Retrieval of perchlorate and other new aerosol species from mass spectra measured by Aerodyne aerosol mass spectrometers (AMS) during previous aircraft missions around the globe

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Introduction and backgrounds

Observational constraints for 3D models

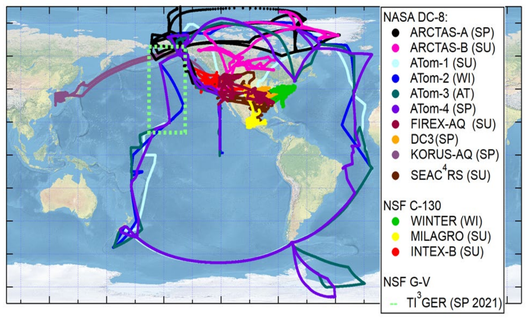

Figure 1. Flight tracks for the airborne campaigns that CU-HR-AMS participated in, during different seasons over the past decade.

- In order to better understand the role of aerosols in the atmosphere, existing 3D chemical transport models (CTMs) need to be constantly evaluated with new observations.
- To that end, measurements of aerosol chemical composition with broad spatial coverage are required.

Newly retrieved AMS species

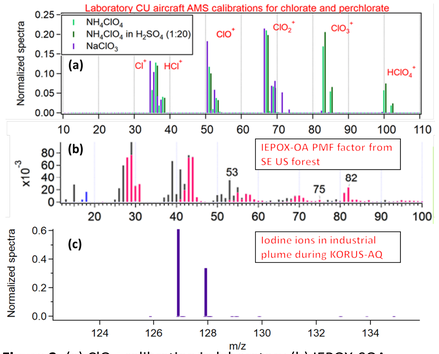

Figure 2. (a) ClO_4^- calibration in laboratory (b) IEPOX-SOA factors identified in SE US [1] (c) iodine factors over Seoul.

- In this work, we retrieved these products for most of the past field campaigns to maximize the spatial and temporal coverage of this dataset.
- In this work, we present the analysis of perchlorate, IEPOX-SOA from the ATom campaign, and particulate iodine from mass spectra acquired from KORUS-AQ campaigns.

Remote transport of IEPOX-SOA

Transported IEPOX-SOA from Brazil

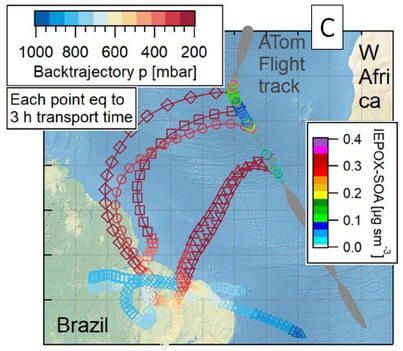

Figure 5. Flight track and 7-day back trajectories for that sampling at 12 km altitude, showing the origin of the IEPOX-SOA precursors

Isoprene epoxydiols driven secondary organic aerosol (IEPOX-SOA)

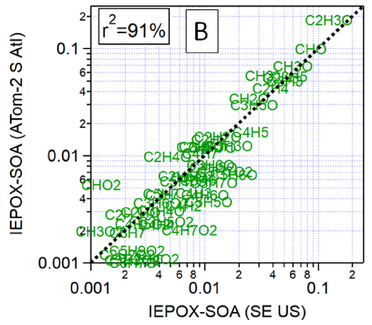

Figure 6. Comparison of the IEPOX-SOA PMF-retrieved spectrum sampled and screened by the tracer method in the South Atlantic during ATom-2 with the IEPOX-SOA spectrum reported over the SE US during SEAC4RS.

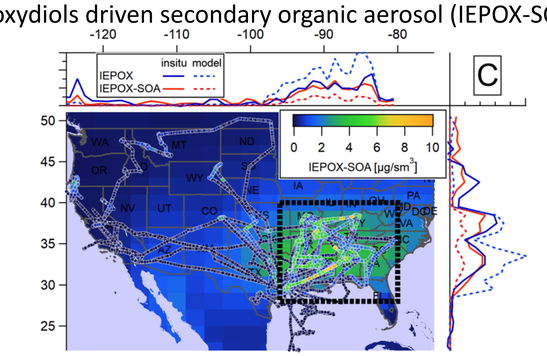

Figure 7. Geographical distribution of IEPOX-SOA and its gas-phase precursor, IEPOX over the continental US during the DC3 and SEAC4RS campaigns [11].

- In most of these environments, IEPOX-SOA formation is favored and can hence be used for further validation.
- There is also some evidence from the ATom dataset that IEPOX might be involved in UT particle nucleation/growth events as recently observed for monoterpenes. [10]
- We will further analyze the in-situ IEPOX-SOA data combined with gas-phase isoprene, IEPOX and back trajectory models to evaluate these recent satellite observations.
- Isoprene is the most dominant non-methane biogenic volatile organic compound (VOC) in the atmosphere (~440-600 TgC per year) and is a major contributor to biogenic SOA (BSOA) globally.
- The Jimenez group previously retrieved IEPOX-SOA from AMS measurements (e.g., Fig. 7) and showed that IEPOX-SOA makes up to ~30% of the total organic aerosols in the pristine amazon forest [1] and over the SE US.[1, 12].
- Constraining IEPOX-SOA with wider spatiotemporal coverage will allow improving CTMs for global biogenic secondary aerosols and evaluating the anthropogenic influence (e.g., sulfate, NO_x). [12]

Observation and modeling of perchlorate (ClO_4^-)

Measurement vs 3D Model comparison

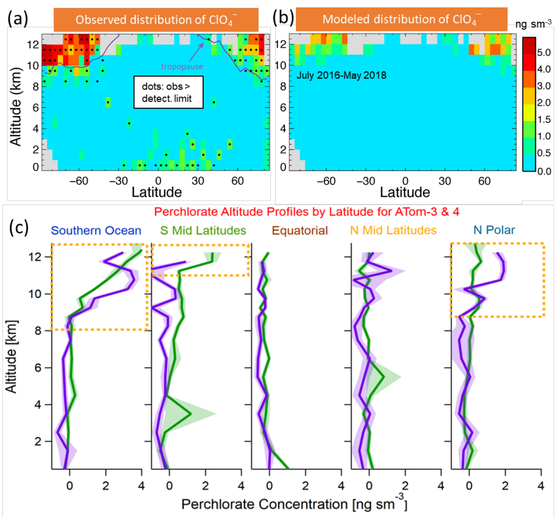

Figure 3. (a,b) Measured and modeled ClO_4^- distribution. (c) Altitude profiles of ClO_4^- as measured by the CU HR-AMS during the ATom-3 and 4 missions, highlighting the two main regions where ClO_4^- was detected, the lower stratosphere (yellow boxes) and (to a much lesser extent) the tropical MBL.

- The largest ClO_4^- concentrations observed during ATom (3-10 ng sm^{-3}) occurred above 9 km over the Southern Ocean.
- Our simulation captures this latitudinal trend, but underestimates the high ClO_4^- values observed at high latitudes in the Southern Hemisphere.
- These preliminary comparisons between a simple $HClO_4$ scheme in GEOS-Chem and ATom observations illustrate the prospects of combining airborne observations with CTM modeling to constrain ClO_4^- chemistry, and highlight potential missing sources.

Comparison of observed and calibrated mass spectra of ClO4-

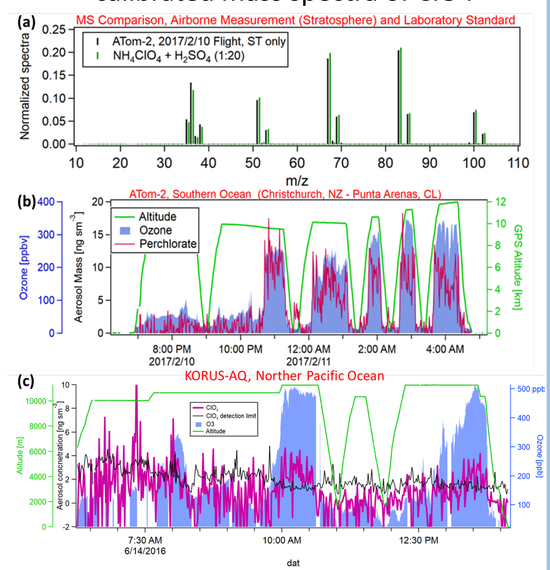

Figure 4. (a) Comparison of the acidic ClO_4^- calibration and the average spectrum measured spectrum during ATom-2. (b,c) Time Series of CU HR-AMS ClO_4^-/ClO_x and O_3 for that flight during ATom and KORUS-AQ.

- ClO_4^- was first identified in the CU HR-AMS data for a flight during ATom-2 that probed deep into the lower stratosphere showing good agreement in fragmentation pattern with laboratory calibration (Fig.4 a,b)
- Chlorine oxides identified during KORUS-AQ (over the northern Pacific ocean) were close to Chlorate until 10:00 AM where Asian outflow was sampled. Afterward, perchlorate enhancements near the stratosphere were observed (Fig.4 c).

Atmospheric sources of perchlorate

- The origin of natural $ClO4^-$ on Earth remains largely unknown. One of the proposed mechanisms is photochemical production in the stratosphere. [2-4]
- Other potential sources suggested include chlorine oxidation with ozone [5], UV [6], or Cl- reaction with lightning [7].
- While the atmospheric sources of perchlorate are highly uncertain, snow and ice core records suggest that chlorofluorocarbons (CFCs) might be important precursors for the photochemical production of perchlorate in the stratosphere. [8,9]

Conclusions

- Global aircraft aerosol chemical composition data sets provide unique constraints for chemical transportation models.
- Enhancement of perchlorate was observed in the lower stratosphere over arctic areas suggesting stratospheric sources.
- In the upper troposphere, IEPOX-SOA transported from Amazonia was sampled, and the mass spectra confirm it is IEPOX-SOA.
- Particulate iodine was identified over Seoul metropolitan areas (SMA) and over the industrial complexes on the west coast of Korea.
- High concentrations of MSA were observed over SMA and the Yellow sea.

Identification of anthropogenic iodine emission & retrieval of MSA

Anthropogenic iodine emission during KORUS-AQ.

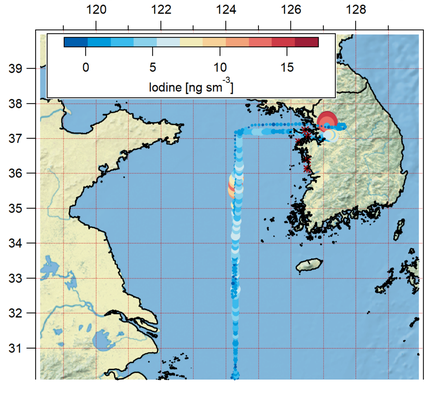

Figure 8. Flight trajectory during RF12 and concentration of particulate iodine in color and size.

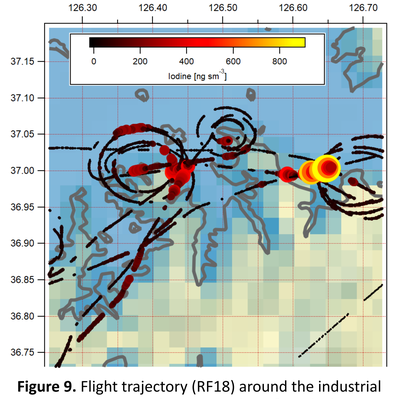

Figure 9. Flight trajectory (RF18) around the industrial complex in Korea and concentration of particulate iodine in color.

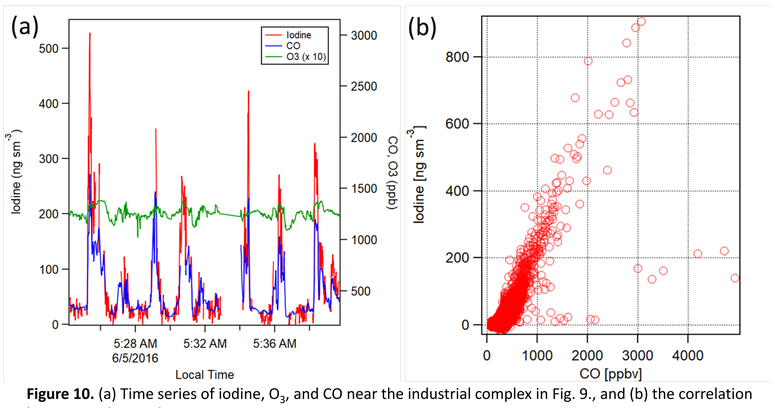

Figure 10. (a) Time series of iodine, O_3, and CO near the industrial complex in Fig. 9., and (b) the correlation between iodine and CO.

- KORUS-AQ data was revisited to retrieve particulate iodine and MSA.
- Significant concentrations were observed over Seoul and over the Yellow sea (~ 10-20 ng sm^{-3}).
- The iodine source in the city is unknown, while the iodine in the yellow sea is likely to originate from marine emissions or transport from China.
- High concentrations (up to 1 µg sm^{-3}) of particulate iodine were observed during a flight over the industrial complex on the west coast of Korea (Figure 9).
- A strong correlation with CO (an indicator of anthropogenic emission) indicates that the observed particulate iodine is primarily emitted from industries, rather than secondary formation. HI^+/I^+ ratio (~ 0.37) in the flight was much lower than that of iodide (~1.5).
- HI^+/I^+ of 5-iodo-2-fulfural was ~ 0.8 [13]. And the HI^+/I^+ ratio observed does not fit our previous calibrations.
- The absence of correlation between iodine and O_3 indicates low gas phase halogen species.

Preliminary retrieval of particulate methanesulfonic acid (MSA)

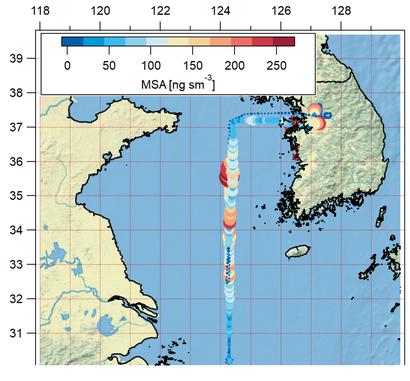

Figure 11. Flight trajectory during RF12 and concentration of particulate MSA in color and size.

- ~ 0.15 µg sm^{-3} of MSA was observed over SMA. Anthropogenic source of MSA is inclusive but MSA in (or near) urban areas were reported previously [14, 15]. MSA observed over the Yellow sea, ~ 0.2 µg sm^{-3}, is ~ 10 times higher than MSA observed over remote oceans (Pacific/Atlantic) during ATom campaigns. [16] Anthropogenic sources of MSA aerosols will be investigated.

Acknowledgements

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