Very Short-Lived Halogen Chemistry in CESM1 (CAM-Chem)

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Chemistry Working Group, Boulder,
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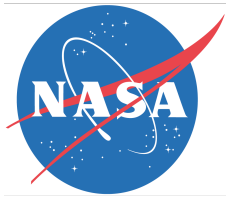


Outline

1. Update the Chemistry Working Group on the Status of VSL chemistry in CAM-Chem

2. Show some preliminary results on Pre-Industrial vs Present-Day simulations with VSL-I only, VSL-Br only, and VSL-ALL.

3. Future research plans.

CAM-Chem with VSL Chemistry

NCAR CESM CESM1 (CAM4-CHEM)

- Global Chemistry-Climate Model
- ~2.0° horizontal resolution
- Running with Specified Dynamics (from CC)

Lamarque et al., *Geosci. Mod. Dev.*, 2012

Tropospheric Halogen Chemistry

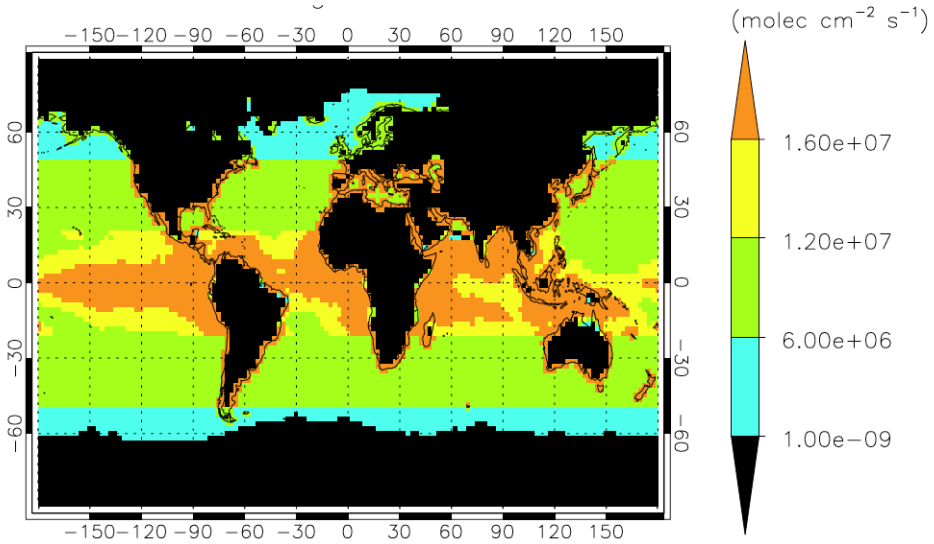
Halogenated sources from the ocean.

- Emissions following Chl-a over tropics
- Catalytic release from sea-salt (9 Rxns)
- Do NOT have polar emission processes

Chemical Processes

- TS1 chemical mechanism (CCMI code base)
- Additional Dry / wet deposition
- Include additional photochemistry (Cl, Br, and I)
- 14 Tropospheric heterogeneous reactions
- 17 Stratospheric heterogeneous reactions
- 9 Additional vsl Organic species included.
- 243 species, 658 photo, thermal, het reactions

$CHBr_3$ Flux in CAM-Chem



Source gas	Global annual flux (Gg yr^{-1})		Lifetime (this study)
	This study	Literature	
$CHBr_3$	533	400[a], 595[b], 448[d]	17 days
CH_2Br_2	67.3	113[c], 62[d]	130 days
CH_2BrCl	10.0	6.8[c]	145 days
$CHBr_2Cl$	19.7	23[c]	56 days
$CHBrCl_2$	22.6	16[c]	46 days
CH_3Br*	climatology	131[c]	1.6 yr[g]
CH_3I**	303	304[e]	5 days
CH_2ICl	234	236[f]	8 h
CH_2IBr	87.3	87[f]	2.5 h
CH_2I_2	116	116[f]	7 min

Total Bromine: 632 Gg Br yr^{-1}
Total Iodine: 600 Gg I yr^{-1}

Ordoñez et al., ACP, 2012; Saiz-Lopez et al., ACP, 2012.

Halogen Chemistry Details

Sea-Salt Aerosol Chemistry,
Production inorganic
X = Cl, Br, or I

$HOX + X^- + H^+ \Rightarrow XY + H_2O$

Ozone Iodine Feedback
Production of I_2, HOI

Flux I_2, HOI is a f{O_3, SST, wind speed}
(Carpenter et al., 2013)

Nitryl Chloride ($ClNO_2$),
Production of Cly

$NO + O_3 \Rightarrow NO_2 + O_2$
$NO_2 + O_3 \Rightarrow NO_3 + O_2$
$NO_3 + NO_2 + M \Rightarrow N_2O_5 + M$
$N_2O_5 + Cl^- \Rightarrow$ particle $\Rightarrow ClNO_2 + NO_3^-$
$ClNO_2 + hv \Rightarrow Cl + NO_2$

Coupled Halogen Chemistry
Increase OddOx Loss?

X = Cl, Br, or I free radicals

$X + O_3 \Rightarrow XO + O_2$
$Y + O_3 \Rightarrow YO + O_2$
$XO + YO \Rightarrow X + Y + O_2$
net: $2O_3 \Rightarrow 3O_2$

Role of NO_x
More OddOx Loss or More Washout?

X = Cl, Br, or I free radicals

$X + O_3 \Rightarrow XO + O_2$
$XO + NO_2 \Rightarrow XONO_2$
$XONO_2 + h\nu \Rightarrow X + NO_3$
$NO_3 + h\nu \Rightarrow NO + O_2$
$NO + O_3 \Rightarrow NO_2 + O_2$
net: $2O_3 \Rightarrow 3O_2$

VSL Scenarios (PI, PD)

Simulation Name	Long-Lived Br, Cl	VSL Br	VSL I
REF	Yes	No	No
VSL_Br	Yes	Yes	No
VSL_I	Yes	No	Yes
VSL_ALL	Yes	Yes	Yes

- All simulations use the same meteorology (from a PD CAM4-Chem sim).
- Anthropogenic emissions have been zeroed for PI conditions.
- NMHC emissions have been reduced by 90% for PI conditions.

Next Two Slides will show PI vs PD species.

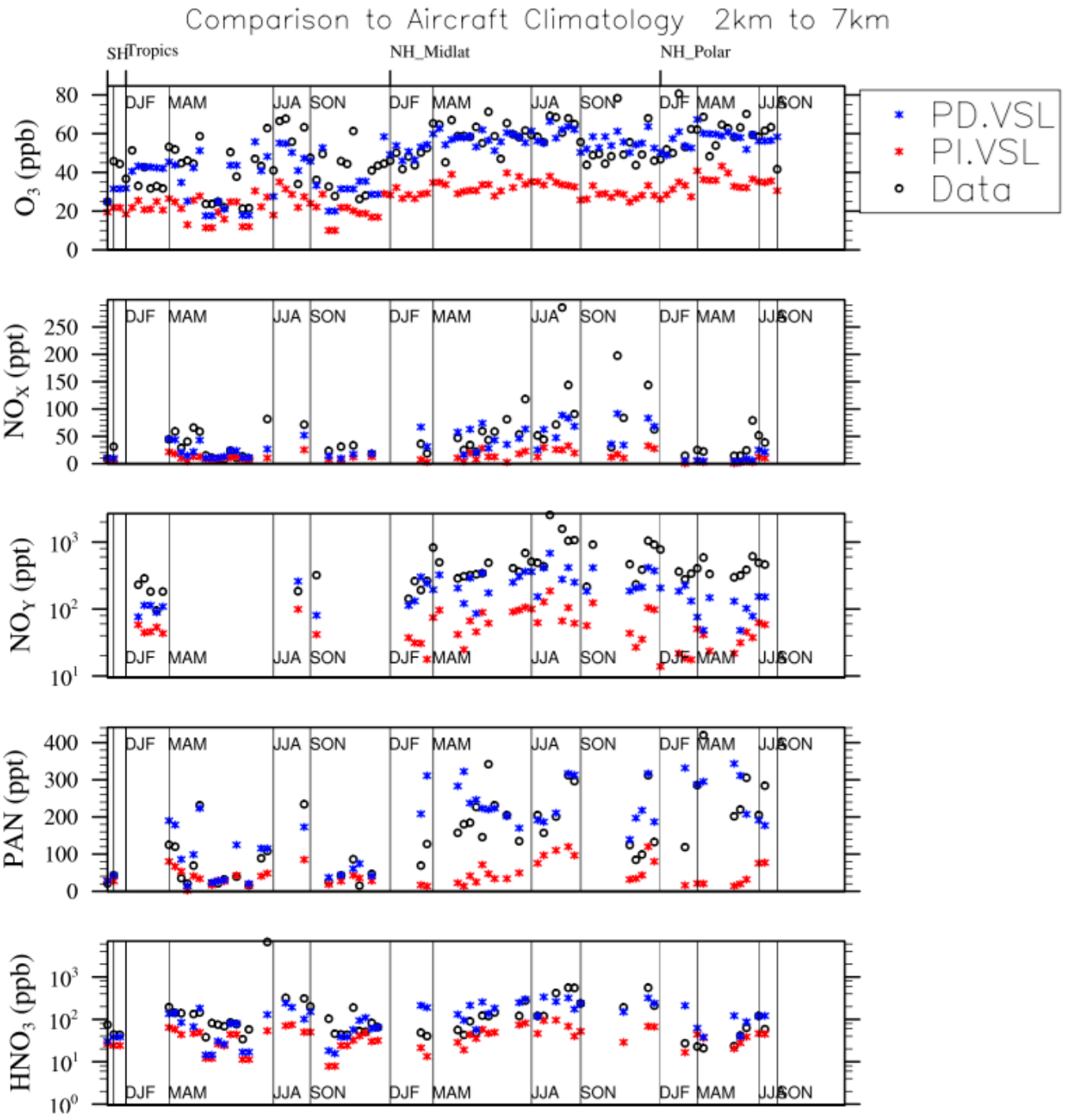


Figure courtesy of Simone Tilmes, NCAR

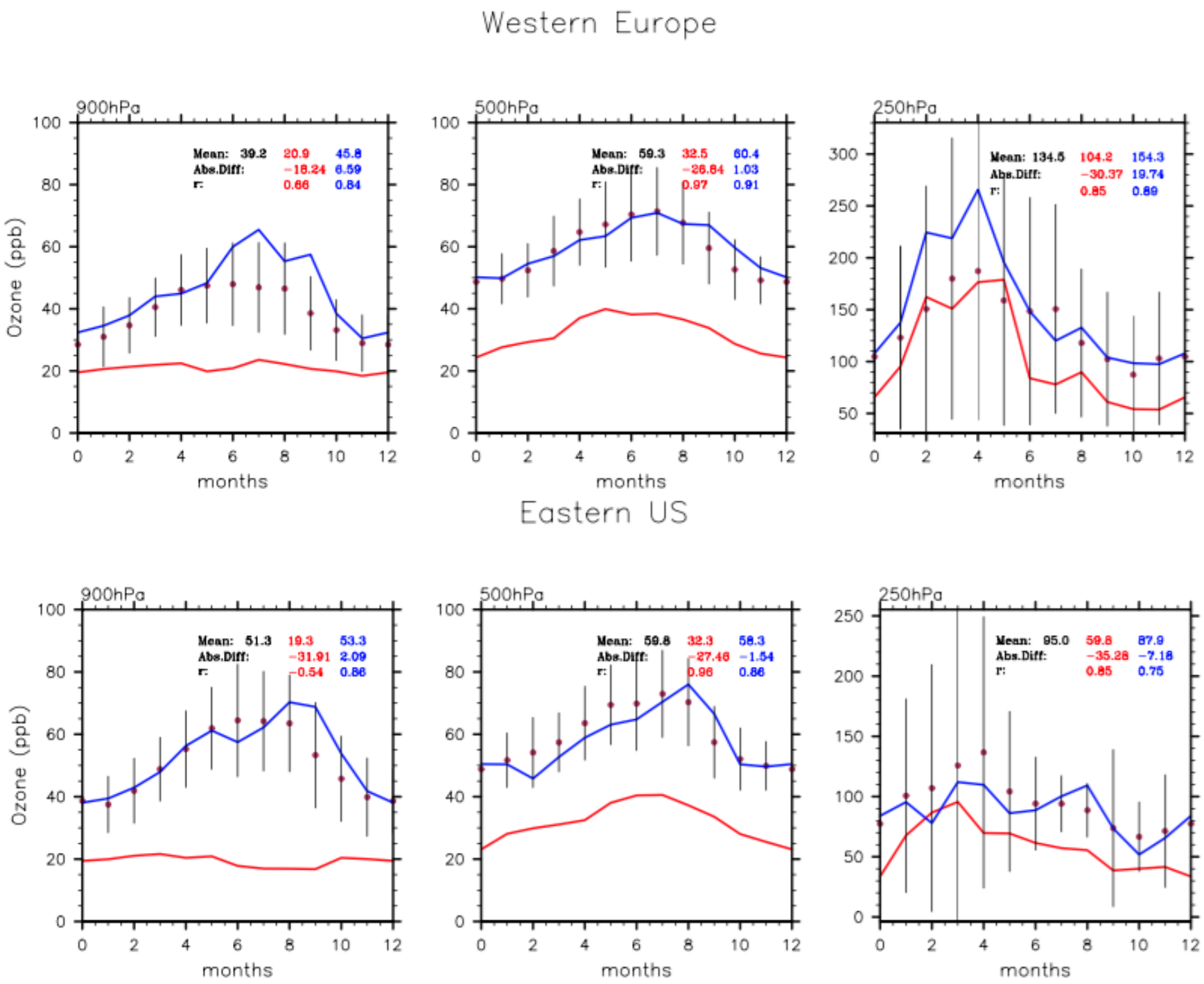


Figure courtesy of Simone Tilmes, NCAR

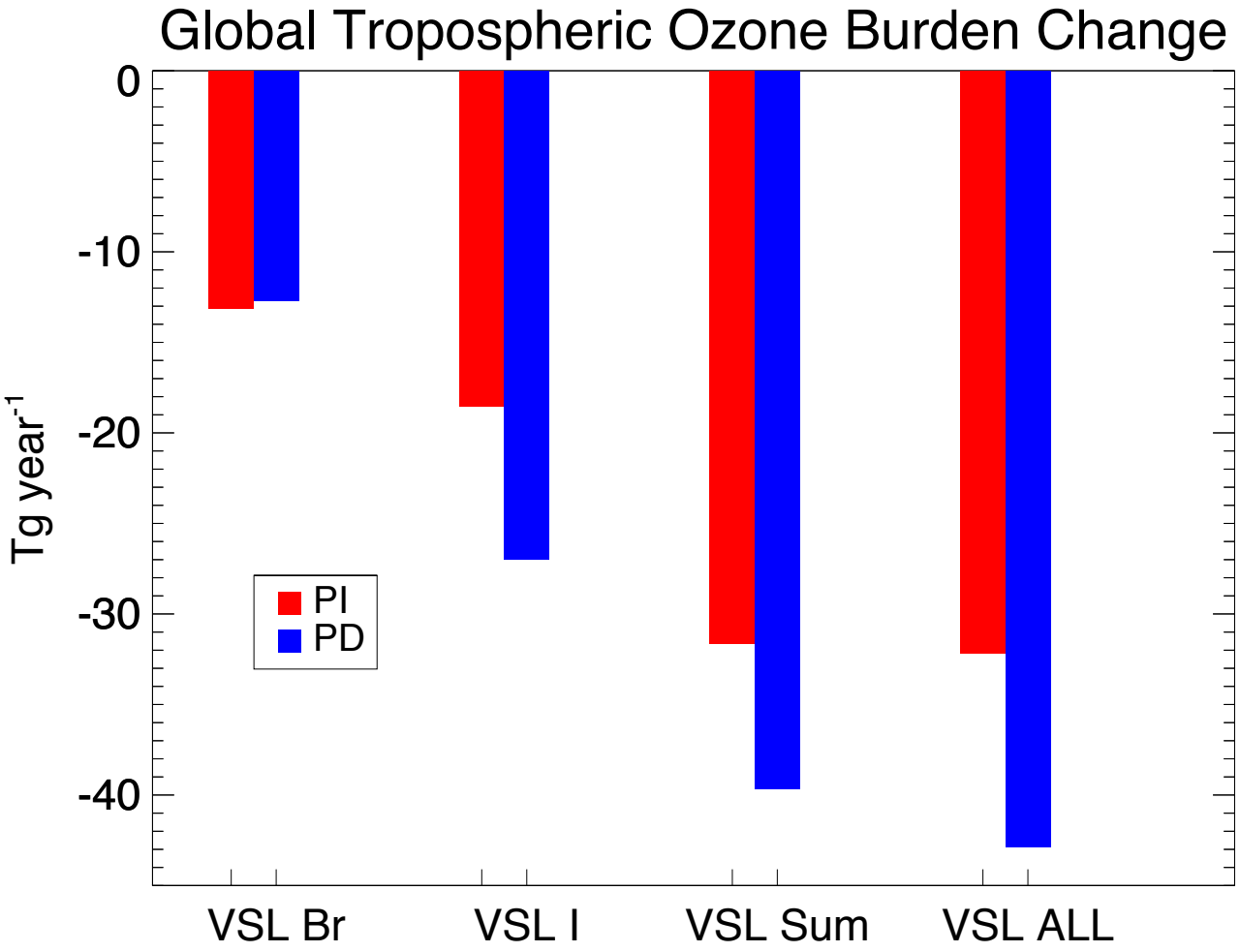
Global Tropospheric Ozone Burdens PI-PD

Simulation Name	Absolute Tg/yr Present-day	Absolute Tg/yr Pre-Industrial	Absolute Tg/yr PD-PI
REF	349	232	117
VSL_Br	336	218	118
VSL_I	322	213	109
VSL_ALL	306	199	107

Note: The tropopause was defined where O_3 is LE 150 hPa (top down). This definition was used from one simulation (PI-REF) for all simulations.

Conclusion: Including VSL chemistry reduces the change in ozone from PI to Pd by 8.5%, therefore the PI to PD radiative forcing will be less when VSL chemistry is included.

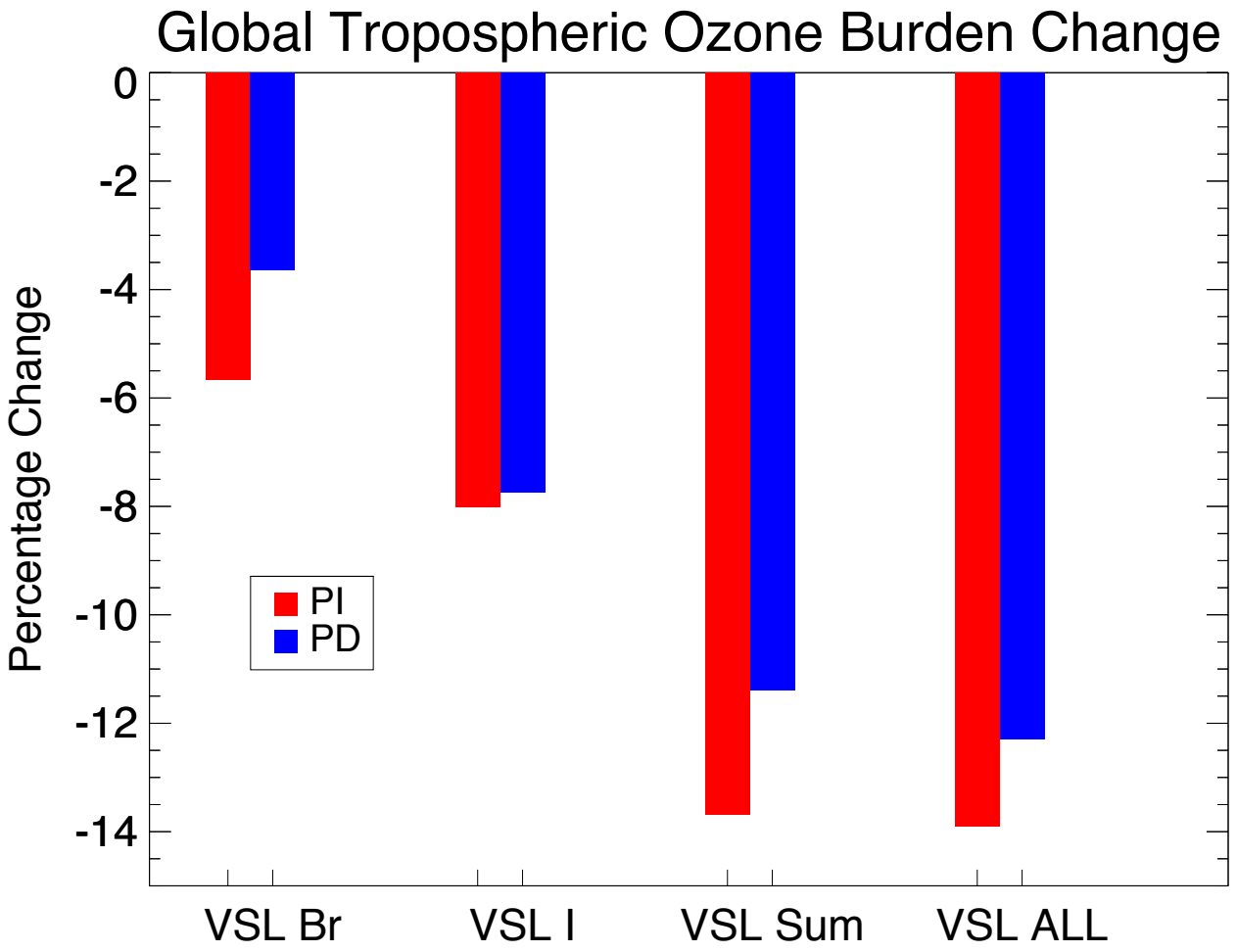
How Linear is the Ozone Change (i.e., does VSL-Br+VSL-I = VSL-ALL)?



Conclusion:

- In PD the total tropospheric burden is less for [VSL-I + VSL-Br] vs VSL-ALL .
- This is not true for the PI period, where [VSL-I + VSL-Br] vs VSL-ALL are equal.

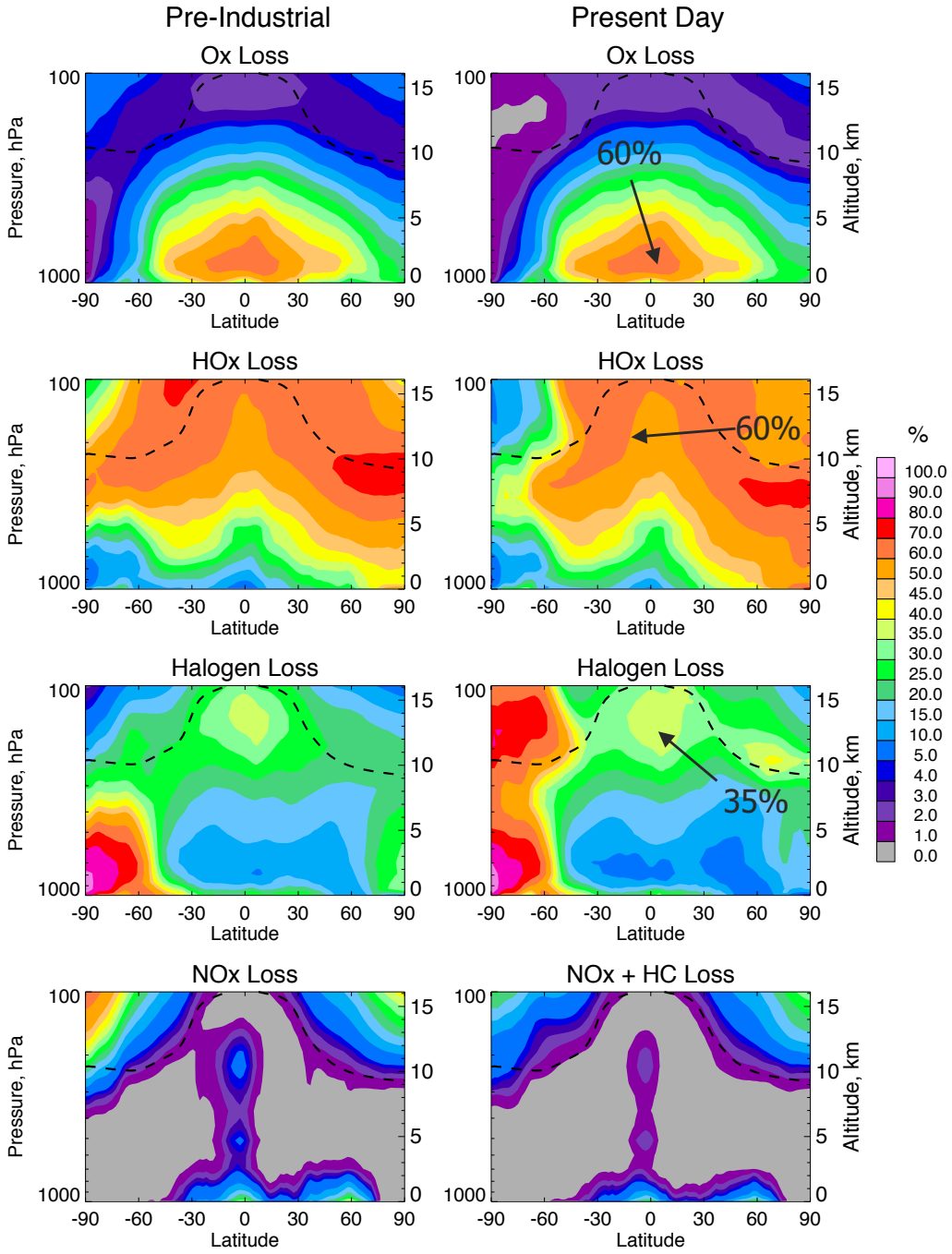
What is the Percentage Change?



Conclusions:

- VSL Bromine is 5.75% and 3.75% for PI and PD respectively.
- VSL Iodine is essentially the same in PI and PD at ~8%.
- VSL ALL is 14% and 11.75% for PI and PD respectively.
- The PI period is more sensitive to VSL chemistry.

OddOx Loss Partitioning (%) *** VSL-ALL



All results are annual average.

OddOx loss Definition (Brasseur and Solomon, 2005):

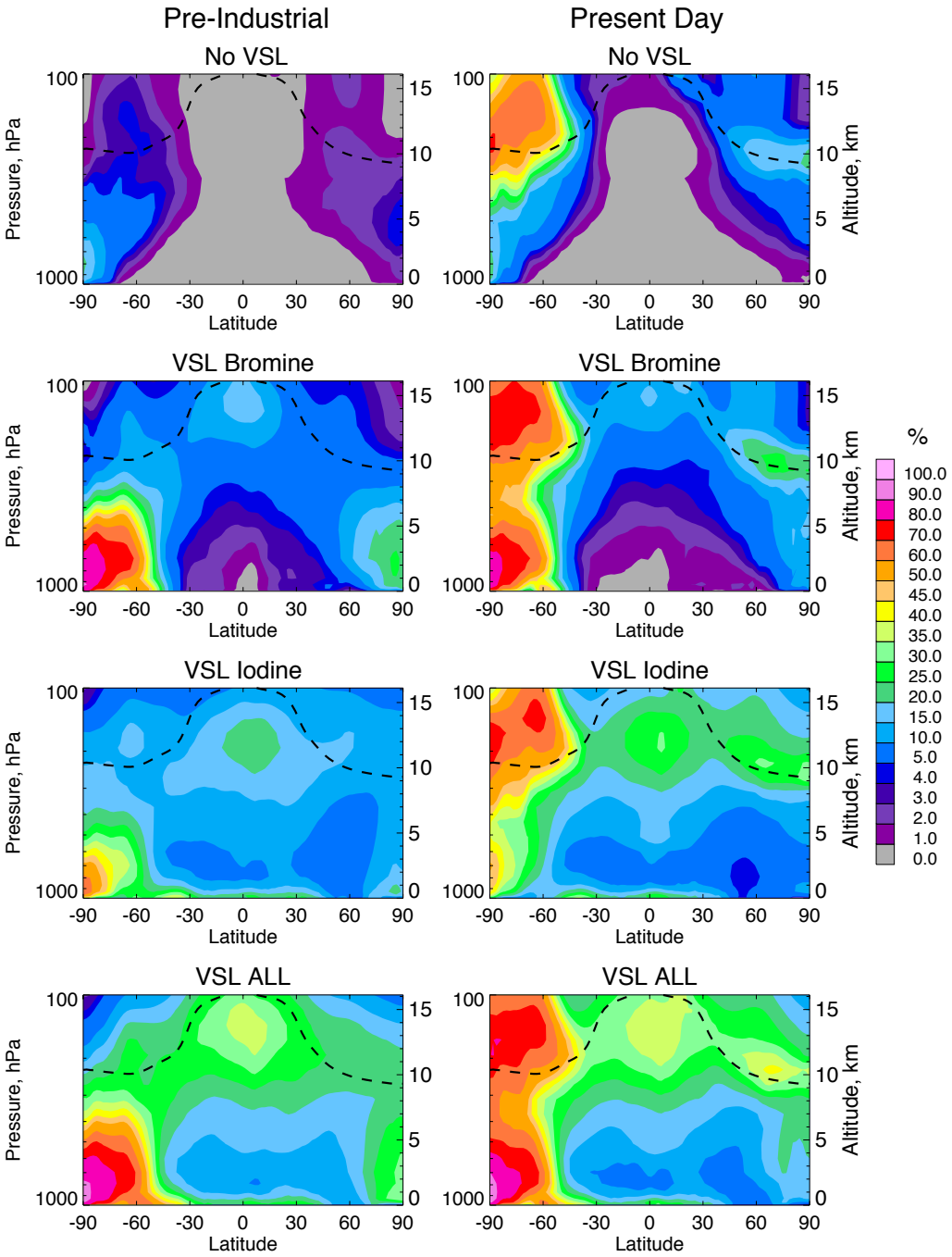
Ox Loss = $2k[O][O_3] + k[O^1D][H_2O]$

HOx Loss = $k[HO_2][O] + k[HO_2][O_3] + k[OH][O] + k[OH][O_3] + k[H][O_3]$

Halogen_Loss = $2k[ClO][O] + 2j[Cl_2O_2] + 2k[ClO][ClO] + 2k[BrO][ClO] + 2k[BrO][BrO] + 2k[BrO][O] + k[ClO][HO_2] + 2k[BrO][HO_2] + 2k[IO][O] + 2j[OIO] + 2k[IO][BrO] + 2k[IO][ClO] + k[IO][HO_2]$

NOx+HC_Loss = $2k[NO_2][O] + 2j[NO_3] + k[C_3H_6][O_3] + .9k[ISOP][O_3] + k[C_2H_4][O_3] + .8k[MVK][O_3] + 0.8k[MACR][O_3] + k[APIN][O_3] + k[BPIN][O_3] + k[LIMON][O_3] + k[MYRC][O_3] + k[BCARY][O_3]$

OddOx Halogen Loss (%)



All results are annual average.

REF: Without VSL chemistry halogen loss in the troposphere is not important, except at high latitudes from transport of BrOy from the stratosphere.

VSL-Br: only has impacts at high latitudes where SSA emissions are important and the UT where breakdown of organics are important.

VSL-I: only is the most important halogen depletion family. Maximum of 30% of the total OddOx loss in the UT.

VSL-All: Halogens are responsible for 5-35% of the local Odd Oxygen Loss!

Conclusions

- We have examined the impact of VSL Bromine and Iodine on Ozone in a Pre-industrial and Present-day model atmopshere.
- Halogens are responsible for 5-35% of the local total Odd Oxygen Loss!
- VSL-Br has impacts at high latitudes where SSA emissions are important and the UT where breakdown of organics are important.
- VSL-I is the most important halogen depletion family. Maximum of 30% of the total OddOx loss in the UT.
- Including VSL chemistry reduces the change in ozone from PI to Pd by 8.5%, therefore the PI to PD radiative forcing will be less when VSL chemistry is included.

Next Step

- Create a "Dynamic Emission" inventory (i.e., obtaining Chl-a for each year instead of climatological average distribution).
- Move VSL code base to CESM2.
- Run past aircraft campaign periods at high horizontal resolution.

Campaign	Date	Location	Aircraft	# of Flights	Whole Air Sampler	# of samples
SEAC4RS	Aug-Sept, 2013	Houston, TX	NASA ER-2	21	U. of Miami: E. Atlas	545
			NASA DC-8	18	U. of Calif, Irvine: D. Blake	~2800
CONTRAST	Jan-Feb, 2014	Guam	NSF/NCAR GV	16	AWAS: U. of Miami, E. Atlas	718
ATTREX	Jan-Feb, 2014	Guam	NASA Global Hawk	8	GWAS: U. of Miami, E. Atlas	676

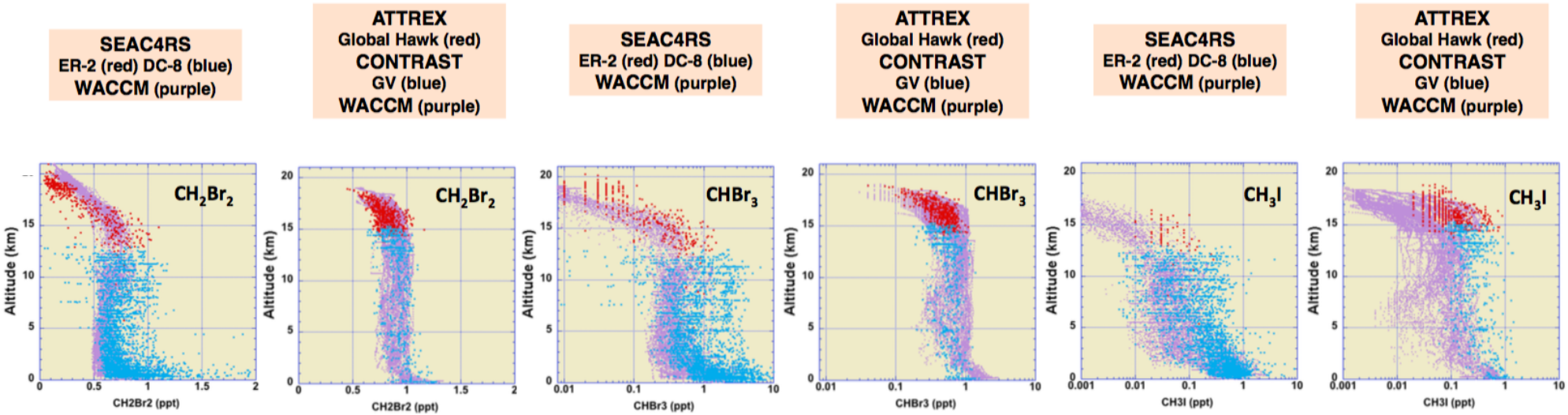


Figure courtesy of Sue Schauffler, Elliot Atlas, et al., AGU 2016.

Planned Missions to Examine.

Table 1: Select aircraft field campaigns that included organic and/or inorganic halogen data.

Field Campaign	Aircraft	Location	Date / Season
NASA Costa Rica AVE	WB-57	Houston/Costa Rica	2006, Winter
NASA TC4	WB-57	Houston/Costa Rica	2007, Summer
NASA ARCTAS	DC8	Alaska	2008, Summer
NSF HIPPO 1	GV	Pacific, Pole-to-Pole	2009, Winter
NSF HIPPO 2	GV	Pacific, Pole-to-Pole	2009, Fall
NSF HIPPO 3	GV	Pacific, Pole-to-Pole	2010, Spring
NSF HIPPO 4	GV	Pacific, Pole-to-Pole	2011, NH Spring/Summer
NSF HIPPO 5	GV	Pacific, Pole-to-Pole	2011, NH Summer/Fall
NSF TORERO	GV	Eastern Pacific	2012, Winter
NASA SEAC4RS	DC-8, ER-2	Western/Central/SE US	2013, Summer
NSF CONTRAST	GV/GH	Western Pacific	2014, Winter
NSF ORCAS	GV	Antarctic	2016, Summer
NASA Atom	DC8	Global	2016, Forward

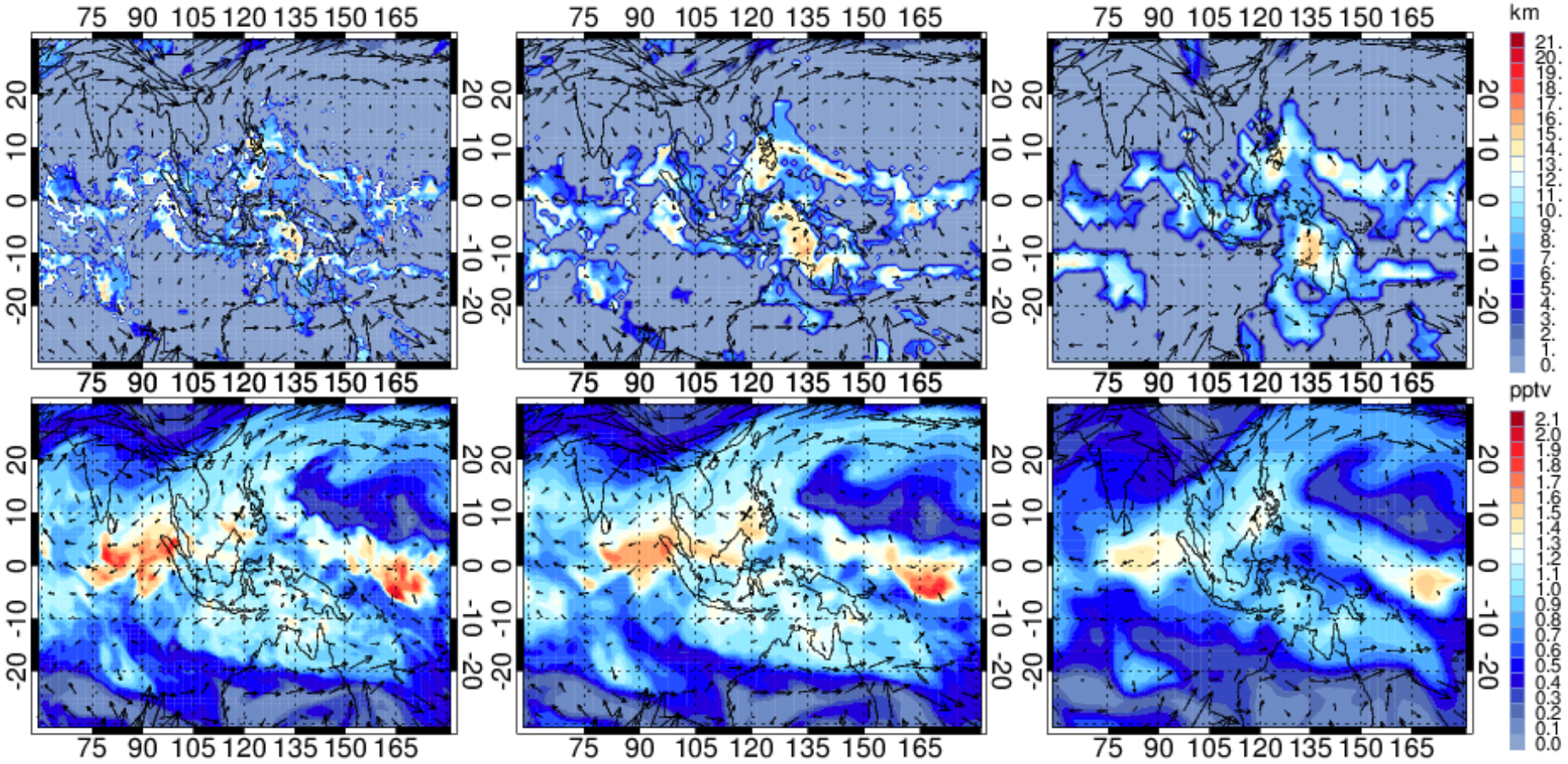
Results will be made available to atmospheric community.

Simulations will be done at ½ degree horizontal resolution.

Impact of Horizontal Resolution on Organic VSL Distributions

Jan 12, 2014

Cloud Top Height top row



Bromoform bottom row

Extra Slide

Oceanic Production of I_2 and HOI is a function of O3, SST, wind speed.

$$\mathrm{ISG} = \mathrm{Flux}(\mathrm{HOI}) + 2 \times \mathrm{Flux}(\mathrm{I_2}), \quad (1)$$

where

$$\mathrm{Flux}(\mathrm{HOI}) = [\mathrm{O_3}] \times \left(4.15 \times 10^5 \times \left(\frac{\sqrt{[\mathrm{I^-_{aq}}]}}{w}\right) - \left(\frac{20.6}{w}\right) - 23\,600 \times \sqrt{[\mathrm{I^-_{aq}}]}\right) \quad (2)$$

$$\mathrm{Flux}(\mathrm{I_2}) = [\mathrm{O_3}] \times [\mathrm{I^-_{aq}}]^{1.3} \times \left(1.74 \times 10^9 - \left(6.54 \times 10^8 \times \ln w\right)\right), \quad (3)$$

with w being the wind speed ($\mathrm{m\,s^{-1}}$), $[\mathrm{O_3}]$ the surface ozone mixing ratio ($\mathrm{nmol\,mol^{-1}}$) and $[\mathrm{I^-_{aq}}]$ the concentration of aqueous iodide ($\mathrm{mol\,dm^{-3}}$) (Carpenter et al., 2013). Based on the work of MacDonald et al. (2014), the sea surface temperature (SST, K) was used as a proxy for describing $[\mathrm{I^-_{aq}}]$:

$$[\mathrm{I^-_{aq}}] = 1.46 \times 10^6 \times \exp\left(\frac{-9134}{\mathrm{SST}}\right). \quad (4)$$

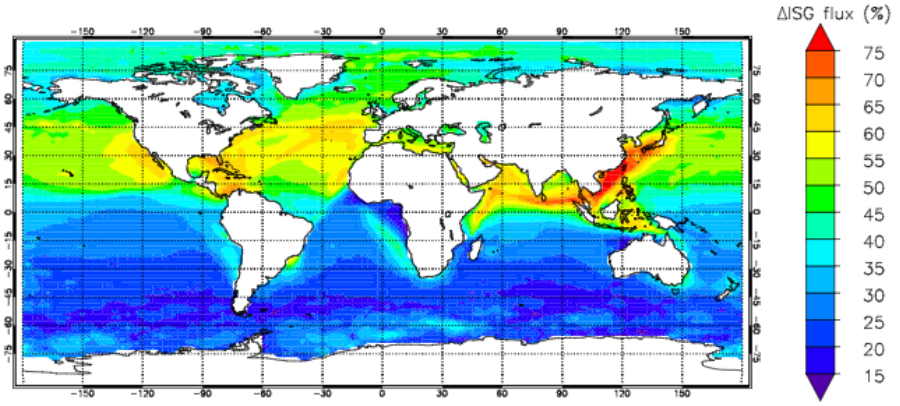


Figure 4. Anthropogenic influence upon the oceanic emission of inorganic iodine. The figure presents the percentage change of the ISG fluxes since pre-industrial times. The annual oceanic flux of ISG for the PD run is shown in Fig. 2.