Is human activity affecting the atmosphere's ability to clean itself of pollutants?

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1 Aim

Using long term trends of alkane and alkyl nitrate concentrations determine the impact of changing anthropogenic emissions on the ozone and hydroxyl radical budgets of the northern hemisphere troposphere since 1950.

2 Motivation

The **oxidizing capacity of the troposphere** reflects the ability of the atmosphere to cleanse itself of anthropogenic and natural pollutants. It is primarily determined by the concentration of **hydroxyl radicals (OH)**, production of which is controlled by a complex series of reactions involving **ozone (O_3)**, **methane (CH_4)**, **carbon monoxide (CO)**, **non-methane volatile organic compounds** (NMVOCs) and **nitrogen oxides (NO_x = NO + NO_2)**.
As emissions of CH_4, CO, $NMVOCs$ and NO_x have changed substantially since pre-industrial times, the tropospheric budgets of OH and O_3 will also have changed. However, there is **no consensus on the long-term trends in OH concentrations**, which leads to very large uncertainties in projected future changes and associated climate impacts.

- There are a few **direct observational data sets** of O_3, CH_4, CO, $NMVOCs$ and NO_x, some of them starting from the 1980s. But there are **none for OH**.
- To extend these time series backward in time, **firn air** samples collected in central Greenland were analysed for a **variety of alkanes (RH) and alkyl nitrates ($RONO_2$)** [2] (Figure 1).
- Being formed during ozone production, **$RONO_2$ can be utilised as a diagnostic of hydrocarbon-NO_x chemistry** (see Section 3).

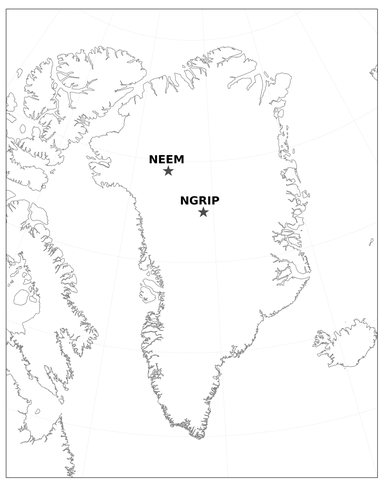

Figure 1: Location of firn air sampling sites in Greenland

- A firn model was used to derive atmospheric histories of six alkanes and six alkyl nitrates from measurements in firn air.
- **The timing of the peak in atmospheric concentrations of alkyl nitrates and their parent alkanes is different** (Figure 2).
- This could be interpreted as representing **a change in the northern hemisphere NO_x or OH concentrations**.

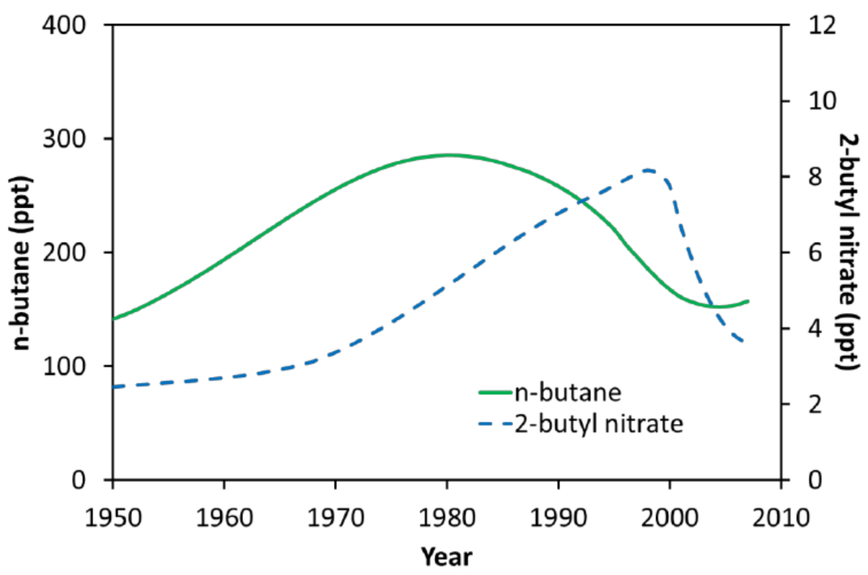

Figure 2: Comparison of the atmospheric histories of 2-butyl nitrate and its parent alkane, n-butane, at NEEM [1]

3 Alkyl Nitrate Chemistry

Alkyl nitrates ($RONO_2$) are formed from the oxidation of alkanes in the presence of NO_x:

$$RH + OH \xrightarrow{O_2} RO_2 \quad (1)$$

$$RO_2 + NO \xrightarrow{1-\alpha_3} RO + NO_2 \quad (2a)$$

$$\boldsymbol{RO_2 + NO \xrightarrow{\alpha_3} RONO_2} \quad (2b)$$

$$RO_2 + HO_2 \rightarrow ROOH \quad (3)$$

$$RONO_2 \xrightarrow{OH,h\nu} RCHO + NO_2 \quad (4)$$

Alkyl nitrate chemical production is thus determined by:

- alkane concentration,
- OH concentration,
- the ratio $\frac{[NO]}{[HO_2]}$.

Alkyl nitrate chemical loss is determined by reaction with OH and photolysis.

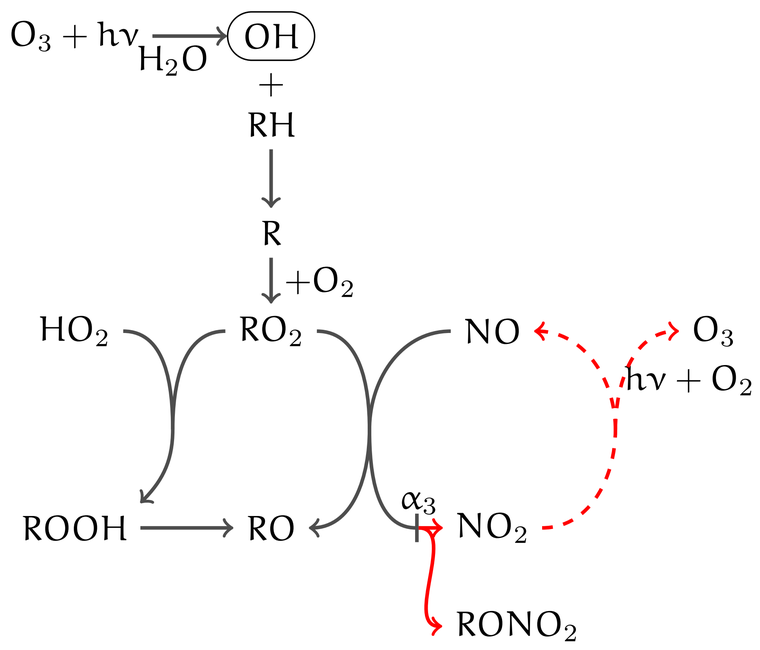

Figure 3: Chemistry related to alkanes and alkyl nitrates, and the link to OH and O_3

4 OXBUDS project

OXidant **BUD**get**S** of the Northern Hemisphere Troposphere Since 1950

Add C_2-C_5 alkyl nitrate chemistry into **UM-UKCA**

Consider impact of emission regions on Arctic composition (also using **NAME** particle dispersion model)

Explore present-day chemistry of the northern hemisphere troposphere

Constrain long-term trends of oxidants in northern hemisphere troposphere

Compare with ACCMIP results and prepare recommendations for the further development of chemistry-climate models

References

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