Survey of accumulation mode particulate halogens (I, Br, ClO_{Λ}^{-}) over the remote atmosphere Dongwook Kim¹, Pedro Campuzano-Jost¹, Benjamin A. Nault^{2,3}, Douglas A. Day¹, Mike Cubison⁴, Jack Dibb³, Yuk Chun Chan⁴, Lyatt Jaegle⁴, Glenn Diskin⁵, Joshua DiGangi⁵, Chelsea Illan⁶, Jeff Peischl⁶ Thomas B. Ryerson⁶, Teresa Campos⁷, Alessandro Franchin⁷, Eric Apel⁷, Rebecca Hornbrook⁷, Alan Hills⁷, Barbara Barletta⁸, Donald Blake⁸, Greg Huey⁹, Lee Mauldin¹, Yandong Tong¹, Rainer Volkamer¹, and Jose L. Jimenez¹ 1. CIRES and Dept. of Chemistry, CU Boulder 2. Aerodyne Inc. 3. School of Engineering, JHU 3. TOFWERK 4. Dept. of Atmospheric and Climate Science, UW 5. NASA Langley 6. NOAA CSL 7. NCAR ACOM 8. Dept. of Chemistry, UCI, 9, Dept. of Atmospheric Sciences, GIT. Introduction and backgrounds Take home messages O₃ loss fraction (%) Simpson et al., Chem. Rev. (2015) **CONTACT:** dongwook.kim@colorado.edu, jose.jimenez@colorado.edu • Quantitative global distribution of particulate halogens by AMS. Eastern Pacific (ppbv day • Most I was iodate, most Br was bromide. More halogens observed in biomass burning (Atlantic) and entral Pacific (ppbv day polluted (Pacific) plumes. Elevated I and ClO_A in the UTLS indicate gas to particle partitioning of I and stratospheric source of ClO₄. • PM₁ I and Br increased in the Arctic concurrently with O₃ depletion & Hg⁰ oxidation. **10-50% of total soluble Br was Br**⁻. **Particulate halogens** O₃ loss rate (ppbv day) Halogens play an important role in controlling oxidation capacity in remote atmosphere. • AMS and filter Br measurements agree. • Bromine oxidizes atmosphere mercury and causes ozone depletion events. Also play important roles in tropospheric O₂ destruction. • Atmospheric iodine has been increasing rapidly recently, potentially destroying stratospheric ozone (Koenig et al., 2020). Enhancement of iodine and perchlorate in the UTLS • 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. Northern Southern Southern Northern Hemisphere Hemisphere Hemisphere Hemisphere Particulate halogens in the Arctic — ATom-1 (Aug) Particulate halogens: — Bromine — Iodine ATom-2 (Jan-Feb) Br₂ — Altitude — O₃ → Hg⁰ — ATom-3 (Oct) others - pBr - pl x4 ■ Br₂ - O₃ - Altitude — ATom-4 (Apr-May) ■ Br₂ TI³GER (Apr) ■ Br 100 ਉ $[H_2O]/[O_3]$ $[H_2O]/[O_3]$ 9:00 PM 10:00 PM • H₂O/O₃ ratio is lower (toward right on the graphs) closer to the stratosphere. Near surface sampling Hg⁰ oxidation & ozone depletion over ice • Gas to particle partitioning of iodine (Koenig et al., PNAS, 2020). Mostly iodate. • Enhancement of particulate & gas phase bromine. Particulate iodine as well. • Particle phase iodide directly react ozone. Iodate can be reduced to iodide. • Concentration of particulate bromine is comparable to that of Br₂ (g). Bromide constitute 10-50% of soluble bromine. Perchlorate likely has stratospheric sources. • The measured particulate bromine is mostly bromide and expected to have fast cycling between gas phase bromines. Biomass burning plumes Bromine in a transported polluted plume Particulate bromine - - AMS Particulate iodine - - AMS Gas-phase iodine (CH₃I) 10000 Organics - 8000 — PALT 6000 Bromine 4000 NASA DC-8: ARCTAS-A ARCTAS-B ATom-1 HCN (ppt) HCN (ppt) ATom-2 Concentration of particulate halogens were proportional to HCN (biomass Transportation of the primary emission and/or secondary ATom-3 burning tracer) over the Atlantic Ocean due to influence from wirefire from production from sea spray aerosols over the Ocean. ATom-4 Africa. Abundance of pBr was as high as Arctic surface. • Emission of methyl halides from wildfires were previously identified. NSF/NCAR G-V: • The concentration of particulate halogens were comparable to the **Aerosol Chemical Composition** TIĞER concentration of methyl halide. Others (0.06 µg sm⁻³) 0.39 µg sm Global distribution of iodine Measurement intercomparison Pacific Basin **Organics** N Mid Latitudes 25 x10 Southern Ocean S Mid Latitudes N Polar Equatorial 1% (BC) Slope = 0.99 Particulate Others 3% (CI bromine [[] 10 1% (Br) measurement by AMS and filter gas-particle (~ 12 km altitude, based method Arctic Southern Ocean, 2017) agreed well. (the comparison was Halogen oxidation state made from urban air plumes during Slope:0.77, Intercept:+0.00729 ng sm⁻³ Slope:0.64, Intercept:+0.0411 ng sm⁻³ 0.25 0.25 **KORUS-AQ Atlantic Basin** lodine Bromine 25 x10⁻³ (mostly IO_3) (mostly Br -) SAGA filter Bromide [ug/sm3] ATom campaign --- 2016 Aug Biomass **–**O− 2017 Jan-Feb Acknowledgements ourning -I Ratio We thank funding from NSF (AGS 2027252), NASA (NNX15AH33A and - +V Ratio 80NSSC21K1342). Dongwook Kim thanks CIRES Graduate Student Research Award and AGU Jerome M. Paros Scholarship in Geophysical Instrumentation. Halogen fragment ion ratio measured by AMS is dependent on References the halogen oxidation state. 0.25 0.25 0.25 Cuevas et al., Nature Comm. (2018), Ball et al., ACP (2018), Wang et al., PNAS. (2015), Over the remote atmosphere, most of particulate iodine is Particulate iodine (ppt) Koenig et al., PNAS (2020), Schill et al., ACPD (2024) iodate (IO₂-) and most particulate bromine is bromide (Br-).