Studying tropospheric chemistry in Australasia

*Using MAX-DOAS measurements*

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Outline

• Introduction: Tropospheric oxidation chemistry in Australasia
• MAX-DOAS

• Results: Lauder, New Zealand and Melbourne, Australia

• Discussion: controls on tropospheric oxidation chemistry
  - $O_3$ production regime
  - OH radical production
  - Tropospheric $O_3$ retrievals
Tropospheric oxidation chemistry

**Australasian perspective**
- Vastly under-sampled
- High but very poorly constrained biogenic VOC emissions
- Important local air quality problems in cities like Melbourne and Sydney
- Interactions between urban and rural airmasses

**And why should you care?**
- Perhaps we’re a real-time case study of your future air quality...?*****
- Oxidation chemistry links to secondary aerosol formation
- MAX-DOAS as a useful tool for this kind of work
MAX-DOAS = Multi-axis differential optical absorption spectroscopy

- Passive solar spectroscopy technique
- Trace gas information in spectra of different elevation angles → Vertically resolved information
- Can measure NO$_2$, HONO, HCHO, glyoxal, halogen oxides, O$_3$
- Ideal for long term measurement campaigns, bottom-up satellite validation
Melbourne and Lauder

UK Atmospheric Science
Conference 2019
Case study 1: Lauder, New Zealand

- Background NDACC site in Central Otago, South Island
- Operated by NIWA

- Expected atmospheric chemistry: low aerosol optical depth, low NOx, possibly bVOCs

- MAX-DOAS measurements ongoing since mid 2016

- Validation possibilities: aerosol optical depth and HCHO column
Case study 1: Lauder, New Zealand

Retrieved surface vmr
0.45 – 0.60 ppb

Retrieved surface vmr
0.20 – 0.40 ppb

HCHO/NO₂ ratio (VCD/VCD)
> 2 = NOₓ limited O₃ production regime
< 1 = VOC limited O₃ production regime
Case study 2: Broadmeadows, Australia

- Operated by Aus BoM, Broadmeadows, northern suburb of Melbourne
- Next to major arterial motorways – expected high NOx
- Also at an urban/rural interface for transported emissions, e.g. bVOCs
- MAX-DOAS measurements ongoing since Dec 2016

My respects to the Wurundjeri traditional owners
Case study 2: Broadmeadows

Directional distribution: NO$_2$

- Seasonal variation evident
- Strongest NO$_2$ at low wind speed indicates local production
- Consistent with adjacent road traffic
Case study 2: Broadmeadows

Autumn

Winter

Spring

Summer

HCHO VCD (molec.cm$^{-2}$)

Mean

$2\times10^{15}$

$4\times10^{15}$

$6\times10^{15}$

$8\times10^{15}$

$1\times10^{16}$

Strong seasonal variation

Clear directional trend, consistent with $bVOC$ emissions from rural areas

Potentially temperature dependent $bVOC$ emissions, biomass burning

Image sourced from Google Maps
Controls on oxidation chemistry: O\textsubscript{3} production regime

\[ R = \frac{\text{HCHO}_{\text{vcd}}}{\text{NO}_2_{\text{vcd}}} \]

- Low R means VOC-limited O\textsubscript{3} production rate, dominated by low wind speeds from the urban sector
- High R means NO\textsubscript{x}-limited conditions, dominated by strong winds from the rural sector
- Discernible influence of rural (bVOC) airmasses on the local atmospheric oxidation chemistry
Case study 2: Broadmeadows – Example vertical profiles

HCHO

12/12/2017

13/12/2017

0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
0.000

0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
0.000

Trace gas mixing ratio (ppmv)

12/12 = Warm but calm conditions

13/12 = Hot, strong north wind
Controls on oxidation chemistry 2

Controls on oxidation chemistry: OH radical production

- $O_3 + h\nu \rightarrow O(^1D) + O_2$
  $O(^1D) + H_2O \rightarrow 2 OH$

- $\text{HONO} + h\nu \rightarrow 2 \text{OH}$

- $\text{HCHO} + h\nu \rightarrow H + \text{HCO}$
  $H + O_2 \rightarrow \text{HO}_2$
  $\text{HCO} + O_2 \rightarrow \text{HO}_2 + \text{CO}$
  $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$

$P_{OH}(O_3) = 2 \times f \times J(O_1D) \times [O_3]$

$P_{OH}(\text{HONO}) = J(\text{HONO}) \times [\text{HONO}]$

$P_{OH}(\text{HCHO}) = 2 \times J(\text{HCHO}) \times [\text{HCHO}]$
Controls on oxidation chemistry:

- Given strong northerly wind conditions, photolysis of HCHO can dominate the local OH radical production.
Tying it all together: trop. O$_3$ retrievals

- Tropospheric O$_3$ retrieval using MAX-DOAS is complicated because of stratospheric ozone
- Following method of Wang et al., 2018:
  \[
  \text{SCD(O}_3\text{ trop)} = \text{SCD(O}_3\text{ total, measured)} - \text{SCD(O}_3\text{ strat, modelled)}
  \]

- First attempts at retrieving trop. O$_3$ profiles look plausible:
Summary

• Nearly three years of MAX-DOAS measurements presented from Australia and NZ
  → Vertical, spatial and temporal analysis of NO₂, HCHO
  → Greater understanding of competing urban/rural influences on tropospheric oxidation capacity
  → Preliminary, promising tropospheric ozone retrievals

• Ongoing work
  → Further work on MAX-DOAS retrievals: O₃ and glyoxal
  → Using these results in modelling studies – e.g. calculating absolute OH concentrations, identifying HCHO source/s
  → Using these results in satellite validation
Thanks for listening

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Aussies are alright, really ;)  
Please come and say g’day!
Case study 1: Lauder, New Zealand

Timeseries HCHO comparison: MAX-DOAS VCD and FTIR VCD
For MAX-DOAS data within 10 min of FTIR data

y = 0.760x + 1.22e14

Pearson’s r = 0.74

The 0.95−confidence bounds are calculated with the bootstrap(quantile) method.

FTIR

MAX-DOAS