Survey of accumulation mode particulate halogens (I, Br, ClO_4^-) over the remote atmosphere

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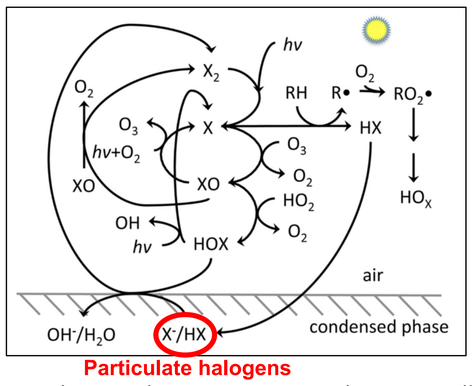
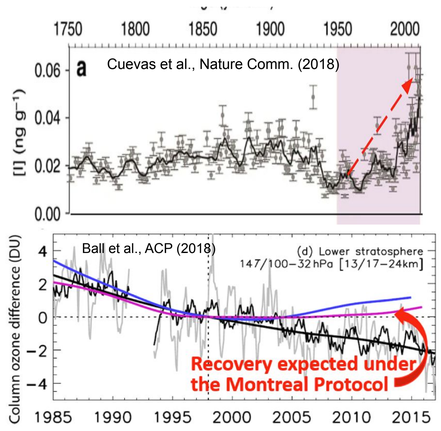
Introduction and backgrounds

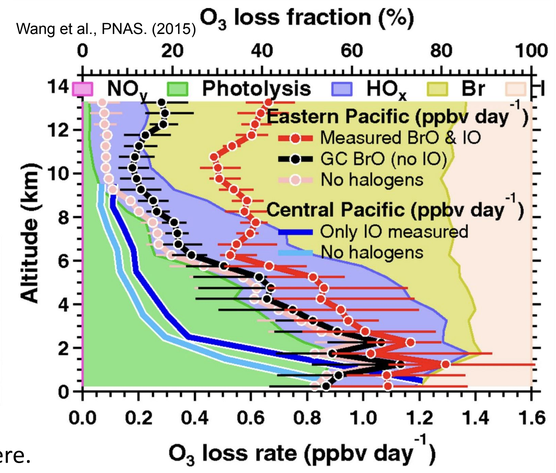
Simpson et al., Chem. Rev. (2015)



Particulate halogens



Wang et al., PNAS. (2015)



- Halogens play an important role in controlling oxidation capacity in remote atmosphere.
- Bromine oxidizes atmosphere mercury and causes ozone depletion events. Also play important roles in tropospheric O_3 destruction.
- Atmospheric iodine has been increasing rapidly recently, potentially destroying stratospheric ozone (Koenig et al., 2020).
- Particle phase halogens are important for their roles as halogen reservoir and as medium for important heterogeneous reactions.
- Abundance of particle phase halogen measurements are highly unknown due to lack of measurements.

Take home messages

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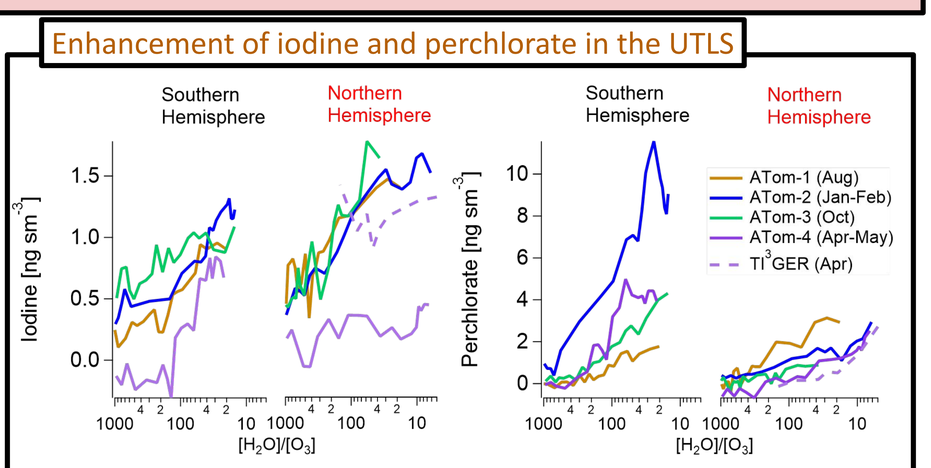
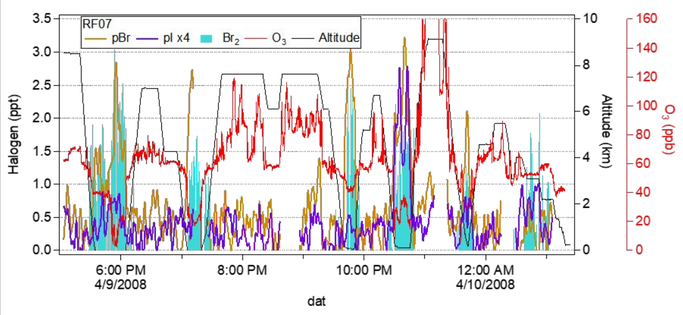
- **Quantitative** global distribution of particulate halogens by AMS.
- Most **I** was **iodate**, most **Br** was **bromide**.
- More halogens observed in **biomass burning** (Atlantic) and **polluted** (Pacific) plumes.
- **Elevated I and ClO_4^- in the UTLS** indicate gas to particle partitioning of I and stratospheric source of ClO_4^-.
- PM_1 **I** and **Br** increased in **the Arctic** concurrently with O_3 depletion & Hg^0 oxidation. **10-50% of total soluble Br was Br^-**.
- AMS and filter Br measurements agree.

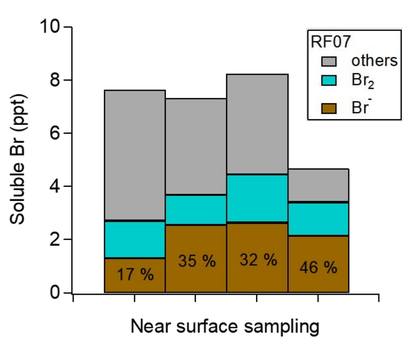
Enhancement of iodine and perchlorate in the UTLS

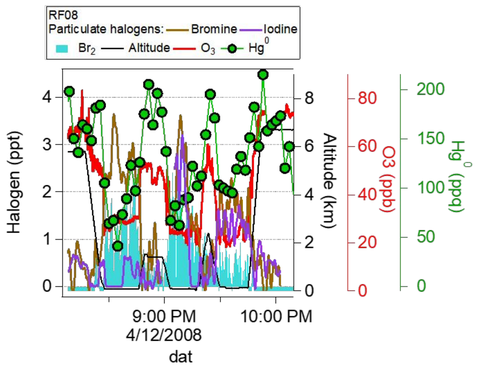


- H_2O/O_3 ratio is lower (toward right on the graphs) closer to the stratosphere.
- Gas to particle partitioning of iodine (Koenig et al., PNAS, 2020). Mostly iodate.
- Particle phase iodide directly react ozone. Iodate can be reduced to iodide.
- Perchlorate likely has stratospheric sources.

Particulate halogens in the Arctic

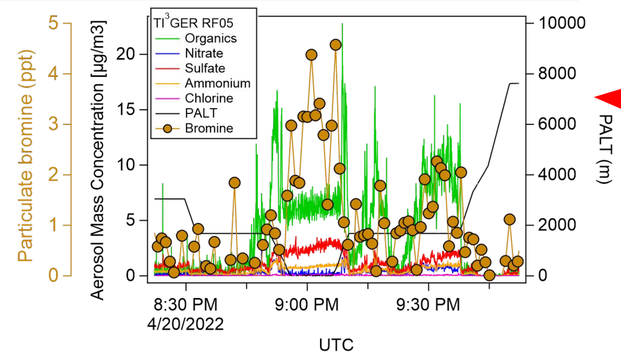




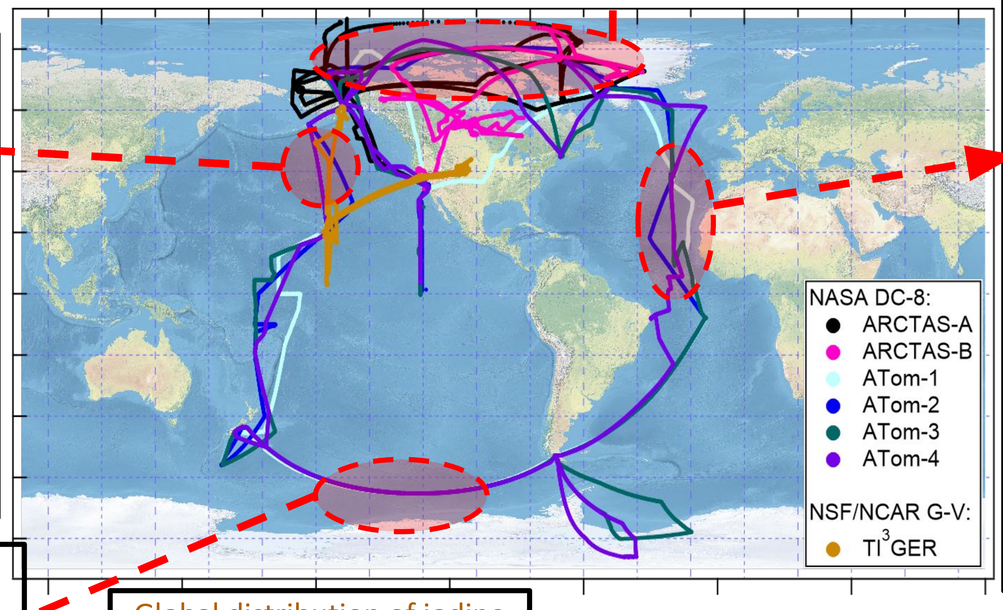


- Hg^0 oxidation & ozone depletion over ice
- Enhancement of particulate & gas phase bromine. Particulate iodine as well.
- Concentration of particulate bromine is comparable to that of Br_2 (g). Bromide constitute 10-50% of soluble bromine.
- The measured particulate bromine is mostly bromide and expected to have fast cycling between gas phase bromines.

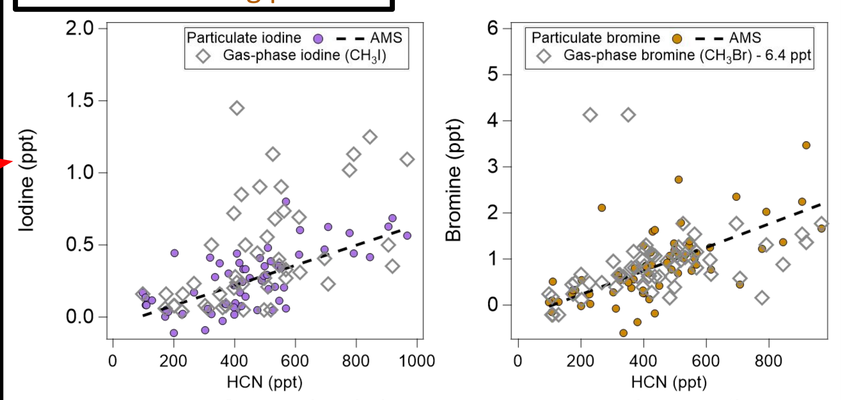
Bromine in a transported polluted plume



- Transportation of the primary emission and/or secondary production from sea spray aerosols over the Ocean.
- Abundance of pBr was as high as Arctic surface.

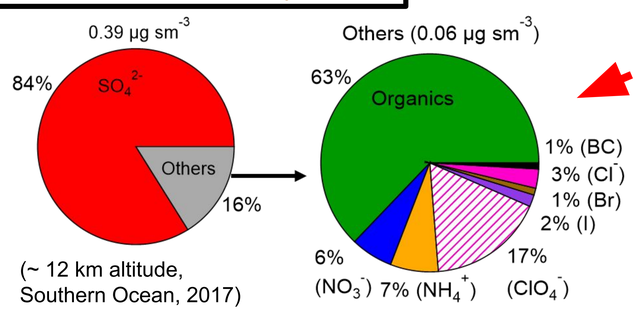


Biomass burning plumes

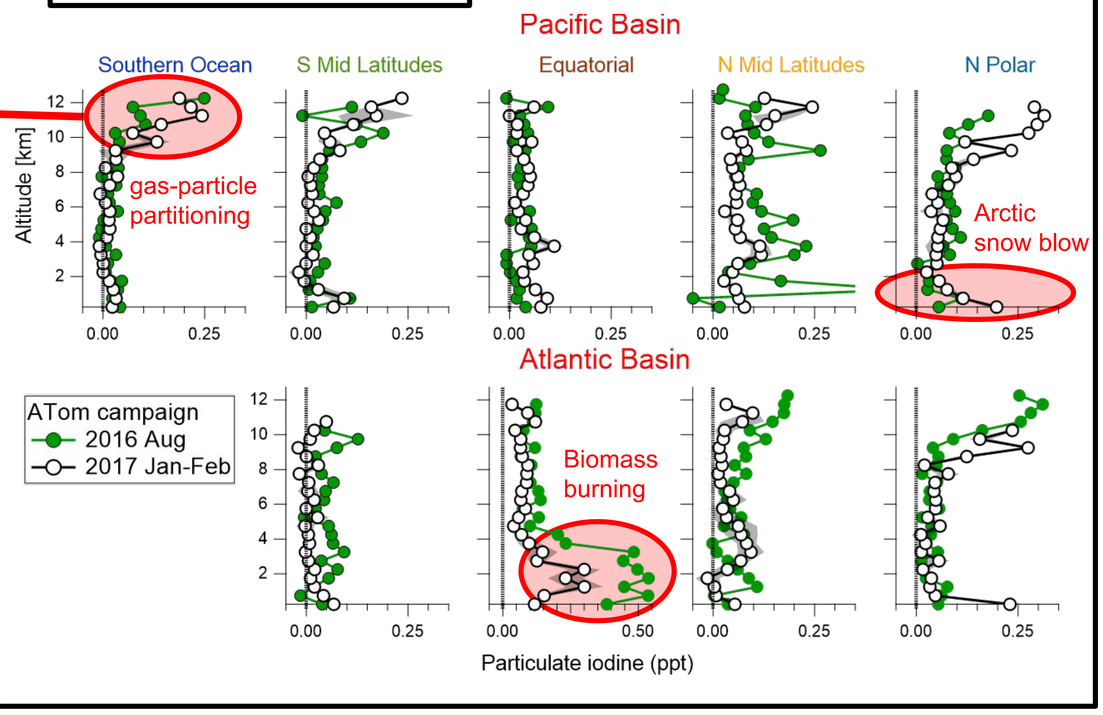


- Concentration of particulate halogens were proportional to HCN (biomass burning tracer) over the Atlantic Ocean due to influence from wirefire from Africa.
- Emission of methyl halides from wildfires were previously identified.
- The concentration of particulate halogens were comparable to the concentration of methyl halide.

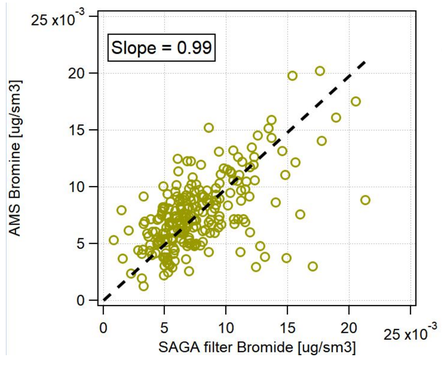
Aerosol Chemical Composition



Global distribution of iodine

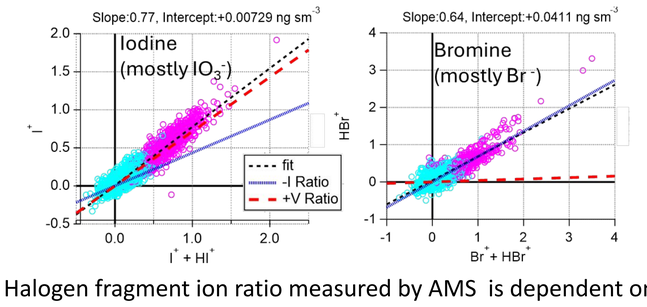


Measurement intercomparison



- Particulate bromine measurement by AMS and filter based method agreed well. (the comparison was made from urban air plumes during KORUS-AQ

Halogen oxidation state



- Halogen fragment ion ratio measured by AMS is dependent on the halogen oxidation state.
- Over the remote atmosphere, most of particulate iodine is iodate (IO_3^-) and most particulate bromine is bromide (Br^-).

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References

Cuevas et al., Nature Comm. (2018), Ball et al., ACP (2018), Wang et al., PNAS. (2015), Koenig et al., PNAS (2020), Schill et al., ACPD (2024)