Observation of $HClO_3$ and $HClO_4$ in the Arctic atmosphere

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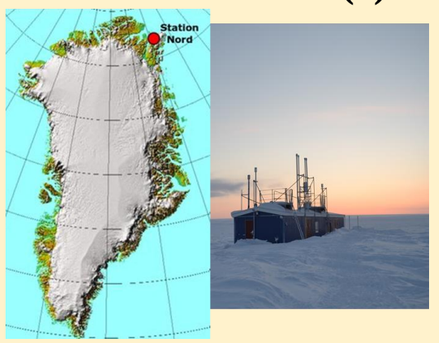
(1) INTRODUCTION AND MOTIVATION

Chlorine in the atmosphere

Cl_2, $ClNO_2$, HCl, BrCl, *etc.* → *Photochemistry* → Atomic Cl → (O_3, HO_x, *etc.*) → ClO_x → Higher ClO_x (*e.g.* $HClO_3$, $HClO_4$) → Atmospheric abundance? / Atmospheric Fate?

- The increased levels of chlorate (ClO_3^-)/perchlorate (ClO_4^-) in ice-core since 1980 likely result from enhanced atmospheric chlorate/perchlorate production (Furdui & Tomassini, 2010; Cole-Dai et al., 2018). However, there is no direct observation of chlorate/perchlorate in the atmosphere to date.

(2) METHODS



- Villum Research Station, Station Nord in high arctic North Greenland (81°36' N, 16°40' W)
- March-May of 2015
- $HClO_3$ and $HClO_4$ were measured by a nitrate chemical ionization atmospheric pressure interface time-of-flight mass spectrometer (NO_3-CI-APi-TOF)

(3) OBSERVATION OF ATMOSPHERIC $HClO_3$ & $HClO_4$

- Enhancement of $HClO_3$ and $HClO_4$ during the ozone depletion events, with concentration up to $6x10^5$ molecule cm^{-3} (Fig.1).
- The enhancement $HClO_3$ and $HClO_4$ maybe contributed by the reduction of O_3 related chemistry and/or related to the surface oxidation chemistry as the air mass was confined to the surface-level during this period.

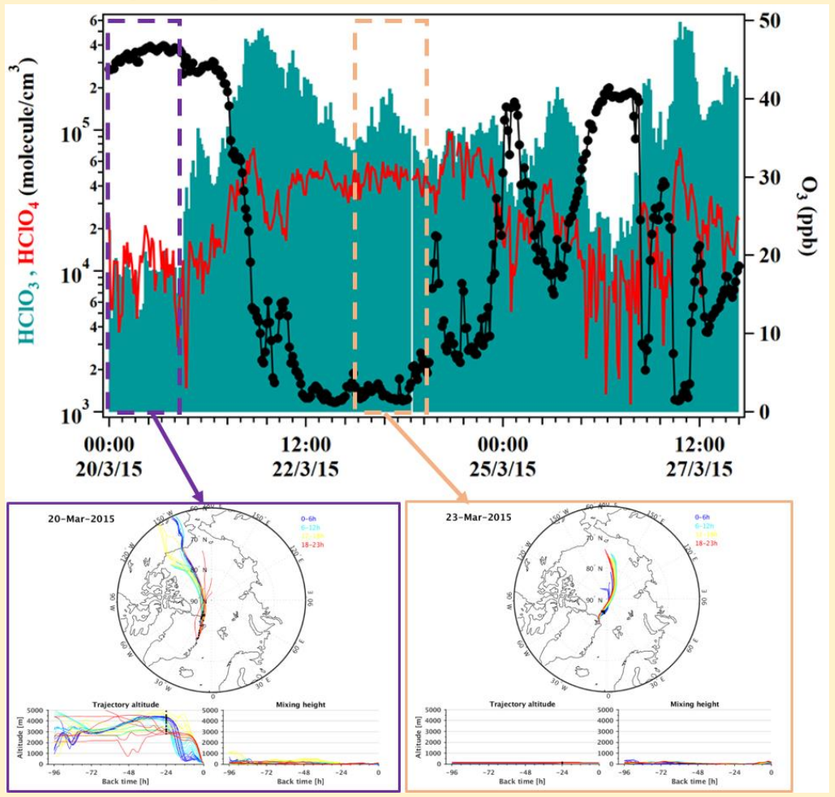


Fig. 1. An example time-series of $HClO_3$ and $HClO_4$ in relation to the O_3. Lower panel shows the air masses were confined to surface-level during the period with enhancement of $HClO_3$ and $HClO_4$.

(4) ATMOSPHERIC FATE OF $HClO_3$ & $HClO_4$

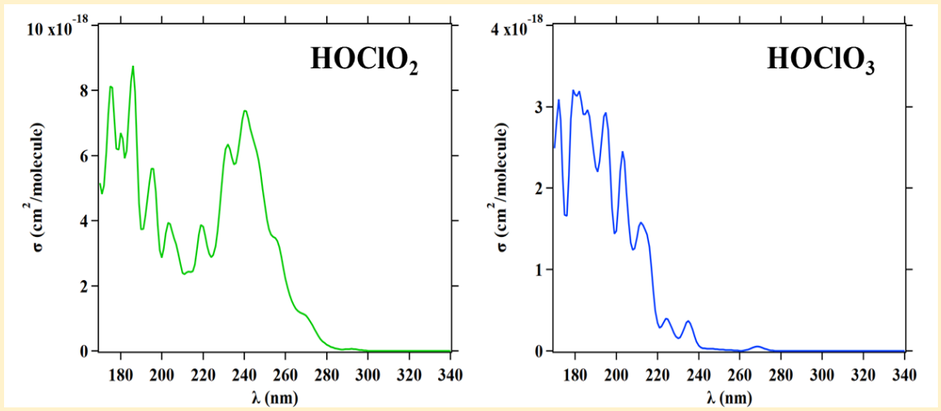


Fig. 2. The estimated cross-section of $HOClO_2$ and $HOClO_3$ in the gas-phase from high-level quantum-chemical methods.

- The high-level quantum-chemical calculations on the ultraviolet-visible absorption spectra and cross-section of $HClO_3$ and $HClO_4$ in the gas-phase (Fig. 2) indicate that these species are **not photoactive in the atmosphere**.
- The fate of $HClO_3$ and $HClO_4$ may end-up in deposition, likely on the surface/ground.

(5) SUMMARY

- First atmospheric observation of the enhancement of $HClO_3$ and $HClO_4$ during the springtime ozone depletion event in Arctic.
- The $HClO_3$ and $HClO_4$ are not photoactive in the atmosphere and may end-up deposit on the surface/ground, therefore, it could be a termination process for the atmospheric chlorine chemistry in Arctic.
- Data analysis is still on-going.

REFERENCE:

V. I. Furdui, F. Tomassini, Trends and Sources of Perchlorate in Arctic Snow. *Environ. Sci. Technol.* **44**, 588-592 (2010).

J. Cole-Dai, K. M. Peterson, J. A. Kennedy, T. S. Cox, D. G. Ferris, Evidence of Influence of Human Activities and Volcanic Eruptions on Environmental Perchlorate from a 300-Year Greenland Ice Core Record. *Environ. Sci. Technol.* **52**, 8373-8380 (2018)

ACKNOWLEDGEMENT:

Financial support from European Research Council (GASPARCON, 714621).
Thanks to the supports from the staff in Villum Research Station and Aarhus University

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