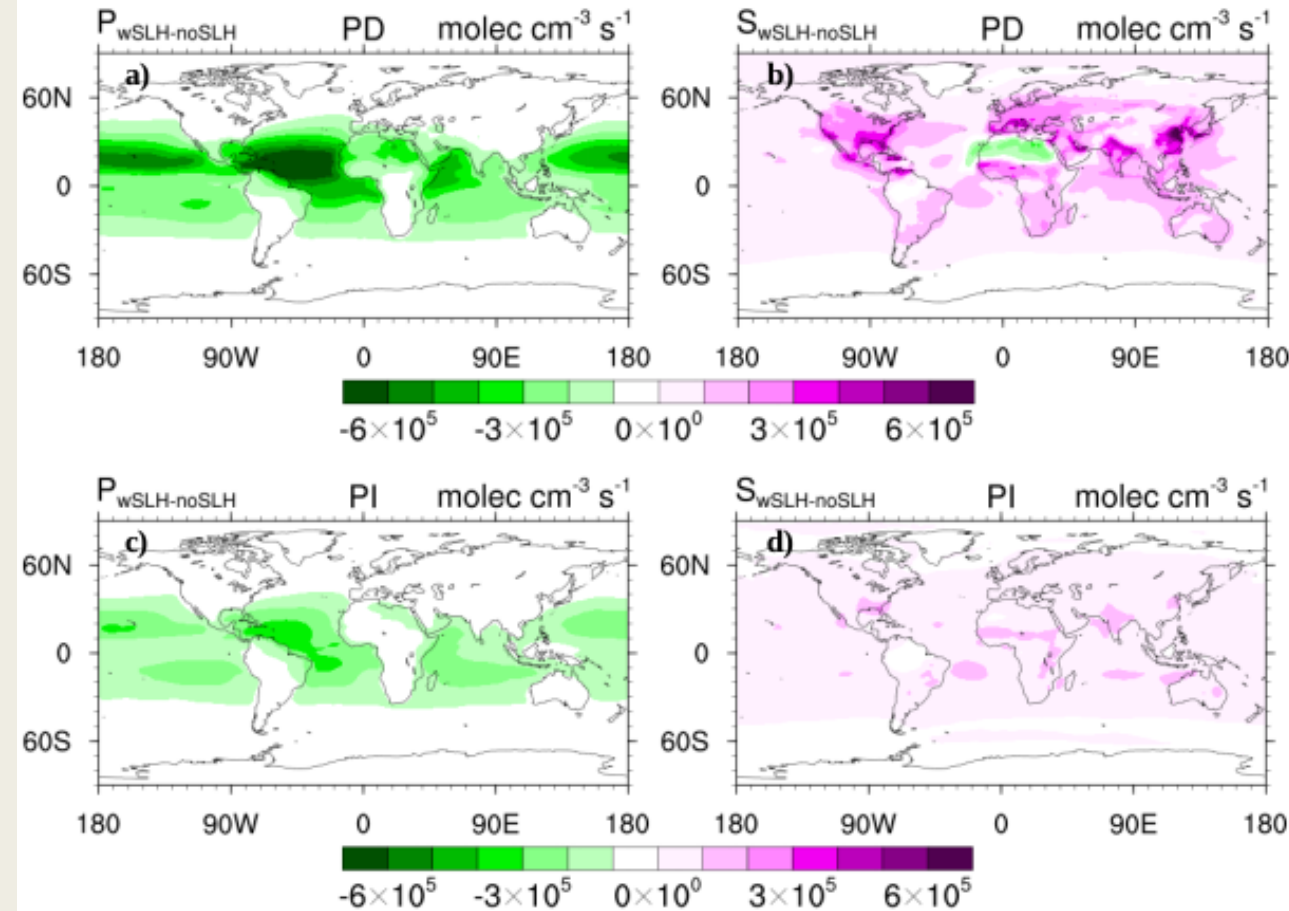
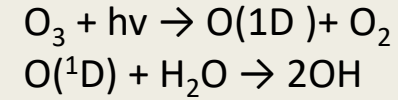
In the PI, lower NO<sub>x</sub> levels favor the formation of reactive chlorine species, resulting in a larger increase in Cl.



# Influence of halogens on the chemical pathways for OH formation

Sources (Tmol yr <sup>-1</sup> )	noSLH_PD	wSLH_PD	noSLH_PI	wSLH_PI
<b>Primary</b>				
O <sup>1</sup> D + H <sub>2</sub> O	87 (47%)	71 (41%)	53 (50%)	41(43%)
<b>Secondary</b>				
NO <sub>x</sub> + HO <sub>2</sub>	59 (31%)	56 (32%)	31 (29%)	28(29%)
O <sub>3</sub> + HO <sub>2</sub>	22 (12%)	17 (10%)	11 (11%)	8(8.5%)
H <sub>2</sub> O <sub>2</sub> + hu	14 (8%)	14 (8%)	8 (8%)	8 (8%)
VOCs, ROOH + hu	5.0 (2.7%)	5.3 (3.0%)	3.4 (3.1%)	3.5 (3.6%)
HOX + hu	-	11.0(6%)	-	7.5(8%)
Others	0.18 (0.1%)	0.2(0.09%)	0.08(0.07%)	0.07(0.07%)
<b>Total Secondary</b>	<b>100 (53%)</b>	<b>103(59%)</b>	<b>54 (50%)</b>	<b>56 (57%)</b>
G (P + S)	187.2	173.7	107.3	97.02
<b>Recycling probability, r (%)</b>	<b>53</b>	<b>59</b>	<b>50</b>	<b>57</b>

Primary Source



- *P* mostly decreases in the tropical and extra-tropical marine regions.
- *S* increases are seen predominantly over the continents

Sources (Tmol yr <sup>-1</sup> )	Lelieveld et al. 2002 <sup>1</sup>	Lelieveld et al. 2016 <sup>2</sup>	noSLH(PD) (this study)
Primary			
O <sup>1</sup> D + H <sub>2</sub> O	91.9	84.0	87
Total S	96.2	167.2	100

# Influence of halogens on recycling OH probability

$$r = 1 - \frac{P}{P + S} \times 100\%$$

Lelieveld, J., et al., 2002

$r$  = recycling probability  
 $P$  = Primary production  
 $S$  = Secondary production

Recycling probability, $r$ (%)	53 (noSLH_PD)	59 (wSLH_PD)	50 (noSLH_PI)	57 (wSLH_PI)
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$r$  at BL (1000-850 hPa)

Tropical BL  $r < 50\%$ , region strongly depends on  $P$ .

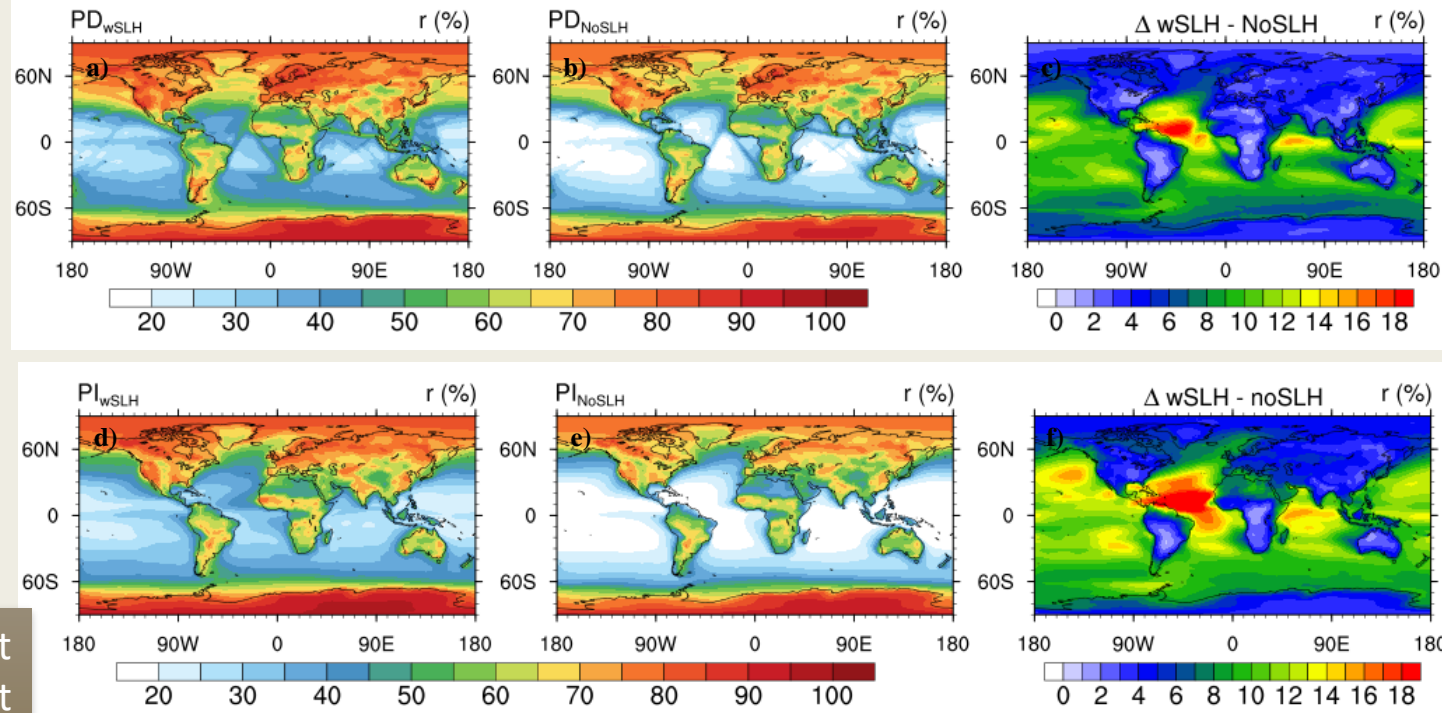
Northern mid-latitudes,  $r > 60\%$ , increasing in  $S$

$r$  values  $\sim 60\%$  over the North Atlantic Ocean, where the photocatalytic chlorine production from Saharan dust is highest

Impact of SLH on OH recycling more pronounced in the PI, especially in the tropics due to the lower contribution of  $S$

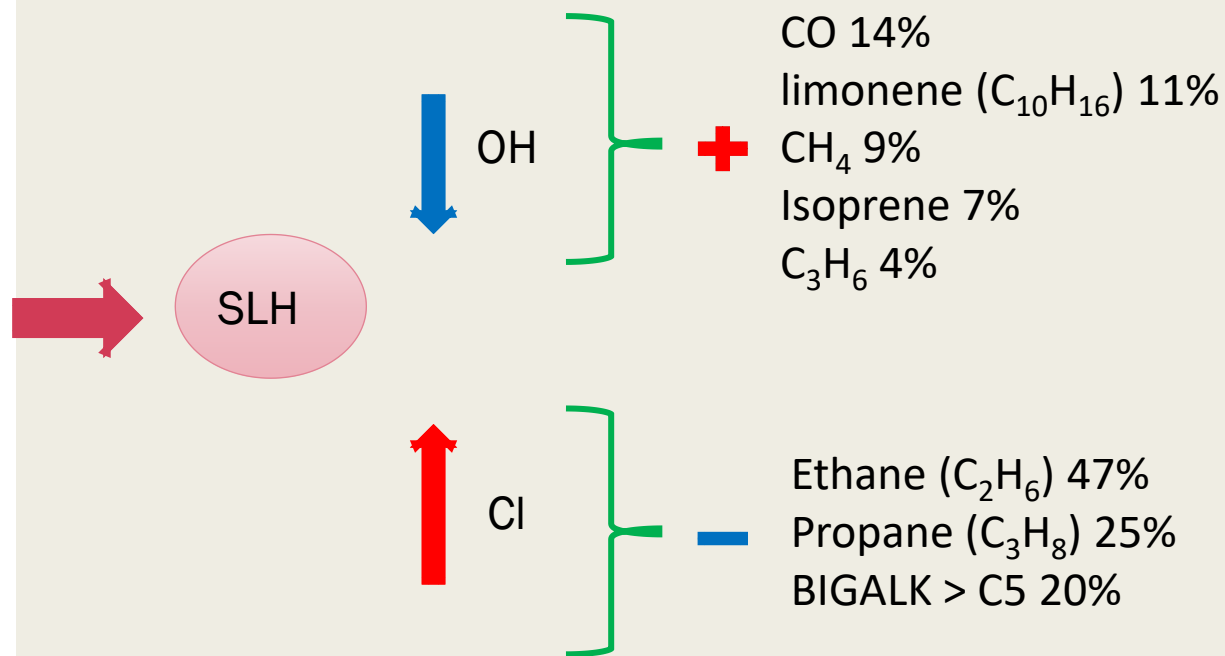
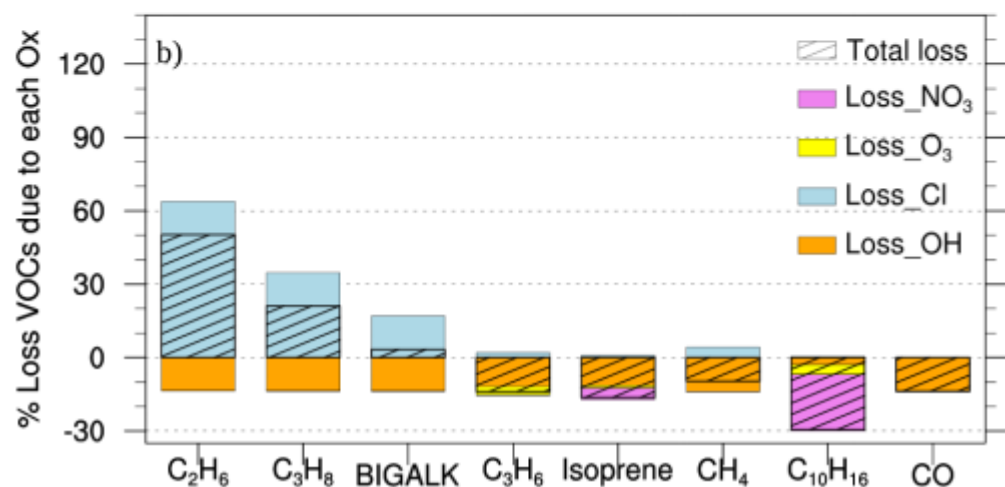
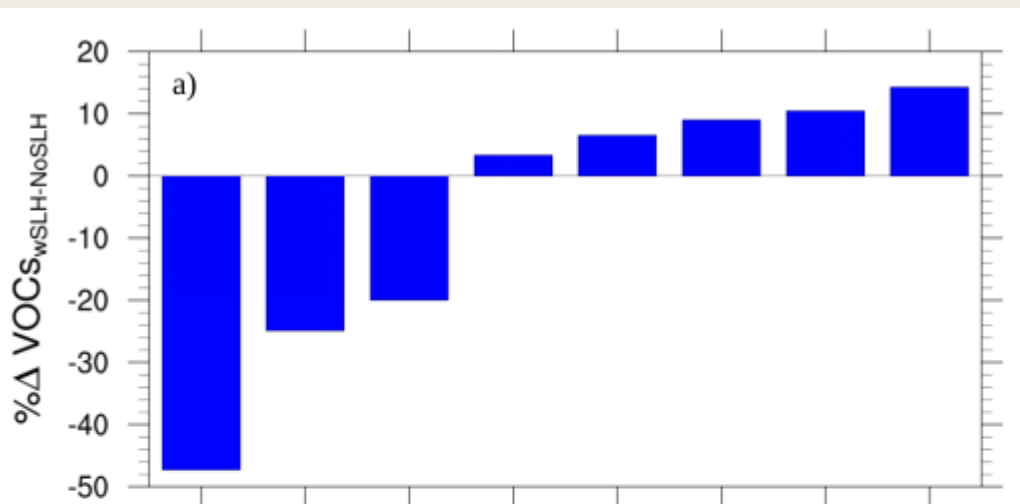
-SLH reduce  $P$  and enhancement  $S$ , therefore, SLH not only reduce OH levels (and the oxidation capacity) but also increase the  $r$ .

-SLH increase the natural resilience of the atmosphere to external perturbations.



# Impact of SLH on the abundance of key organic compounds

We investigated how the addition of SLH along with the difference in the reaction rates between VOCs with OH and Cl leads to positive/negative changes in the burdens of different VOCs

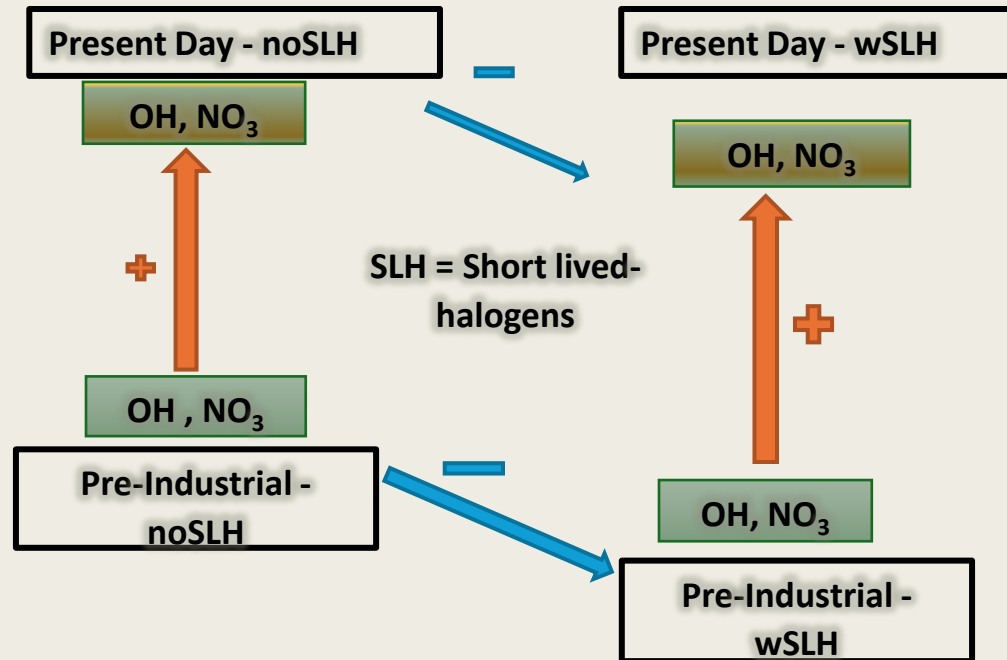


Percentage of changes in some principal VOCs due to the inclusion of SLH for PD

- This contrasting effect of SLH on the abundance of VOCs results from the faster oxidation of some VOCs by Cl than by OH.
- In the presence of SLH, reaction with Cl is the main loss pathway for C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and big-alkanes and, as a consequence, their burden decreases in the presence of halogen chemistry, despite the decrease in OH levels.

# Summary and Conclusions

**Substantial Reduction in Oxidation Capacity:** SLHs significantly decrease atmospheric oxidation by reducing the combined concentration of major oxidants ( $O_3$ , OH,  $NO_3$ ).



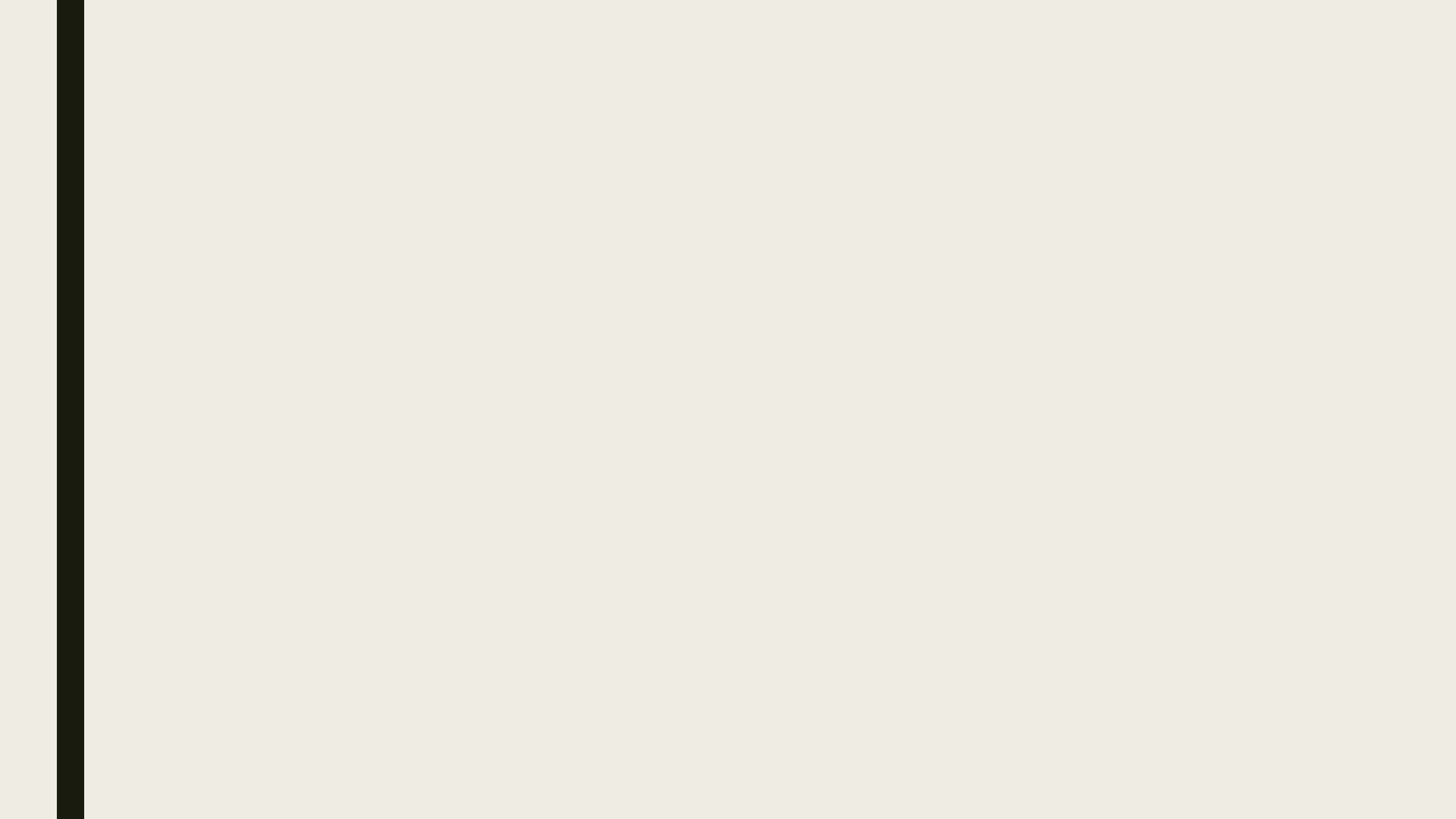
**Enhanced Impact in the Pre-industrial Atmosphere:** Impact of SLHs on atmospheric oxidation more prominent in the PI atmosphere. SLHs account for a quarter of OH and half of  $NO_3$  concentrations in the PI boundary layer

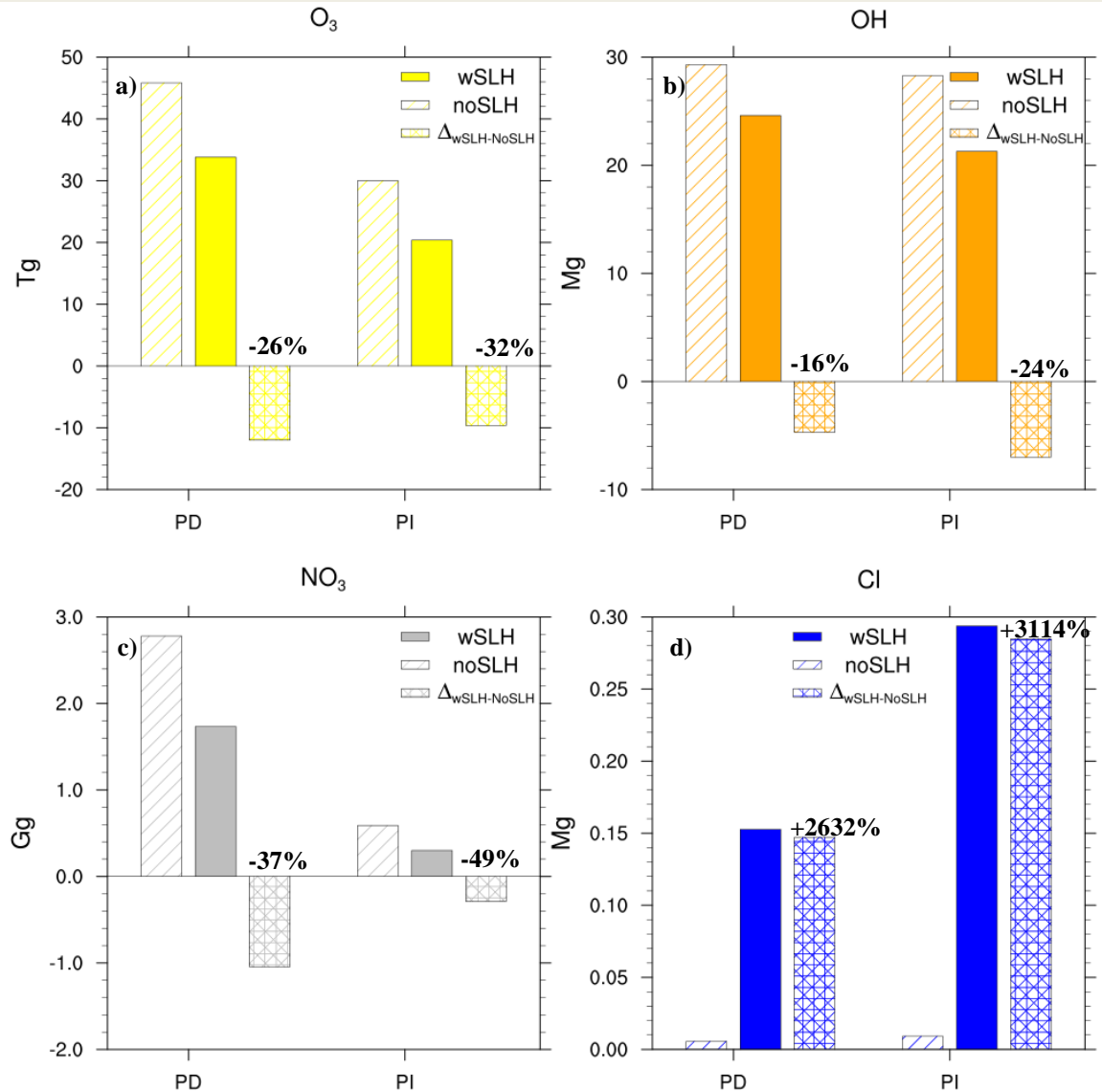
**Increased OH recycling:** SLHs reduce the dependence of OH on primary production and increase OH recycling efficiency.

**Complex Interactions with VOCs:** The interplay between oxidants, SLHs, and VOCs leads to substantial changes in the burden of key organic compounds, impacting air quality and potentially aerosol formation.

Complex and multi-directional chemical interactions between SLH and atmospheric oxidants, currently unaccounted for in air quality and climate assessments. Incorporate a detailed SLH emissions and chemistry into air quality and climate models will improve their predictive skills on atmospheric oxidation in past, present, and future climates.

Thanks!!





**Global integrated burden of main oxidants (OH, O<sub>3</sub>, NO<sub>3</sub>, and Cl) at the boundary layer (BL, 1000-850 hPa) and their relative changes due to the inclusion of SLH in the present-day (PD) and pre-industrial (PI) atmospheres.**

Burdens of OH, NO<sub>3</sub>, O<sub>3</sub> and Cl (expressed in Mg) in the boundary layer (BL, 1000-850 hPa) for *wSLH*, *wSLH noMDSA* and *noSLH* simulations for present (PD) and pre-industrial (PI) periods and its respectively relative percentage of change (%Δ) in oxidant concentrations due to SLH. %Δ = ((OxwSLH - OxnoSLH) / OxnoSLH) \* 100%, Ox= OH, NO<sub>3</sub>, O<sub>3</sub> and Cl.

PD										
OH						O <sub>3</sub>				
	wSLH	wSLH <sup>noMDSA</sup>	noSLH	%ΔMDSA-noHAL	%ΔnoMDSA-noHAL	wSLH	wSLH <sup>noMDSA</sup>	noSLH	%ΔMDSA-noHAL	%ΔnoMDSA-noHAL
Global	24	26	29	<b>-16</b>	<b>-13</b>	3.4x10 <sup>7</sup>	3.6x10 <sup>7</sup>	4.6x10 <sup>7</sup>	<b>-26</b>	<b>-22</b>
NO <sub>3</sub>						Cl				
Global	1.7x10 <sup>3</sup>	1.9x10 <sup>3</sup>	2.8x10 <sup>3</sup>	-38	-30	0.15	0.05	5.6x10 <sup>-3</sup>	2632	792
PI										
OH						O <sub>3</sub>				
	wSLH	wSLH <sup>noMDSA</sup>	noSLH	%ΔMDSA-noHAL	%ΔnoMDSA-noHAL	wSLH	wSLH <sup>noMDSA</sup>	noSLH	%ΔMDSA-noHAL	%ΔnoMDSA-noHAL
Global	21	23	28	<b>-25</b>	<b>-17</b>	2.0x10 <sup>7</sup>	2.3x10 <sup>7</sup>	3.0x10 <sup>7</sup>	<b>-32</b>	<b>-24</b>
NO <sub>3</sub>						Cl				
Global	3.0x10 <sup>2</sup>	4x10 <sup>2</sup>	5.9x10 <sup>2</sup>	-49	-33	0.29	0.05	9.1x10 <sup>-3</sup>	3114	423



