Quantification of anthropogenic and pyrogenic particulate bromine by an Aerodyne aerosol mass spectrometer (AMS)

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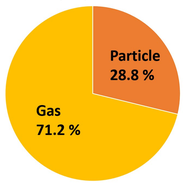
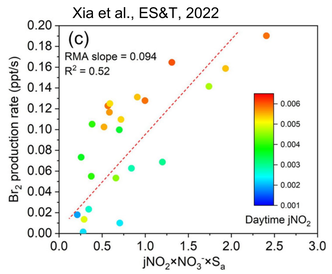
Introduction and background

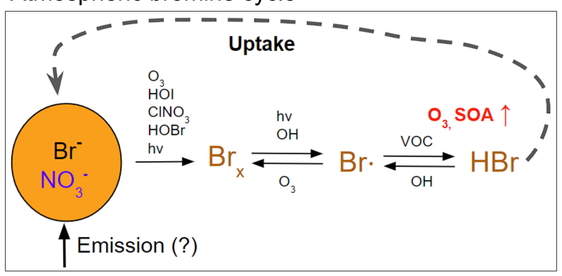
Wang et al., 2021, ACP)
In the troposphere



Xia et al., ES&T, 2022

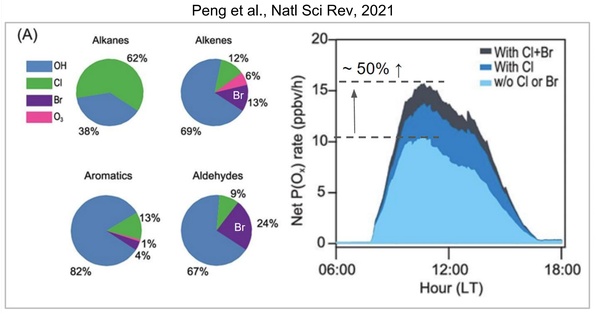


Atmospheric bromine cycle

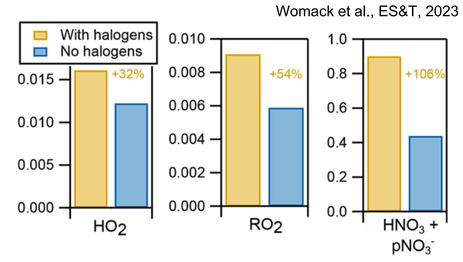


- Troposphere: ~ 30% of bromine is thought to be in particle phase (GEOS-Chem, Wang et al., 2021)
- Bromide is recycled to gas phase by various heterogeneous reactions and by photolysis of nitrate.
- Reactive Br_2 gas forms Br· radical oxidizing VOCs in the atmosphere thereby enhancing O_3 and leading to secondary organic aerosol (SOA).
- HBr partitions preferentially into particle phase (pKa = -9.0), similar to sulfuric acid.

Peng et al., Natl Sci Rev, 2021



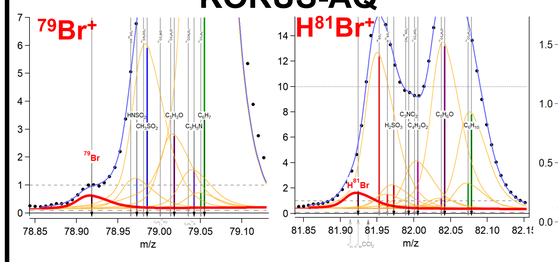
Womack et al., ES&T, 2023



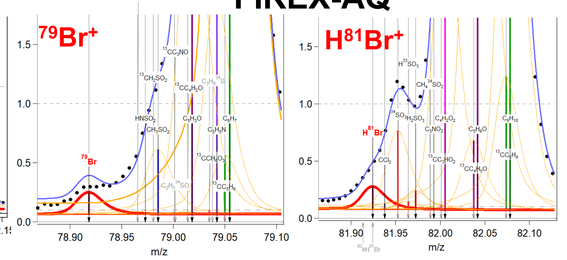
- Halogen radicals oxidize VOCs. Bromine radical reacts efficiently with aldehydes and alkenes while chlorine radical reacts more efficiently with alkanes.
- Bromine radical contributed ~ 15% increase to the O_3 production near coal burning site (Peng et al. 2021)
- Emission of bromine gas leads to nitrate production

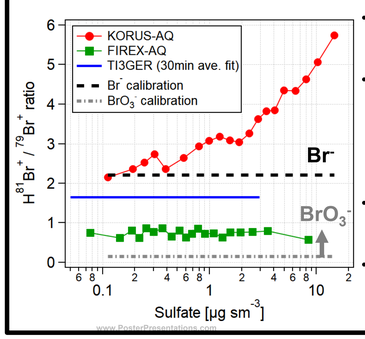
Quantification Method

KORUS-AQ



FIREX-AQ





- $^{79}Br^+$ and $H^{81}Br^+$ are the main ions from particulate bromine (both bromide and bromate) with minimum interference from other ions.
- For KORUS-AQ, $H^{81}Br^+$ has too much interference with sulfate during urban sampling. Thus, $^{79}Br^+$ was used for bromine quantification since it was reasonably well separated from adjacent ions.
- For FIREX-AQ, $H^{81}Br^+$ was used since it had less sulfate interference while $^{79}Br^+$ fit was interfered by large organic ion tail.
- $H^{81}Br^+$/ $^{79}Br^+$ ratio was significantly affected by sulfate during KORUS-AQ.

Observation of Particulate Bromine (pBr)

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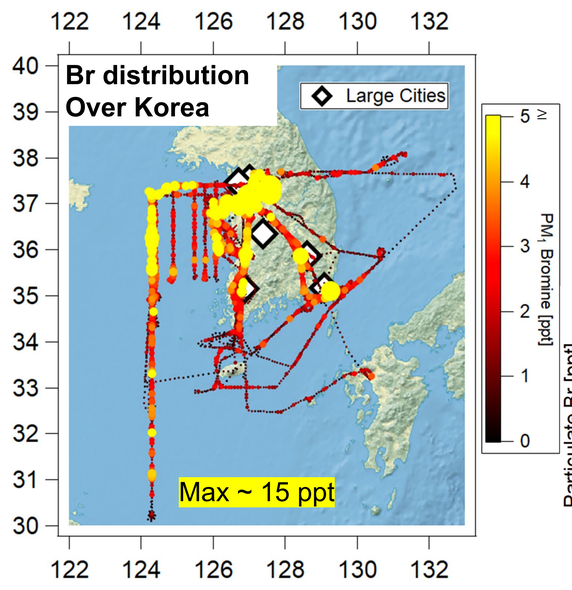
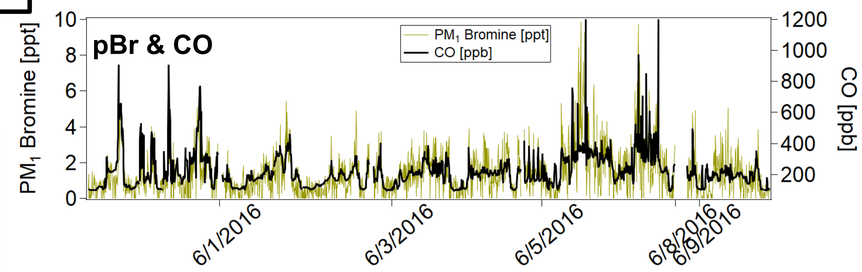
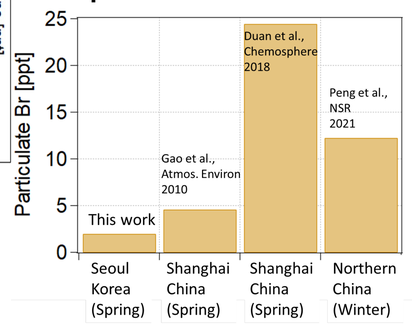
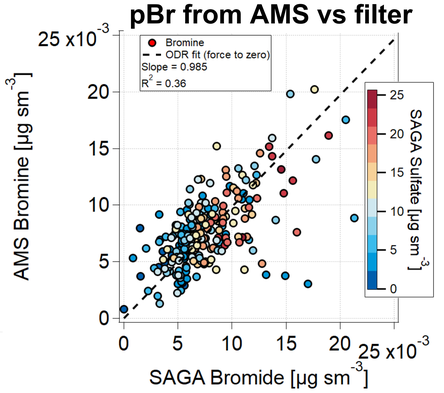




pBr in Korea vs China

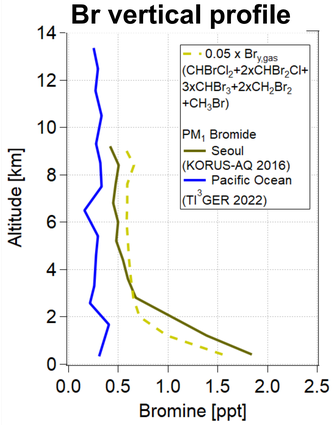


pBr from AMS vs filter

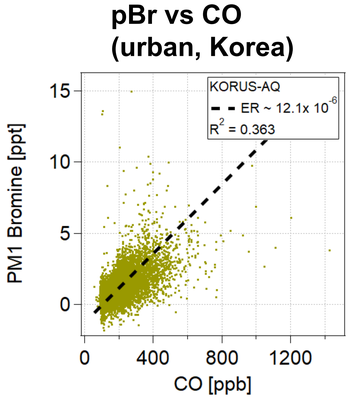


- Enhanced pBr was observed over large cities and plume transported from China.
- pBr enhancement tracks well with CO, suggesting the source of pBr is related to combustion activity (or general urban activities).
- Near surface pBr concentration over Seoul was 2-10 times lower than pBr measured in Shanghai in the same season (Spring)
- Independent filter-based bromide matched well with AMS bromine measurement.

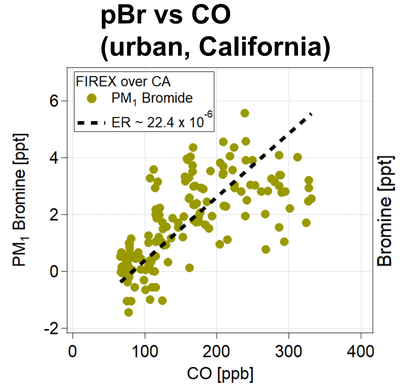
Br vertical profile

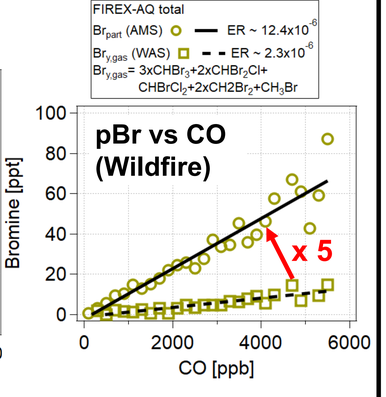


pBr vs CO (urban, Korea)



pBr vs CO (urban, California)





- During KORUS-AQ, gas-phase bromine concentrations were ~ 20 times higher than pBr. And pBr concentration in the free troposphere were ~ 2 times higher than that of remote Pacific Ocean measurement. Such enhancement in the free troposphere may have been impacted by Chinese emission.
- pBr/CO emission ratio (ER) over California was ~ 2 times higher than Korea.
- PBr/CO ER in fire plume was ~ 5 times higher than gas-phase Br/CO.
- Simple extrapolation of the ER gives annual 24 Gg Br (anthropogenic) and 14 Gg Br (pyrogenic) of pBr emission.
- Still, each source account for < 0.1 % of oceanic Br emission contributing small amount to the global Br budget.
- However, wildfires may inject bromine into the stratosphere potentially contributing to stratospheric Br budget.

Take home messages

- Bromine chemistry can be important for regional aerosol and O_3 formation.
- High-time resolution of non-refractory pBr measurement was demonstrated using AMS.
- Depending on the dominant ambient aerosols, different tracer ions may need to be used.
- AMS based pBr measurement agreed well width filter-based bromide measurement over Korea.
- In urban areas, gas-phase bromine is dominant. In fire plumes, particulate bromine is dominant.
- Estimated annual pBr emission: 24 Gg Br (anthropogenic) and 14 Gg Br (pyrogenic)
- Injection of wildfire-Br into the stratosphere merits further investigation.

Acknowledgements

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