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Arctic Halogens Reduce Ozone in the Northern Mid-latitudes

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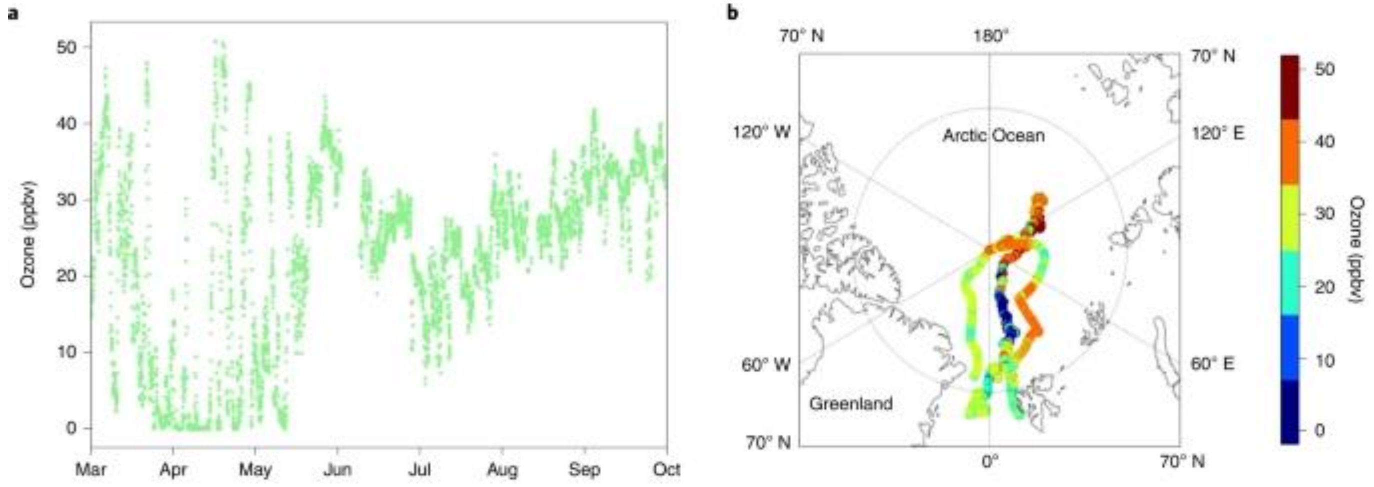
30th CESM Workshop, Boulder, June 2025

Arctic Halogens and Tropospheric Ozone Depletion

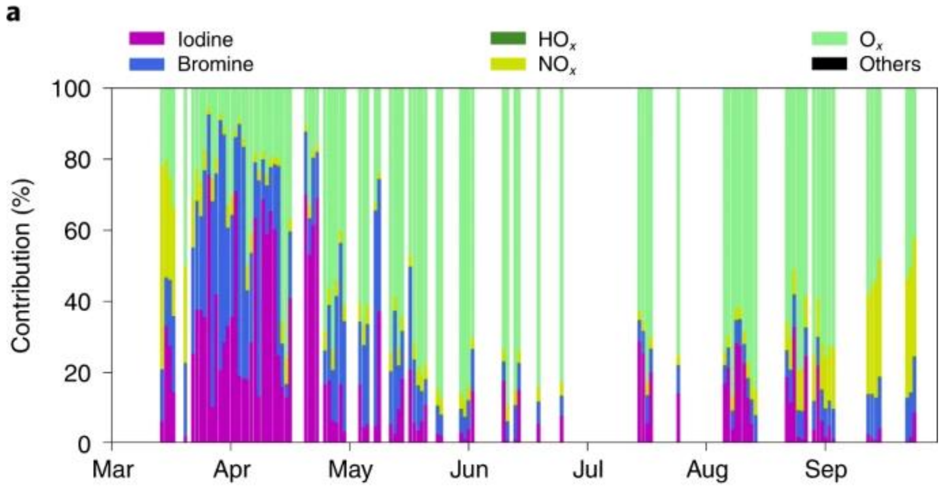
Halogen-driven ozone depletion events (ODEs) affect the springtime polar boundary layer in the Arctic. These events release large amounts of inorganic bromine from the sea-ice surface, sea-salt aerosols, and blowing snow, resulting in regional plumes with **enhanced BrO (bromine explosions) during spring** (Barrie et al., 1988; Begoin et al., 2010).

High levels of **reactive bromine**, lead to the rapid destruction of polar tropospheric ozone during spring. In addition, **iodine has also been shown** to contribute to Arctic ozone destruction either in the presence or in the absence of ODEs, surpassing the role played by bromine when the whole sunlit period is considered (Benavent et al., 2022).

Surface O_3 during MOSAiC



Ozone loss by family



How large is the influence of Arctic Halogens in ozone over the NH mid-latitudes?

Polar Halogens Module (CAM4-Chem)

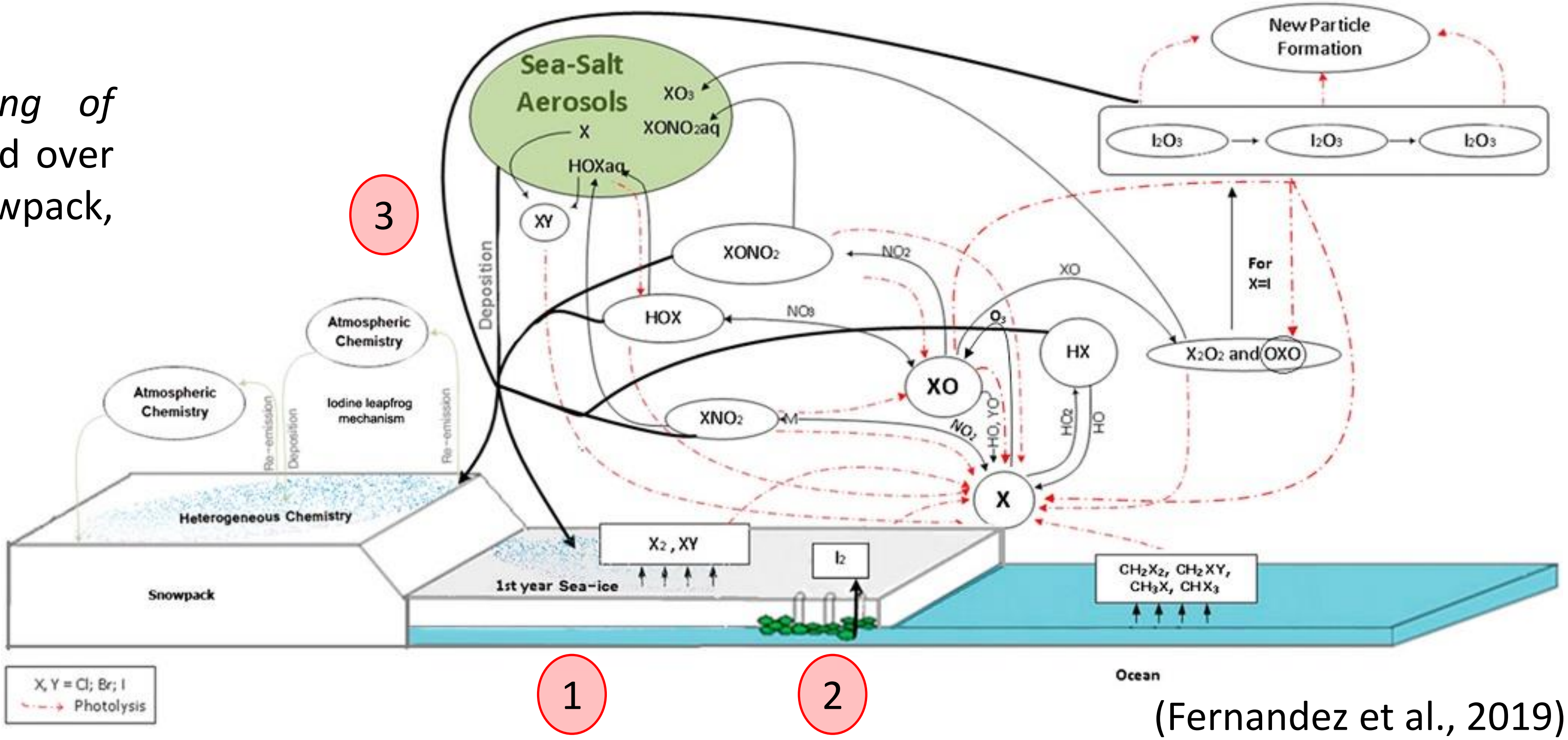
The **online polar halogens module** includes parameterized representations of:

1. the *photochemical release of gas-phase bromine* and chlorine from 1st-year sea-ice,

2. the *brine diffusion of reactive iodine* biologically produced underneath the sea-ice,

3. the *heterogeneous recycling of inorganic halogens* deposited over sea-salt aerosols, the snowpack, and sea-ice covered areas.

Polar Halogens Emissions add up to the default oceanic halogen emissions considered in CAM-Chem

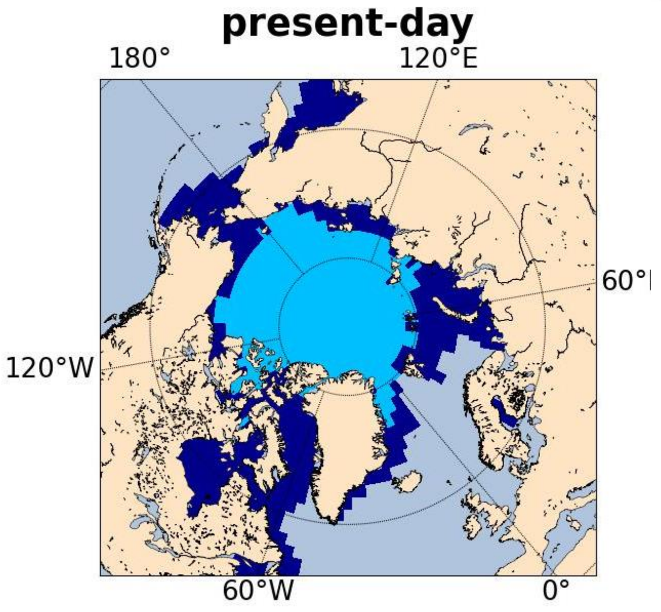


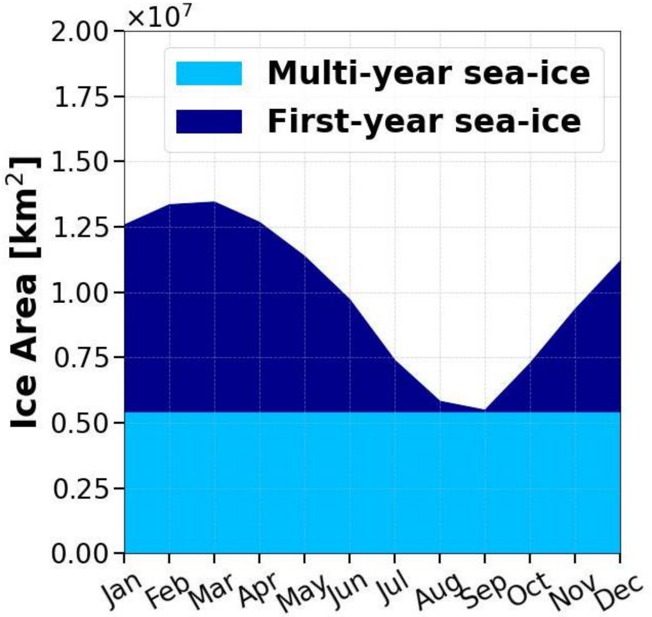
(Fernandez et al., 2019)

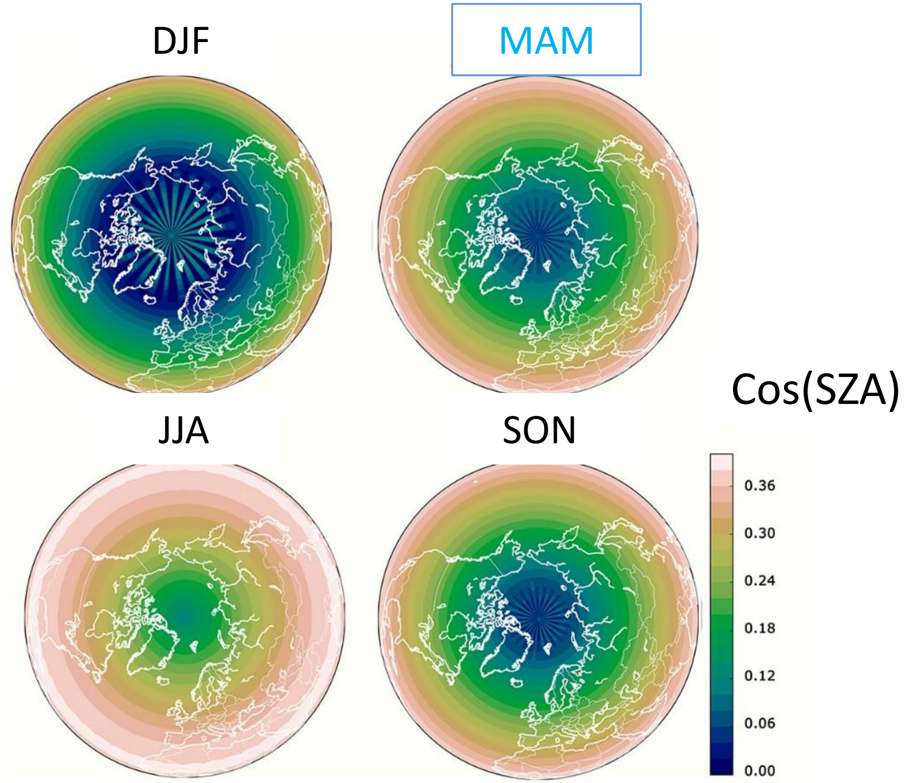
Polar Halogens Module (CAM4-Chem)

The parameterized **strength of the sea-ice halogen flux** depends on:

i) the *seasonal changes of sea-ice* surfaces and sea-salt aerosol abundance;
ii) the *net solar irradiance* reaching the Arctic surface at each latitude, longitude, and time of day;
iii) the *instantaneous surface air temperature* in each model grid-point;
iv) the *chemical partitioning between reactive and reservoir species* conforming each halogen family.







Has the impact of Arctic halogens on ozone changed since preindustrial times?

Model Experiments Design

- **Three independent sensitivities:**
  - i) a benchmark scenario neglecting the contribution of natural halogens (NoSLH ; gray)
  - ii) natural halogens scenario considering only oceanic emissions **(SLH^{ocean} ; blue)**
  - iii) polar halogens scenario considering sea-ice emissions and recycling in the Arctic **($SLH^{ocean+ice}$; red)**

- **Latitudinal bands defined** with identical geographical area (~7% of the Earth's surface):
  - **Arctic (60ºN to 90ºN)**
  - **NH mid-latitudes (47ºN to 60ºN).**

- **Five years-long cyclical** simulations were performed during two different **time periods,** considering SST, sea-ice conditions, and LBCs representative of:
  - **Present-day: 2000-2004.**
  - **Preindustrial: 1850-1854.**

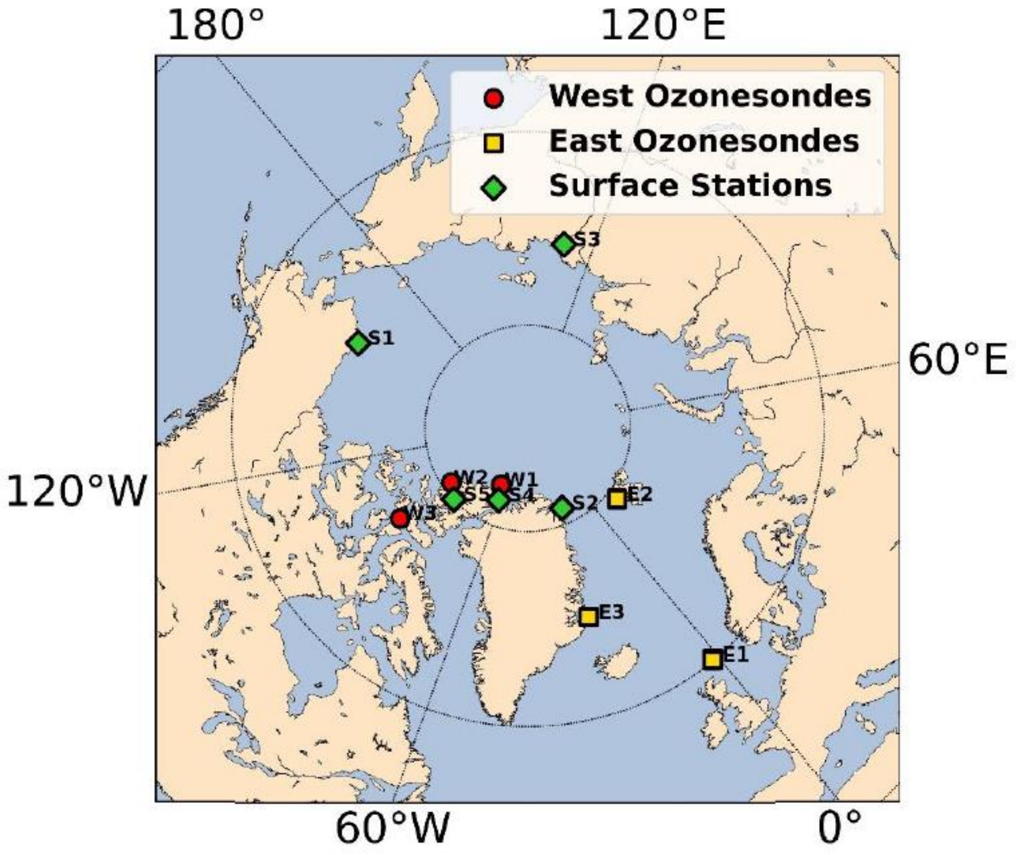
- The model was run in **specified dynamics (SD)** with forced meteorological fields obtained from a free-running CAM-Chem simulation omitting the contribution of SLH.

- Spatial resolution of **1.9º lat by 2.5º lon**, and **26 vertical levels** from the surface up to ~3 hPa (~40 km)

Model Evaluation

We used the 1995-2011 ozonesonde climatology compiled by Tilmes et al. (2012; https://www.earthsystemgrid.org/dataset/ozone_climatology_1995_2011.html).

In addition, we compared model output against Arctic surface ozone observations from the NOAA-GML (https://gml.noaa.gov/ozwv/surfoz/data.html), as well as the EBAS (NILU) database (https://doi.nilu.no).



The **ozonesonde climatology during 1995-2011** for Arctic stations has been separated between:

NH Polar West locations at Alert (W1), Eureka (W2) and Resolute (W3);

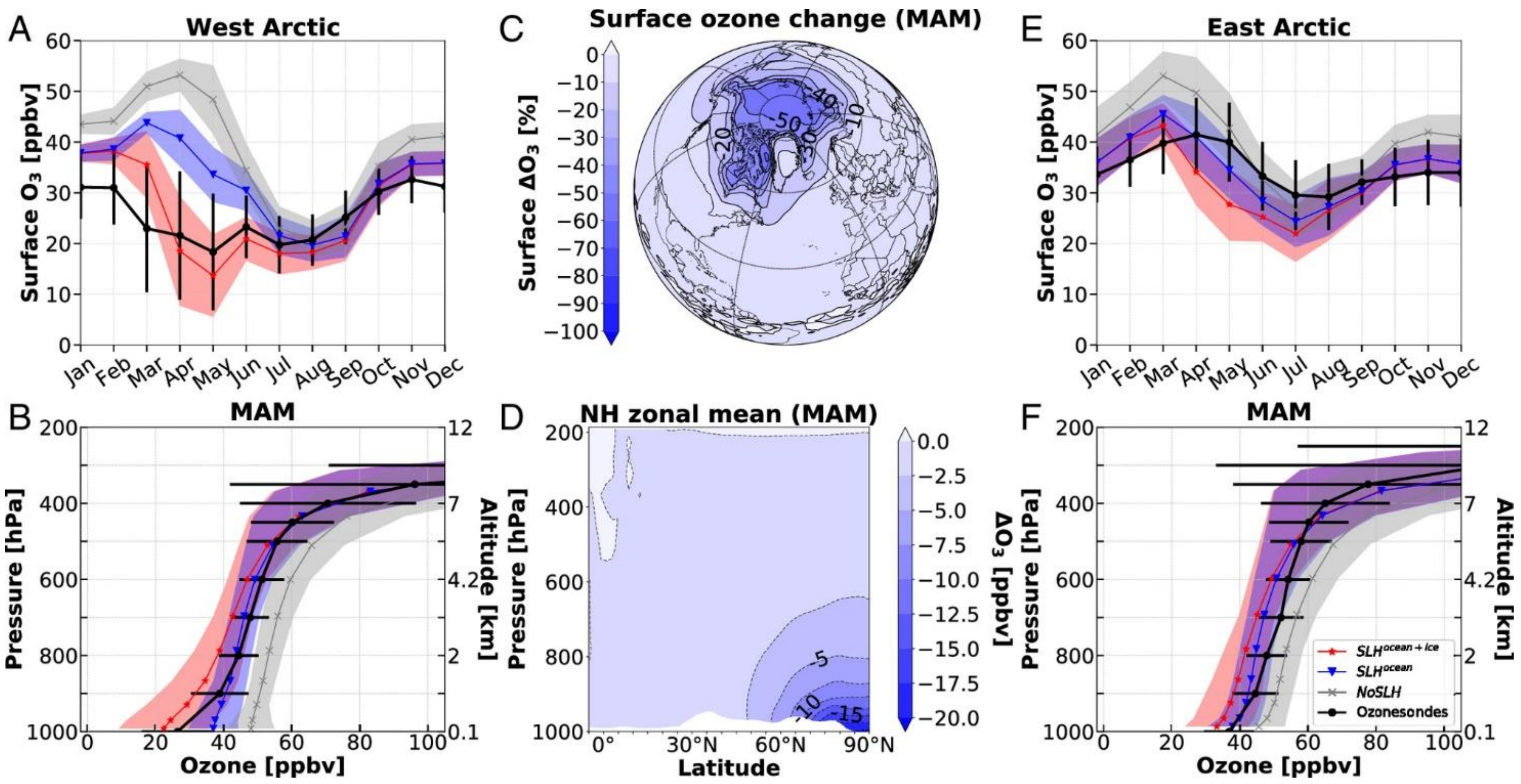
NH Polar East locations at Lerwick (E1), Ny Alesund (E2) and Scorebysund (E3).

Surface ozone stations: Barrow (S1), Villum (S2), Tiksi (S3), Alert (S4) and Eureka (S5). Three-year long hourly observational datasets for all stations have been averaged for the period 2011-2013, with the exception of Alert (2010-2012) and Eureka (2017-2019) for which the closest dates to the other stations were used.

Results

Effect of Arctic Halogens on Polar Ozone

Seasonal, Geographical, Latitudinal and Vertical Impacts



Model Sensitivities:

- NoSLH (gray)
- SLH^{ocean} (blue)
- SLH$^{ocean+ice}$ (red)

Ozone Change:

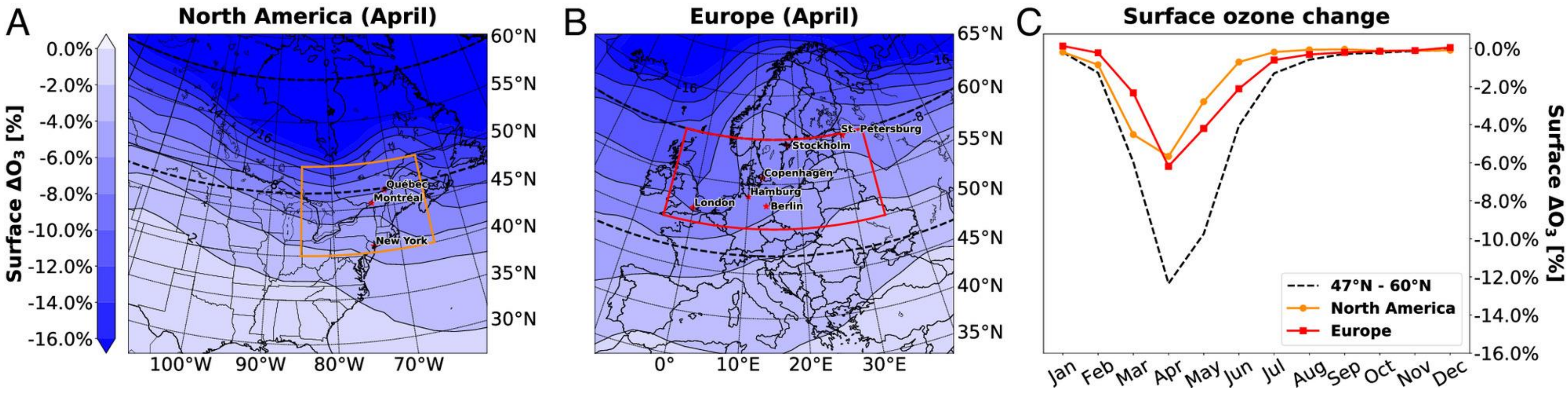
ΔO_3 = **SLH$^{ocean+ice}$ (red)** – **SLH^{ocean} (blue)**

The sea-ice halogen-driven surface ozone depletion alters the pan-Arctic ozone seasonal cycle by ***introducing a local minimum during April and May***

Including Arctic halogens in the model results in an ***improved representation of the surface ozone seasonal cycle*** and springtime vertical profiles, *mostly over the west Arctic*

The larger impact over western follows the regional enhancements of reactive halogens in coastal, which in turn depend on the spatial and ***seasonal distribution of 1st-year sea-ice controlling the strength of Arctic halogen emissions***.

Effect of Arctic Halogens on O_3 over NH mid-latitudes



- During synoptic subpolar intrusions, regional transport of **“low-ozone and halogen-rich”** air masses influence populated regions in the NH mid-latitudes

- The reduction in background surface ozone reaches:
  - ΔO_3 = −2.2 ppbv (−5%) over the north-east US / south-east Canada
  - ΔO_3 = −2.1 ppbv (−6%) northern Europe

Effect of Arctic Halogens on Polar and extra-polar Ozone

Table 1. Impact of Arctic sea-ice halogens on ozone abundance in the North Hemisphere

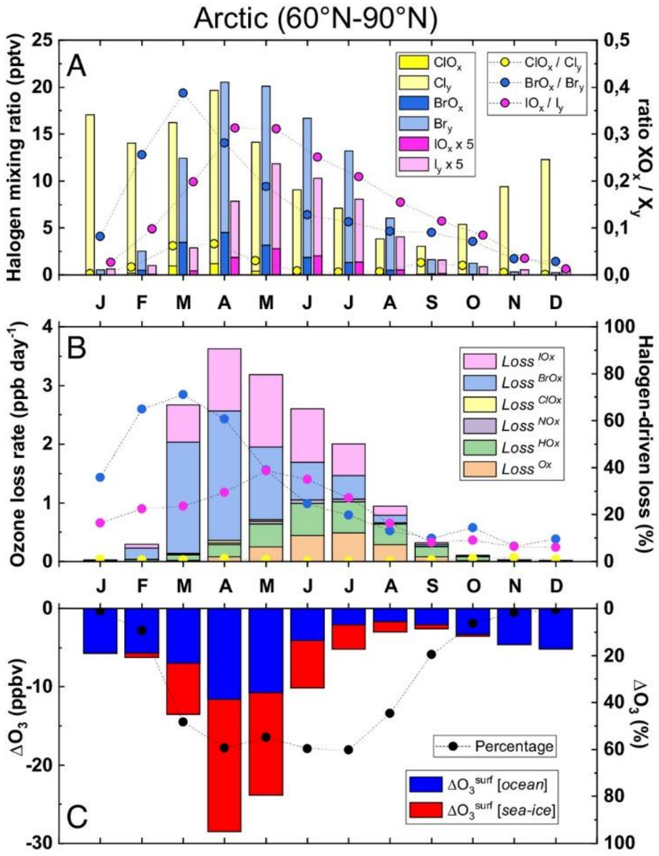
Region	Latitude	Period	Surface ΔO_3[*sea-ice*]		Tropospheric ΔO_3[*sea-ice*]	
			ppbv	%	DU	%
				present-day		
Arctic	60°N to 90°N	April	−16.9	−43	−2.5	−7
NH mid-latitudes	47°N to 60°N	MAM*	−4.0	−11	−1.4	−4
North Hemisphere	0°N to 90°N	ANNUAL	−0.8	−2	−1.1	−3

- The largest change in ozone is located over the Arctic and close to the surface (−16.9 ppbv in April, ~43%)
- In the NH mid-latitudes, sea-ice halogens reduce background surface ozone by −4.0 ppbv (−11%) during boreal spring
- Our results show that Arctic halogens lead to an annual mean NH surface ozone reduction of −2%.

Seasonality of Arctic Halogen-driven Ozone Chemical Loss

Present-day

Polar-Cap (60°N to 90°N)



Halogen Partitioning
(Cl, Br, I)

Ozone Chemical Loss
($Loss^{Cl}$, $Loss^{Br}$, $Loss^{I}$)

Ozone Change

Ozone Change:

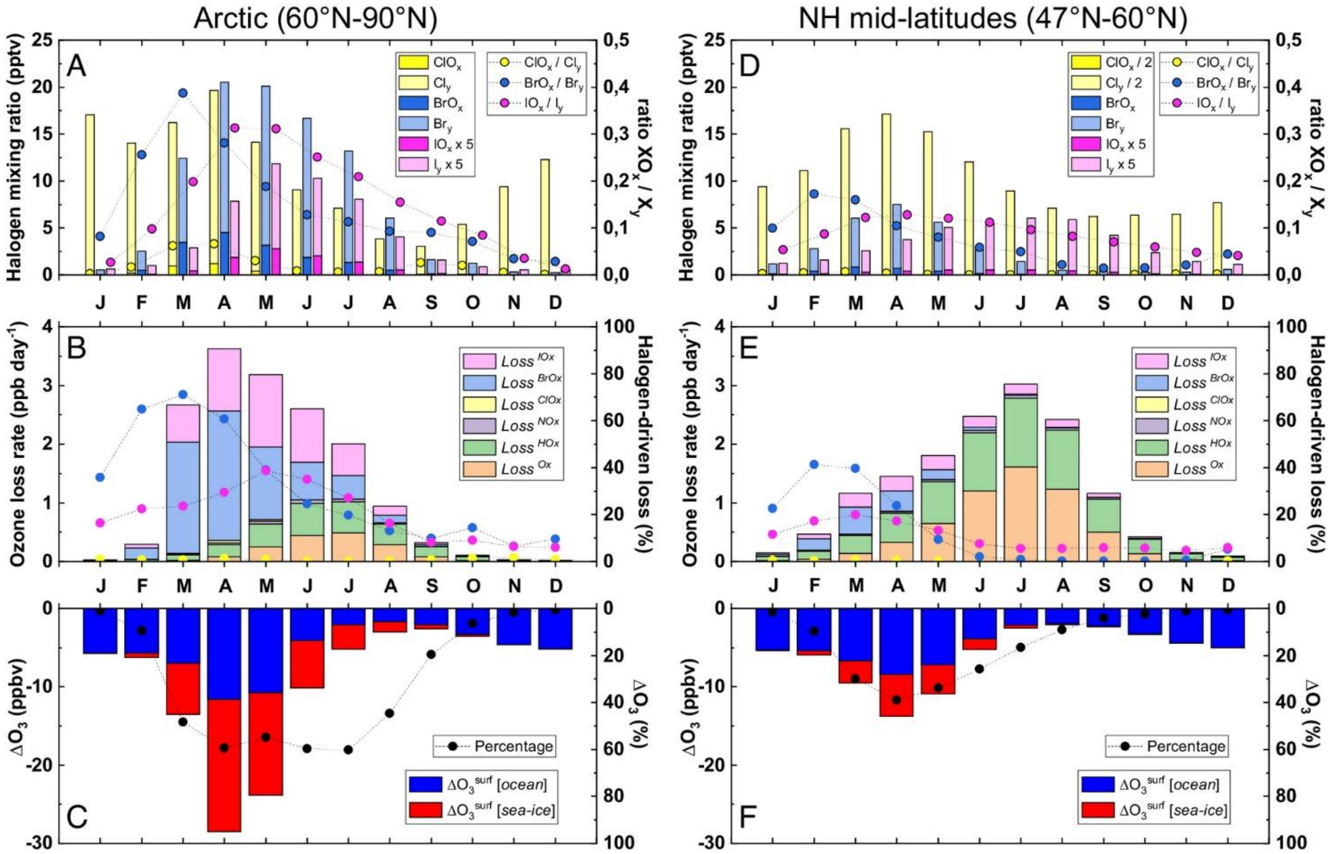
ΔO_3[sea-ice] = $SLH^{ocean+ice}$ – SLH^{ocean}

ΔO_3[ocean] = SLH^{ocean} – NoSLH

- The total ozone destruction by halogens peaks during spring and decreases rapidly into the summer:
  - the larger sea-ice halogen emissions during spring
  - the ***change in halogen partitioning*** from reactive species (Br and BrO) to reservoir species (Br_y)
- Springtime ODEs over the Arctic ***are dominated by bromine cycles, closely followed by iodine*** and with a minor contribution of chlorine.
- The net change in surface ozone due to Arctic halogens (ΔO_3[sea-ice]) is significantly larger than that arising from oceanic halogens (ΔO_3[ocean]) and mirrors the seasonal variation of the total ozone.

Seasonality of Arctic Halogen-driven Ozone Chemical Loss

Present-day　　　　Present-day



Ozone Change:

$$\Delta O_3^{sea\text{-}ice} = SLH^{ocean+ice} - SLH^{ocean}$$

$$\Delta O_3^{ocean} = SLH^{ocean} - NoSLH$$

NH Mid-Latitudes (47°N to 60°N)

- Arctic halogens contribute ~40% to the total halogen-driven surface ozone reduction over the NH mid-latitudes (47°N to 60°N) during spring
- The dominant ozone destruction channels over the NH mid-latitudes are ***Loss^{Ox}* and *Loss^{HOx}*** , which peak during the summer where halogen-driven ozone loss remains at ~8%.
- *Loss^{BrOx}* (~24%) and *Loss^{IOx}* (~17%) cycles enhance the springtime extrapolar ozone chemical loss, indicating that halogen chemistry remains active within the air masses exported from the Arctic to the NH mid-latitudes

Arctic Halogen-driven ΔO_3 during the Anthropocene

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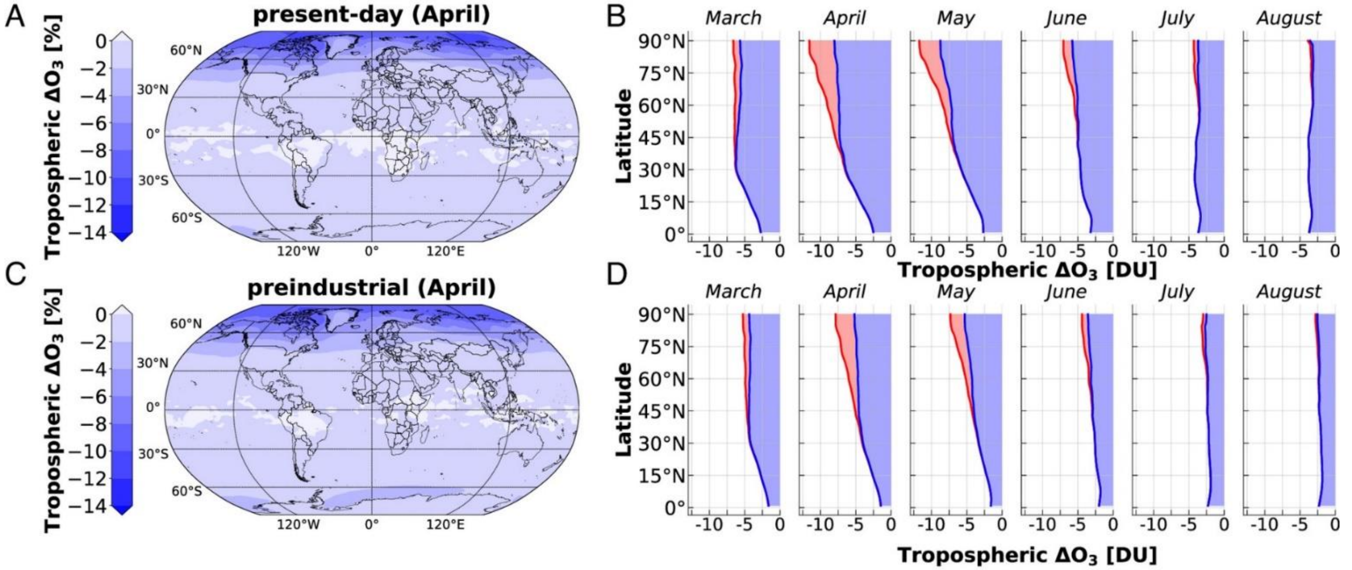
North Hemisphere	0°N to 90°N	ANNUAL	−0.8	−2	−1.1	−3
				preindustrial		
Arctic	60°N to 90°N	April	−12.5	−49	−1.9	−7
NH mid-latitudes	47°N to 60°N	MAM*	−3.1	−14	−0.7	−3
North Hemisphere	0°N to 90°N	ANNUAL	−0.6	−4	−0.1	−0.4

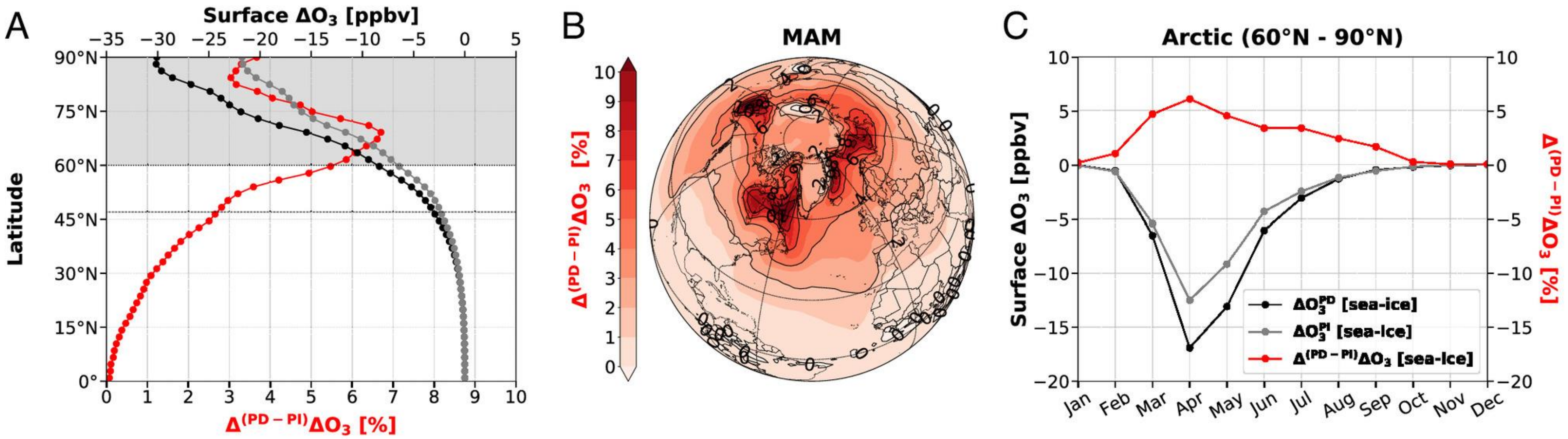
*MAM stands fof boreal spring mean (March, April, and May).



Absolute Ozone changes are larger during present-day

Relative influence of Arctic Halogens is larger during pre-industrial

Arctic Halogen-driven ΔO_3 during the Anthropocene



- The ***partitioning shift from reactive to reservoir species is lower than during present-day***, which in turn results in larger BrOx/Bry and IOx /Iy ratios during preindustrial times (driven by the NOx changes between periods).

- ***the absolute present-day halogen-driven ozone depletion is larger than in preindustrial times***, although *in relative terms the influence of Arctic sea-ice halogens on ozone over the NH has decreased* during the Anthropocene.

Conclusions

Previous research has focused on the influence of mid-latitude anthropogenic pollution on Arctic ozone levels, while here we focus on ***the regional export of halogen-rich and ozone-poor air masses*** from the Arctic to the NH mid-latitudes.

Our results show that considering Arctic sea-ice halogens in CAM-Chem helps to reproduce the abundance and seasonality of polar surface ozone, inducing a ***seasonal pulse that alters background ozone and air quality over populated areas*** in the north-east US and northern Europe.

Future changes in sea-ice coverage and ***shifting from multi-year to first-year sea-ice fractions*** is expected to induce photochemical alterations of polar halogen emissions and consequently alter the oxidation and deposition of anthropogenic emissions into the Arctic Ecosystems (e.g., mercury mobilization).

CONTACT

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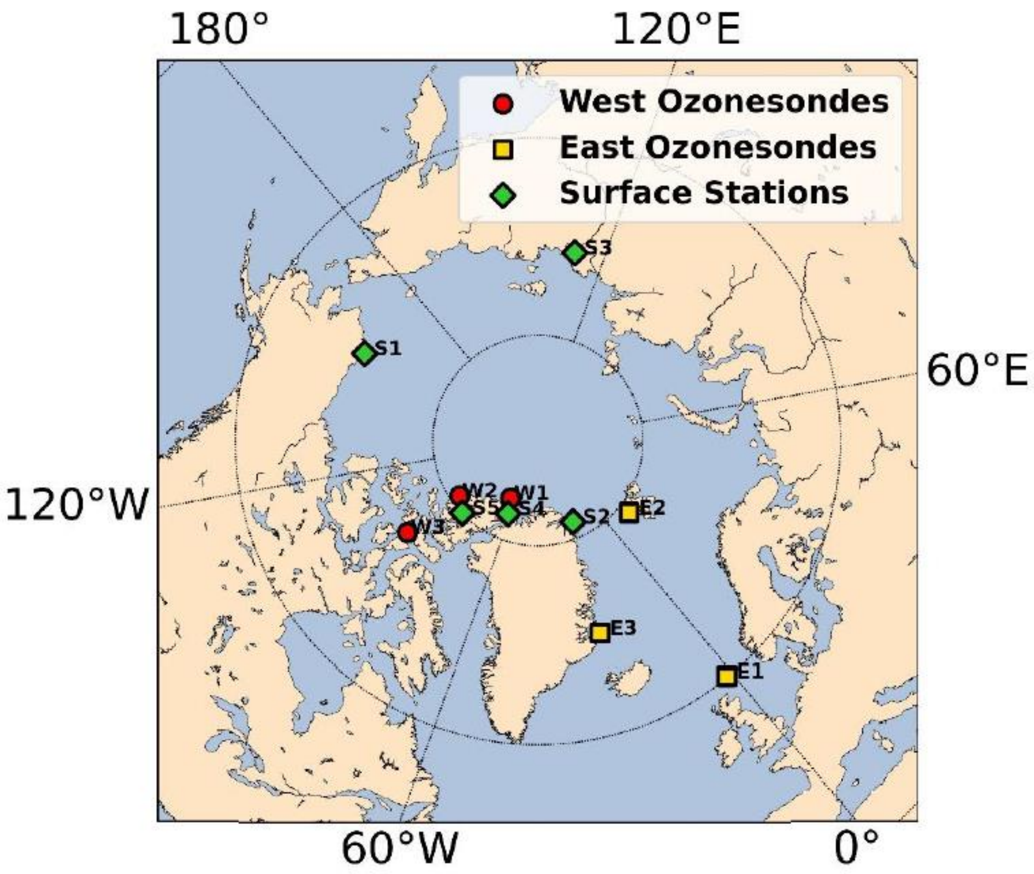
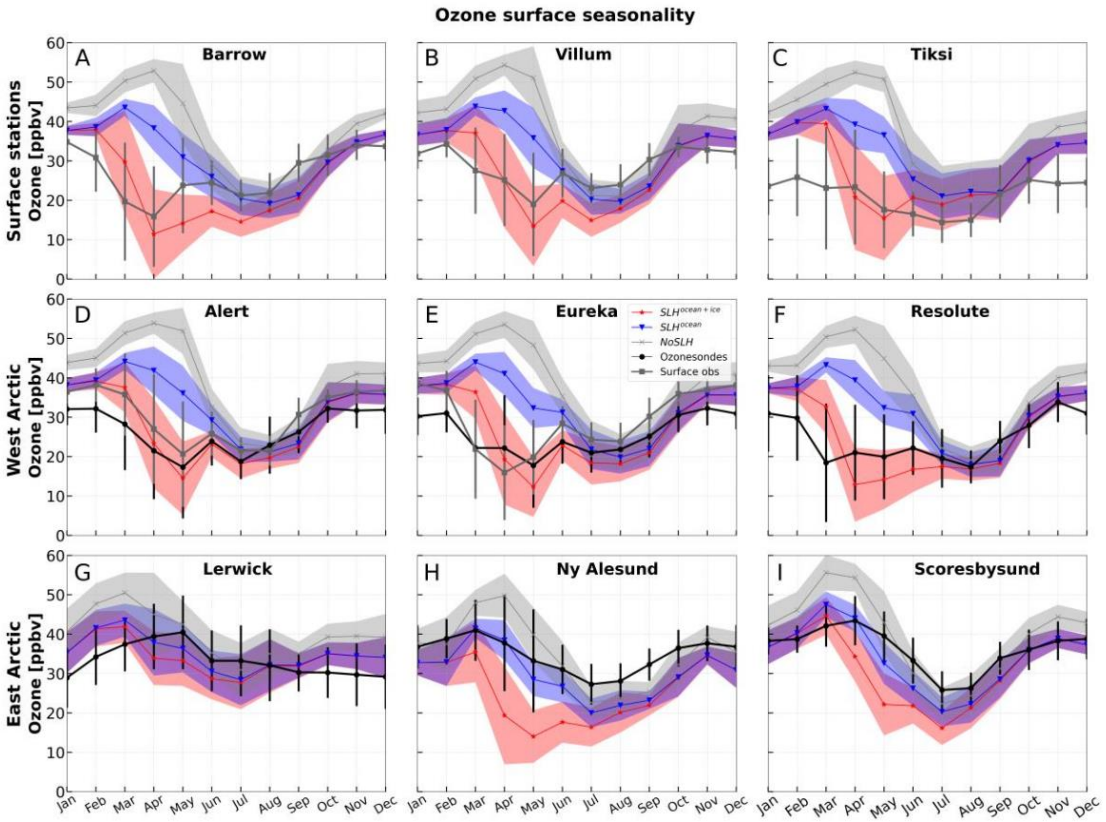
Fernandez et al., 2024 (*PNAS 2024 Vol. 121, No. 39, e2401975121, doi.org/10.1073/pnas.2401975121*)

Additional Slides

Individual Observational Sites





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Observations:
- **Near-Ground Ozonesonde climatology (black)**
- Surface Arctic Stations NOAA + Villum (gray)

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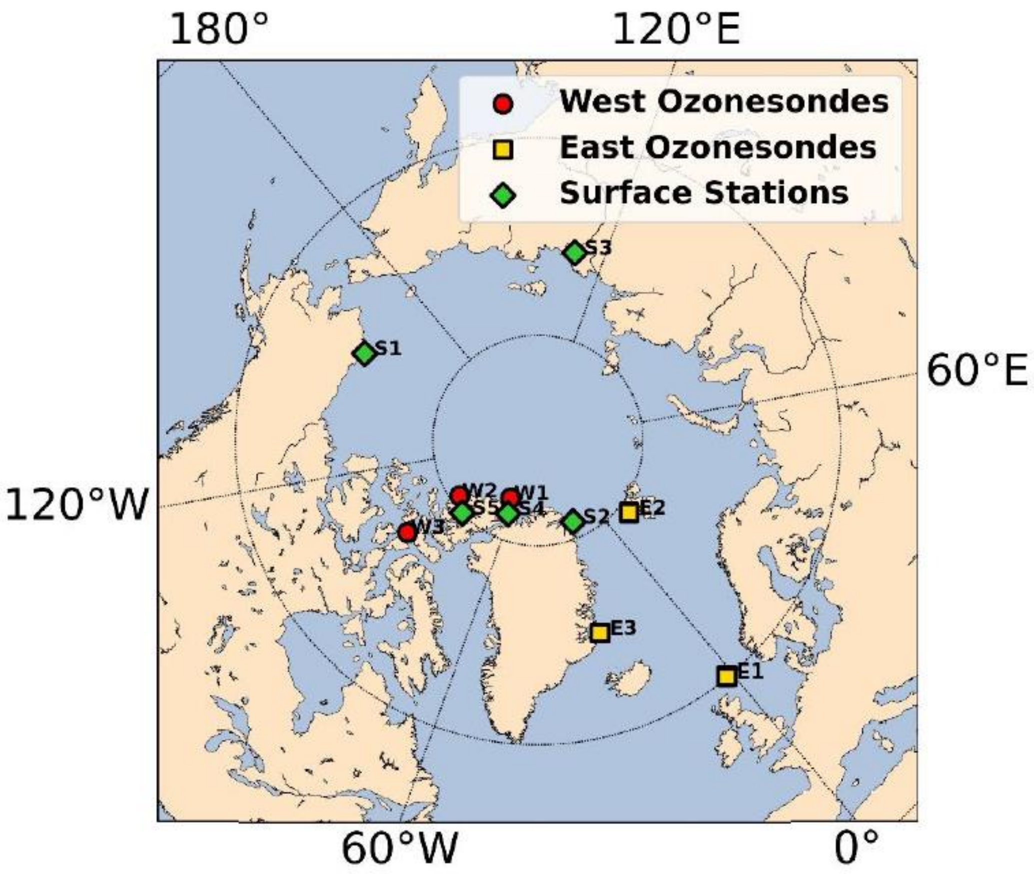

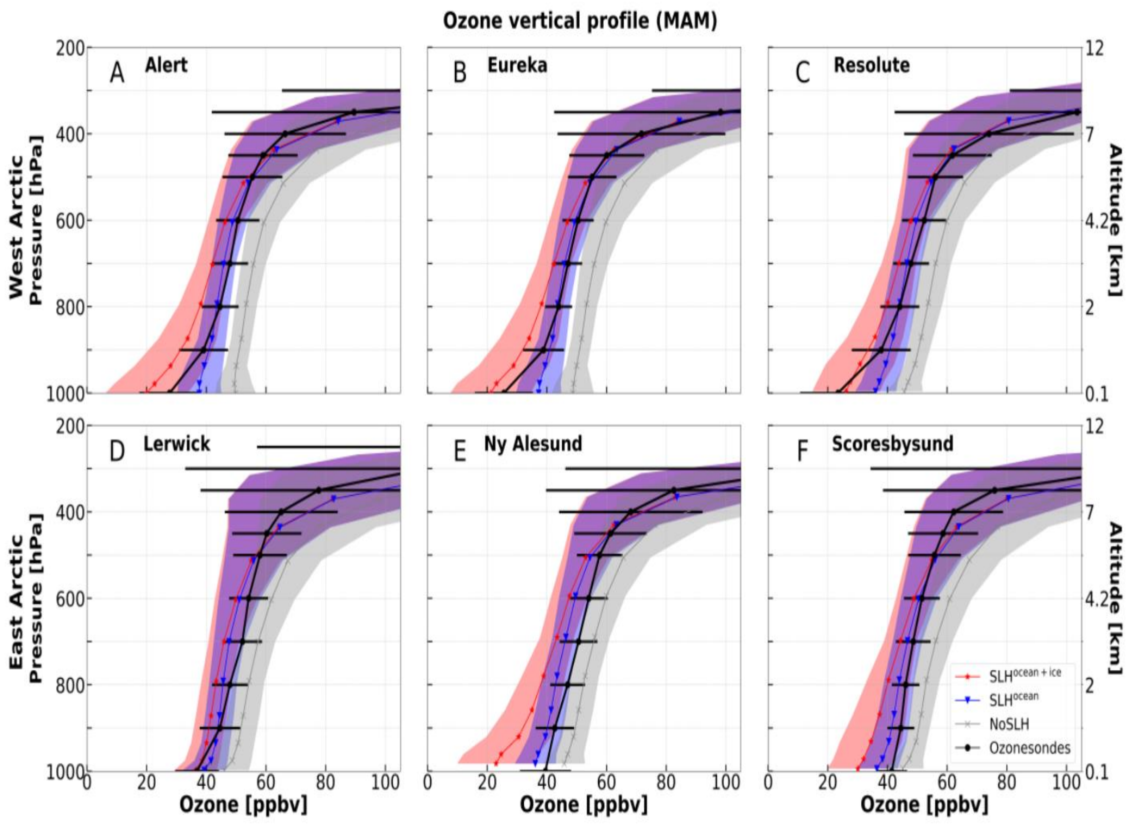

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