Investigation of chlorine radical chemistry in the Eyjafjallajökull volcanic plume using depletions in NMHCs

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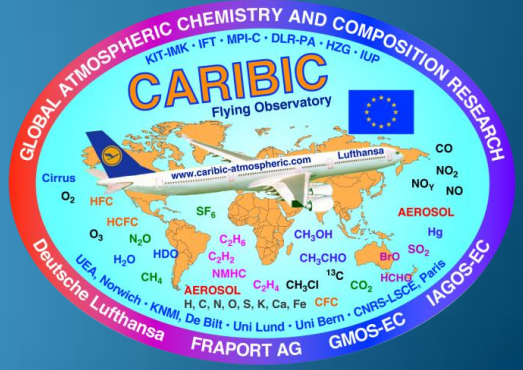
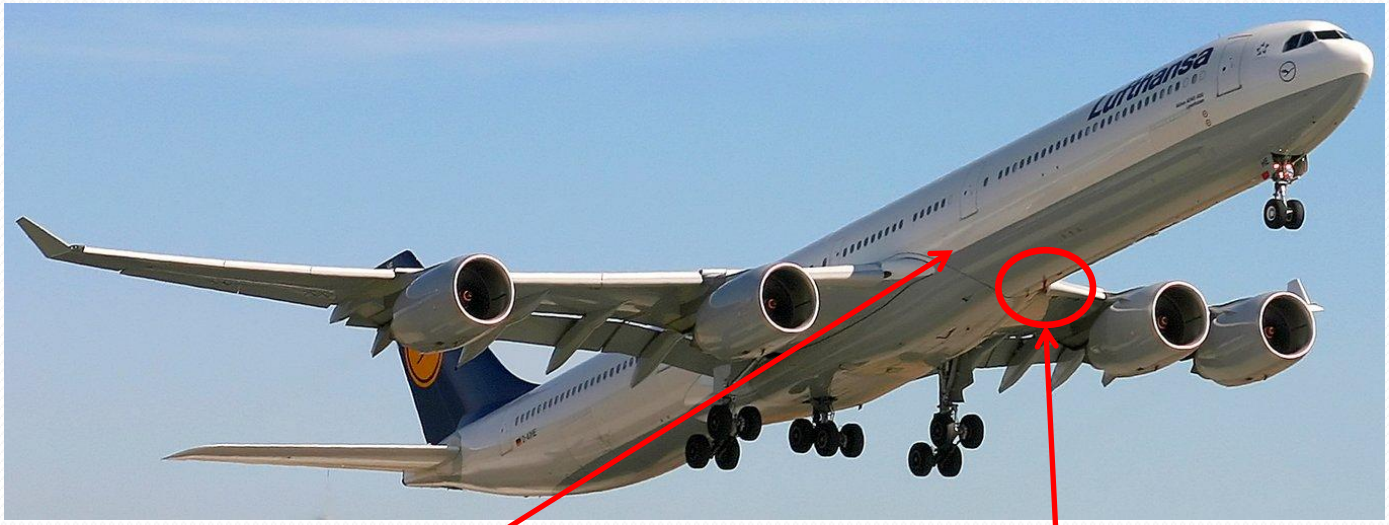
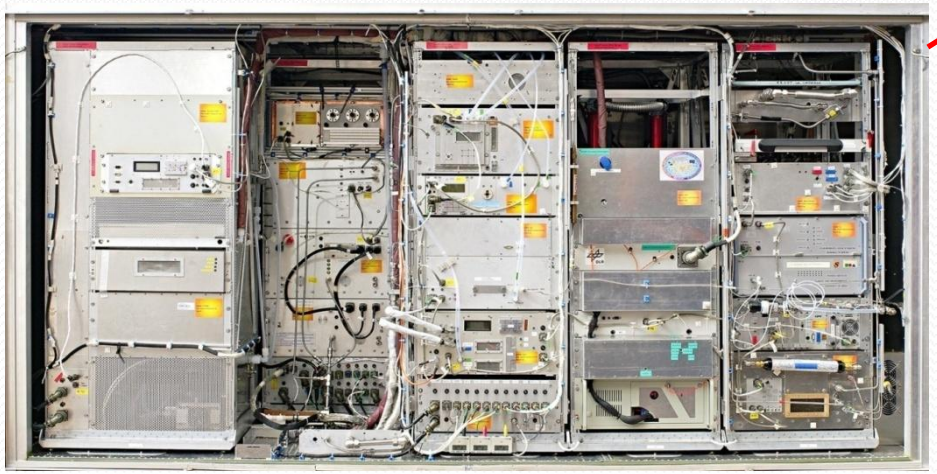


CARIBIC: The Flying Observatory

Civil
Aircraft for the
Regular
Investigation of
the atmosphere
Based on an
Instrument
Container

Lufthansa Airbus A340-600



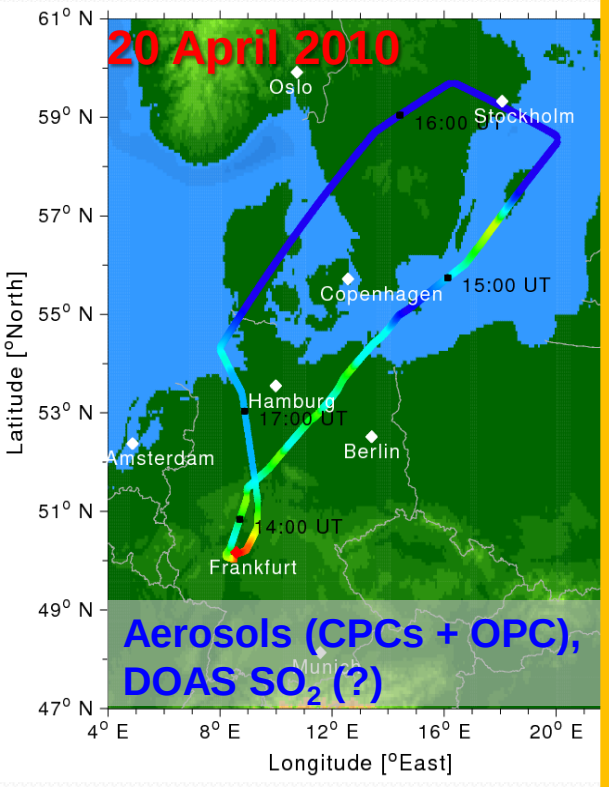


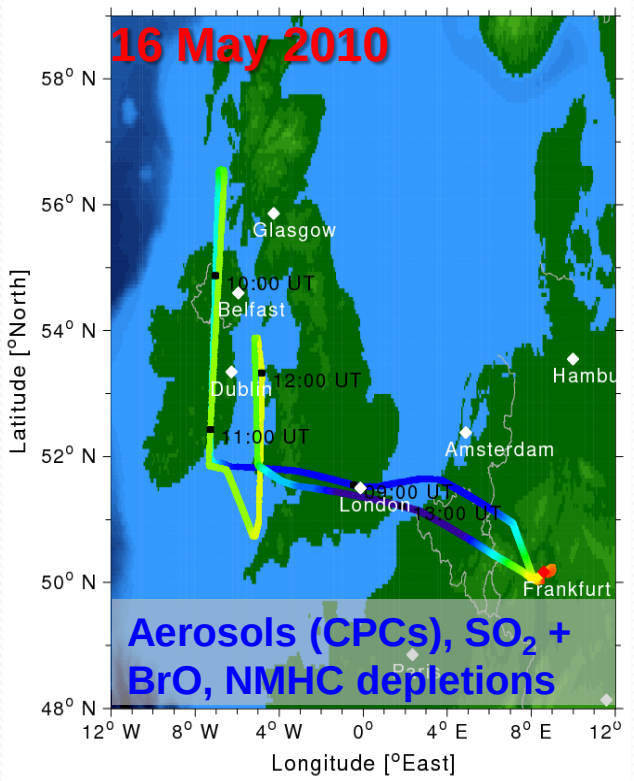
measurement container: installed once per month in the cargo bay for 4 flights

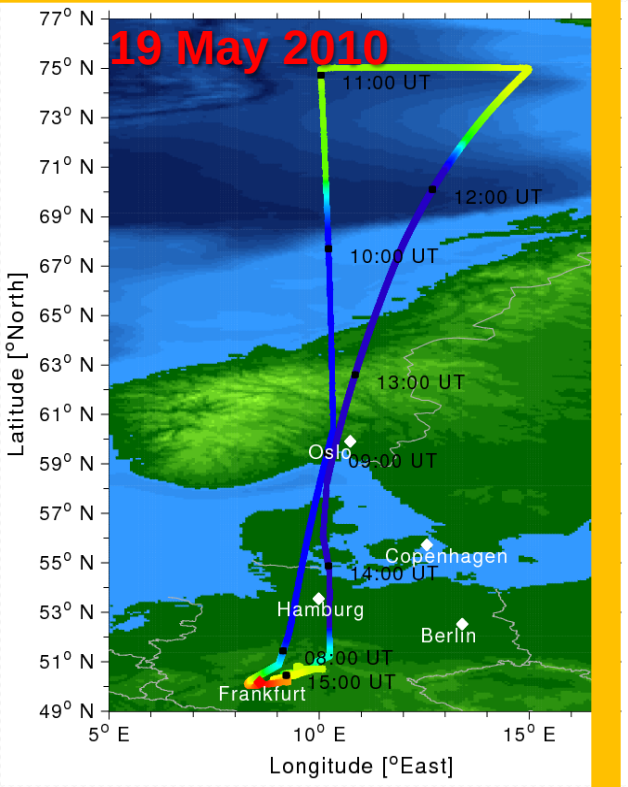
Permanantly installed inlet system

Eyjafjallajökull Flights

- 20 April: little ash, diluted in low altitude, small peak in SO_2
- 16 May: clear identification of SO_2 & BrO
- 19 May: clear identification of ash (aerosols)



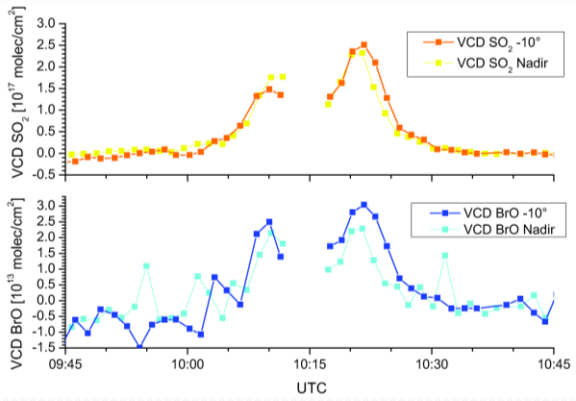


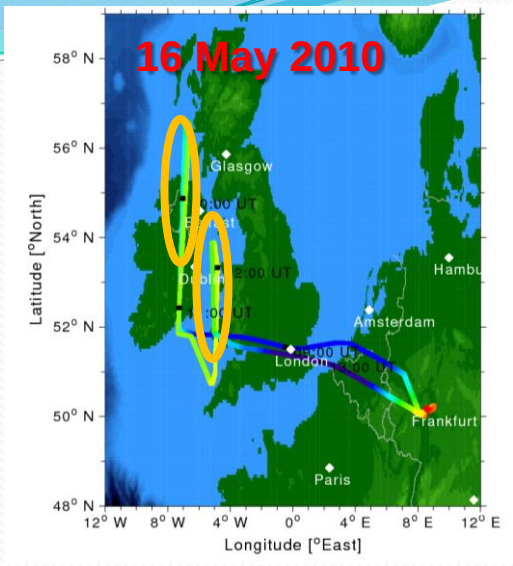


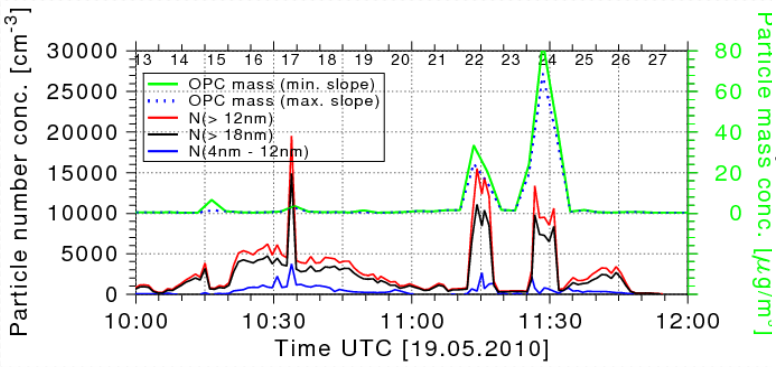
(Rauthe-Schöch et al., submitted to ACPD, 2011)

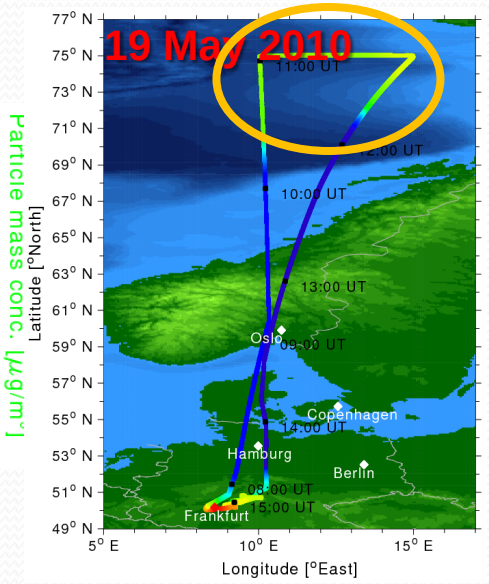
Eyjafjallajökull Flights

- 16 May
  - 7 samples collected in 2 plume sections
  - Coincident with enhanced SO_2 and BrO
  - 35-53 h transit times from volcano
- 19 May:
  - 9 plume samples
  - Coincident with enhanced particles
  - 18-24 h transit times from volcano





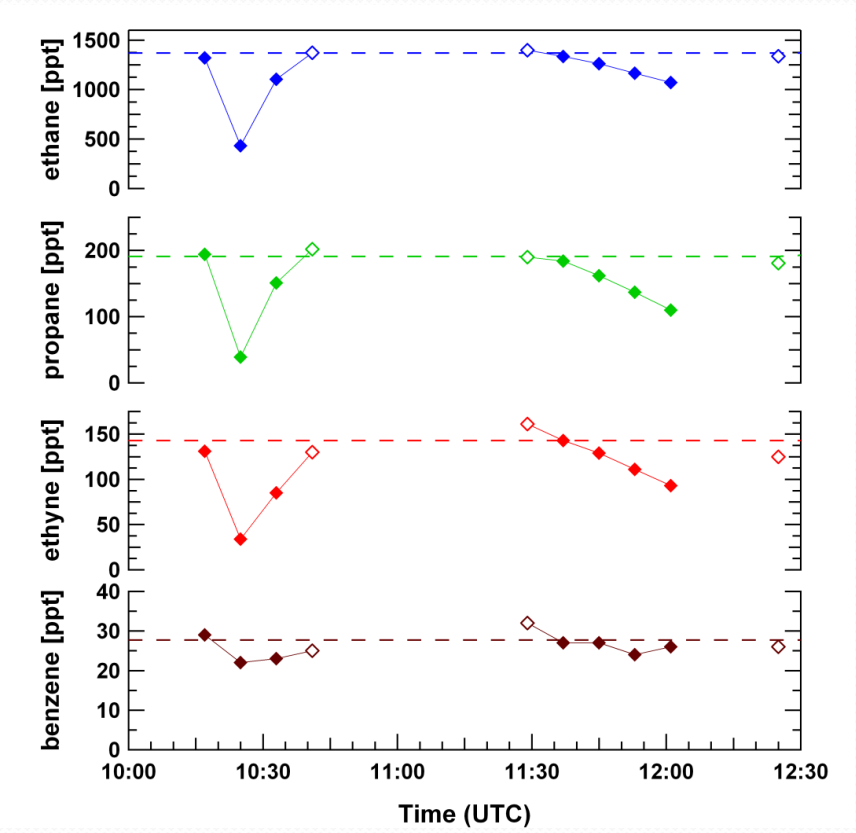




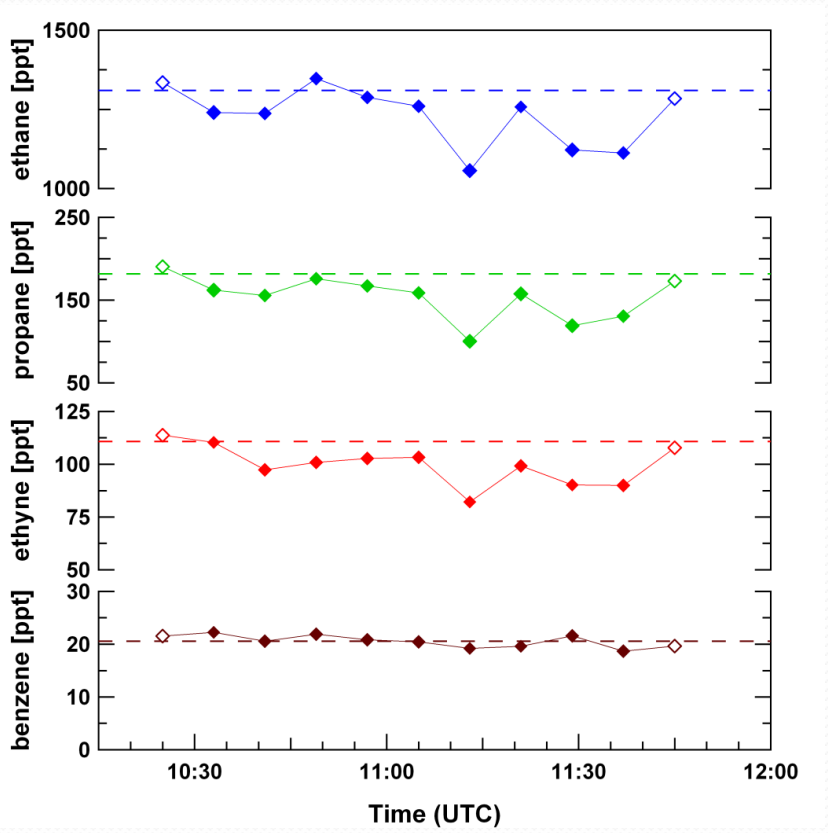
NMHC Depletions

- NMHCs in plume samples up to 70% lower than background

  …with the exception of benzene



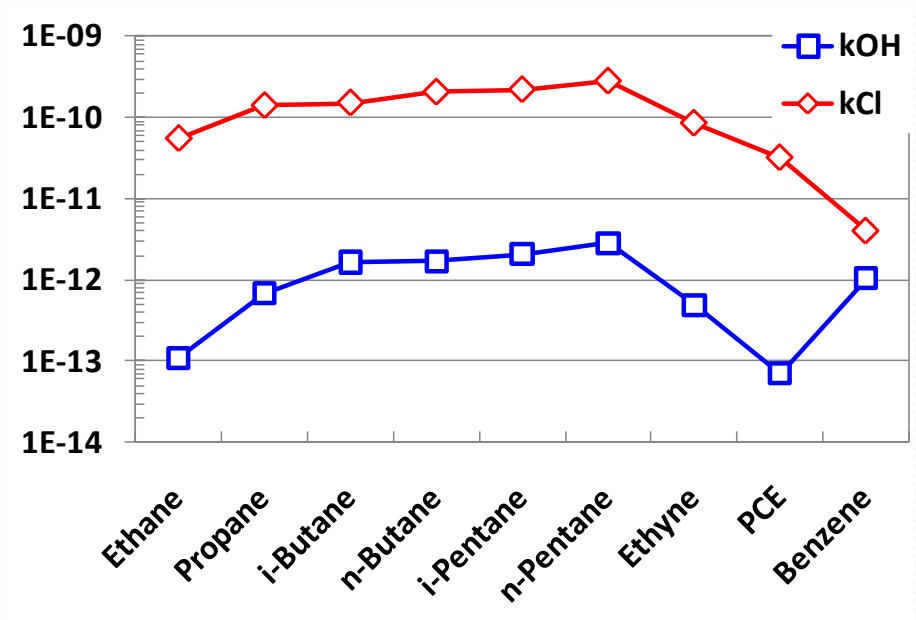
16 May 2010

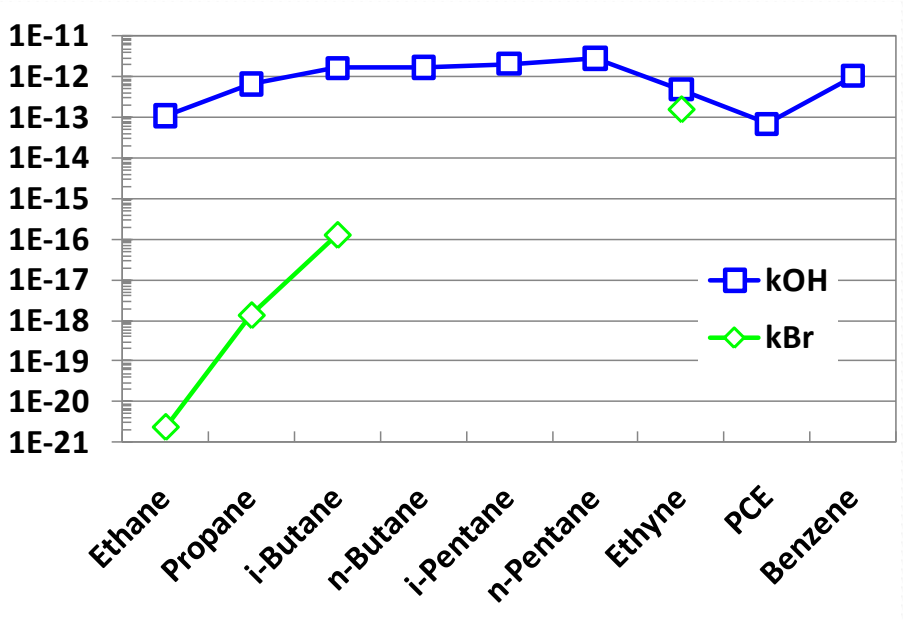


19 May 2010

Removal of NMHCs

- Typically, primary loss is reaction with OH
- Reaction with Cl much faster than with OH
  - Exception: benzene ($k_{Cl} \approx k_{OH}$)
- Reaction with Br very slow
  - Exception: ethyne ($k_{Br} \approx k_{OH}$)

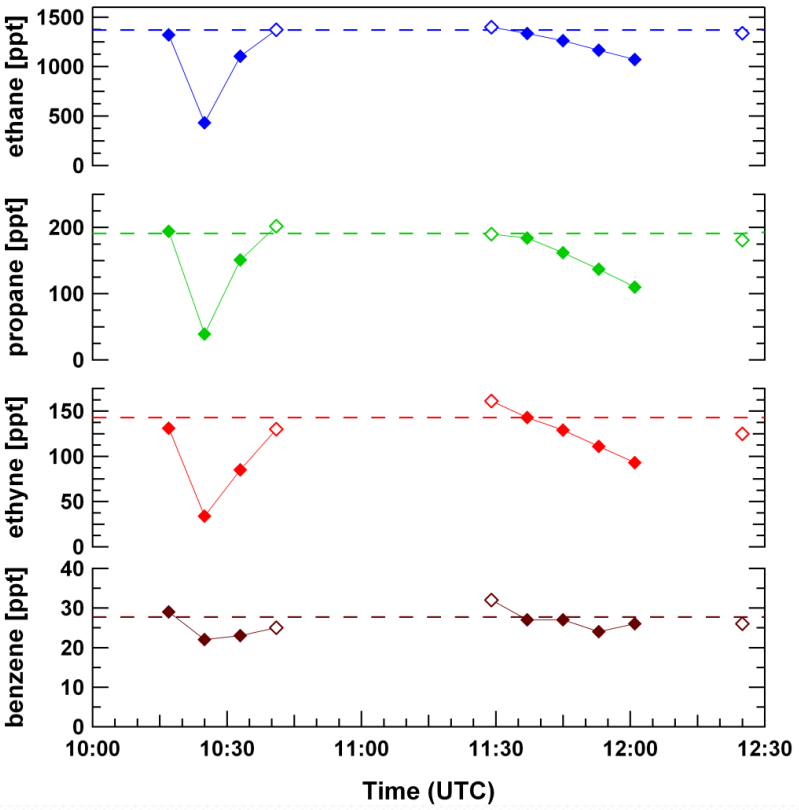




NMHC Depletions

- NMHCs in plume samples up to 70% lower than background

  …except for benzene → Cl chemistry?



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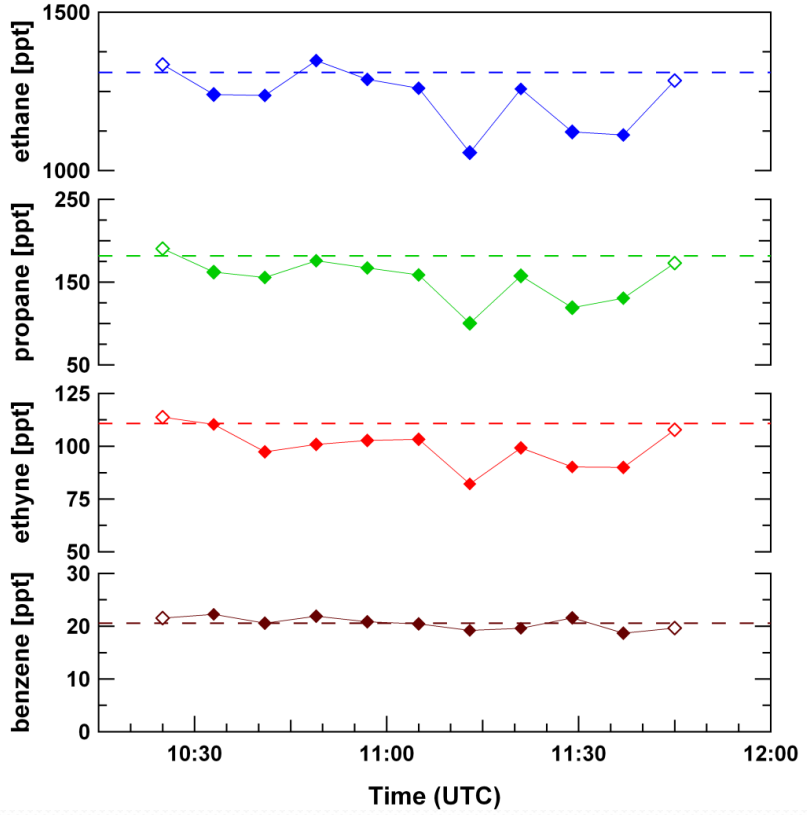

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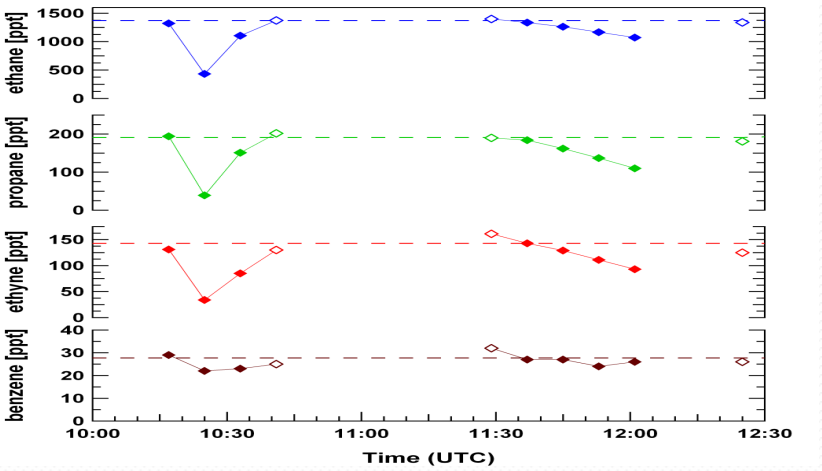

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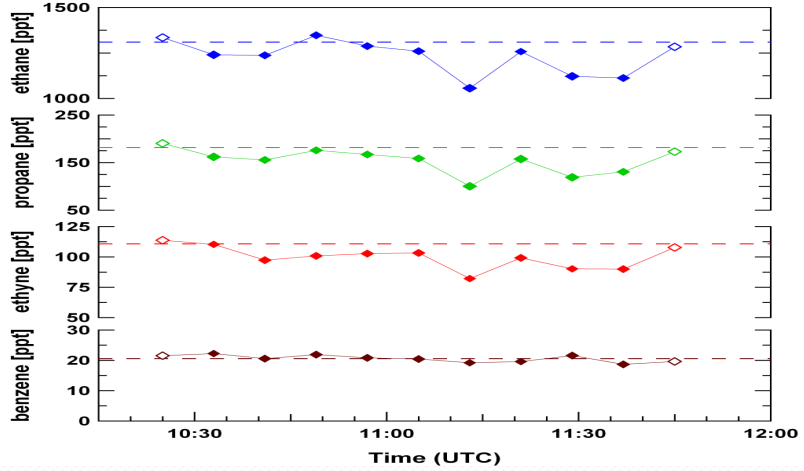


19 May 2010

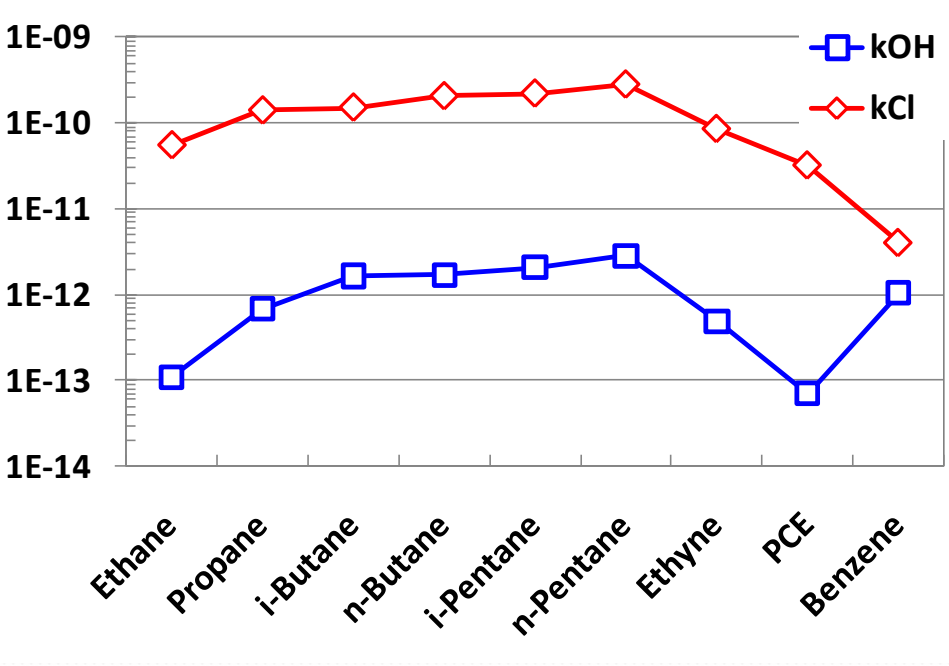
- Br chemistry considered, but
  - Ethyne not significantly more depleted
  - No evidence of Br influencing these NMHCs

Estimating Cl from NMHC depletions

- Depletions of NMHCs related to reaction kinetics through:

$$\ln([HC]_{plume}/[HC]_{bkgd}) = -k_{Cl}\langle[Cl]\rangle\Delta t$$ [*Jobson et al., 1994*]

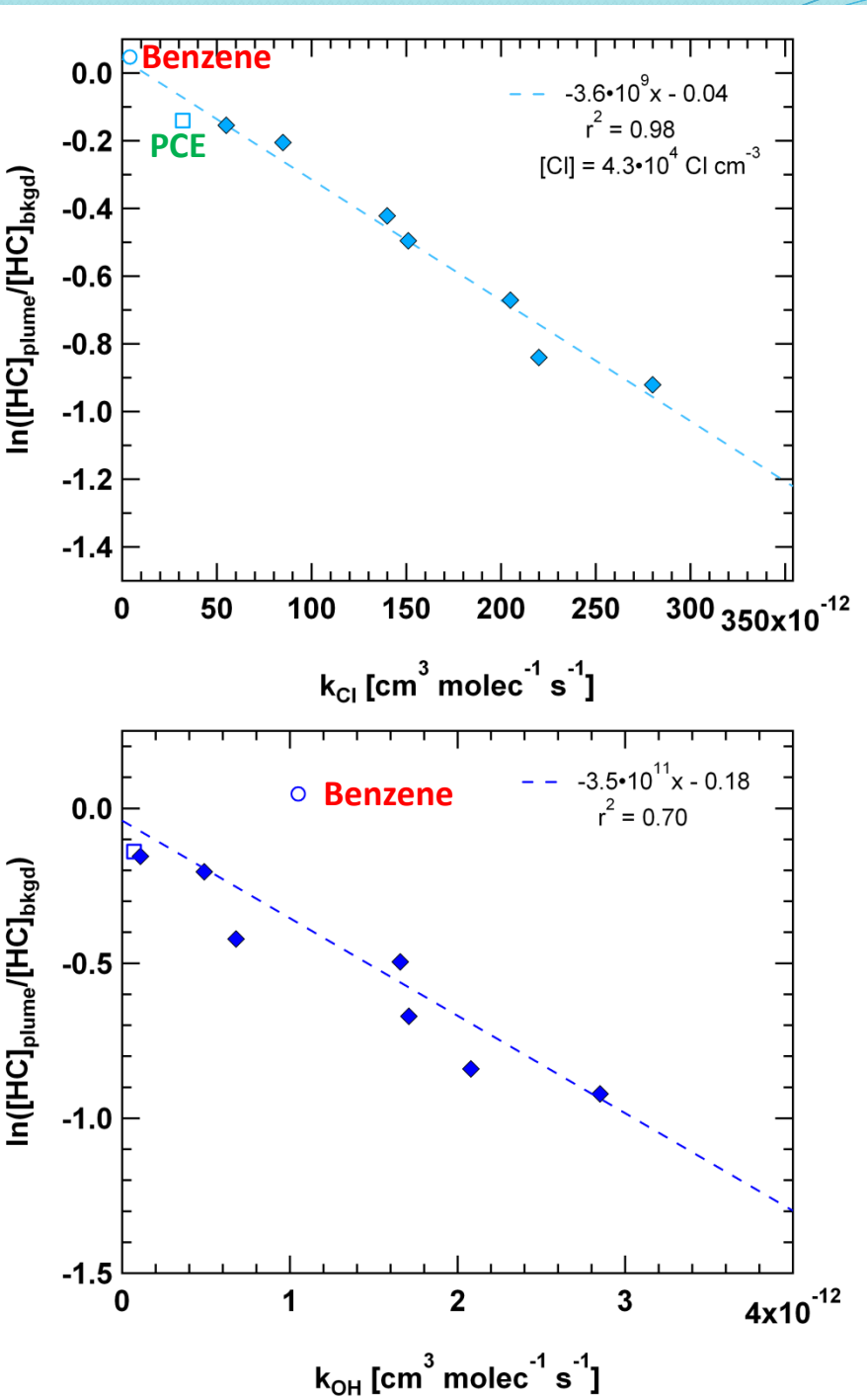
- [Cl] can be estimated from the slope of the correlation between the ratio and k_{Cl}
- Δt estimated from backward trajectories



Cl Estimates

- Good correlations for 15/16 samples
  - Poorer correlations if OH replaces Cl
    - Benzene obvious outlier
  - PCE (C_2Cl_4) agreed with NMHCs
- Estimated [Cl]
  - 19 May:1.5–6.0x10^4 cm^{-3} (mean 2.8x10^4)
  - 16 May: 1.3–6.6x10^4 cm^{-3} (mean 3.6x10^4)

(Baker et al., 2011. submitted to GRL)



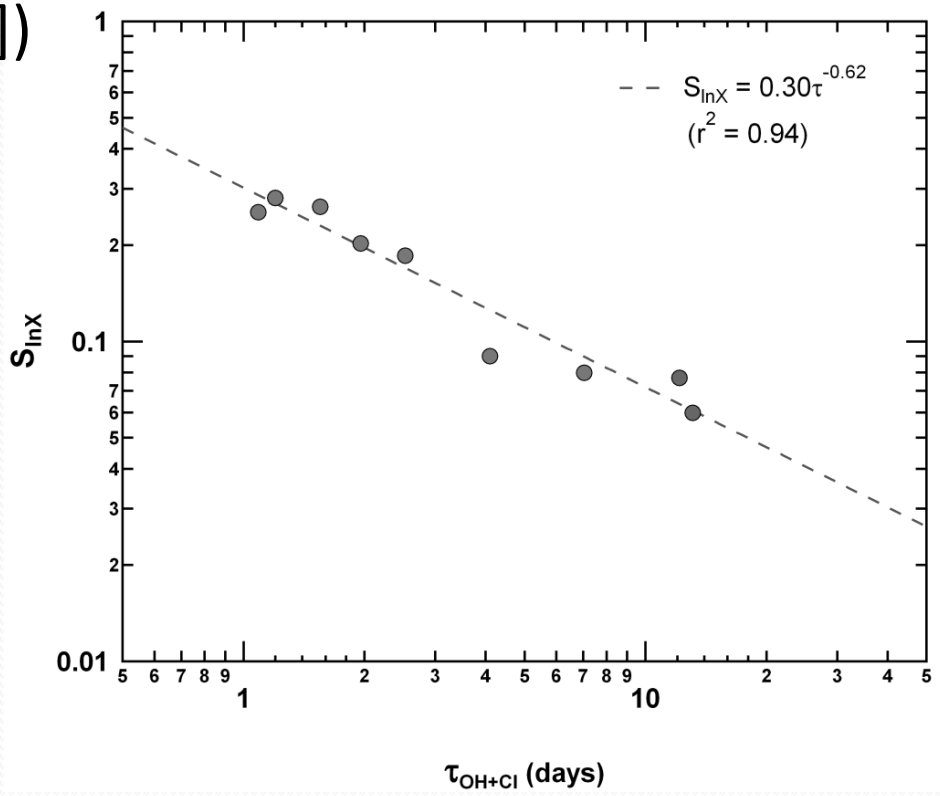
Relative Abundances of OH and Cl

- Estimate relative abundances (influences) of OH and Cl using relationship between local lifetime and variability:

$S_{lnX} = A\tau^{-b}$ [*Jobson et al., 1998, 1999; Pszenny et al., 2007*]

where $\tau = 1 / (k_{OH}[OH] + k_{Cl}[Cl])$

- Examined for flight on 19 May
  - Describes plume variability surprisingly well
- Optimal ratio [OH]/[Cl] = 32
- Using mean Cl of 2.8×10^4 Cl cm^{-3} gives OH = $0.9 \cdot 10^6$ cm^{-3}



Summary

- 2 of 3 CARIBIC volcanic flights extensively probed the Eyjafjallajökull volcanic plume.
- 7 whole air samples collected in the plume on 16 May, 9 samples on 19 May
- NMHCs (and PCE) depleted in plume samples
  - Patterns characteristic of reaction with Cl
  - Estimated [Cl] between 1.3×10^4 and 6.6×10^4 Cl cm^{-3}
- Examination of relationship between NMHC variability and local lifetime found optimal [OH]/[Cl] of 32
  - Corresponds to OH = $0.9 \cdot 10^6$ cm^{-3} using mean Cl

Acknowledgements

We would like to thank Lufthansa for providing for these special research flights, in particular Captain Martin Hoell, Andreas Waibel and Thomas Dauer, and the entire CARIBIC team for their tremendous effort put into flight execution.

Thank you for your attention!

References:

Baker et al. (2011): Investigation of chlorine radical chemistry in the Eyjafjallajökull volcanic plume using depletions in non-methane hydrocarbons, *submitted to GRL.*

Rauthe-Schöch, et al. (2011): CARIBIC aircraft measurements of Eyjafjallajökull volcanic plumes in April/May 2010, *submitted to ACP* Eyjafjallajökull special issue**. POSTER XY164 Thursday 17:30-19:00**

Heue et al. (2010): SO_2 and BrO observation in the plume of the Eyjafjallajökull volcano 2010: CARIBIC and GOME-2 retrievals, *ACP* Eyjafjallajökull special issue. **TALK Friday 9:45 Room 8**

Jobson, et al. (1994): Measurements of C2-C6 hydrocarbons during the Polar Sunrise1992 Experiment: Evidence for Cl atom and Br atom chemistry, *J. Geophys. Res.*, *99*(D12), 25355-25368.

Jobson, et al. (1998): Spatial and temporal variability of nonmethane hydrocarbon mixing ratios and their relation to photochemical lifetime, *J. Geophys. Res.*, *103*(D11), 13557-13567.

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