Studying tropospheric chemistry in Australasia

Using MAX-DOAS measurements

Robert Ryan,
PhD student, School of Earth Sciences, The University of Melbourne

rgryan@student.unimelb.edu.au

rsquared_aus

Acknowledgments

Robyn Schofield, Peter Rayner (University of Melbourne)
Steve Rhodes, Matt Tully (B.Meteorology, Melbourne)
Stephen Wilson, Nicholas Jones (University of Wollongong)
Richard Querel, Paul Johnston (NIWA NZ)
Udo Frieß, Johannes Lampel (IUP Heidelberg, Germany)

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

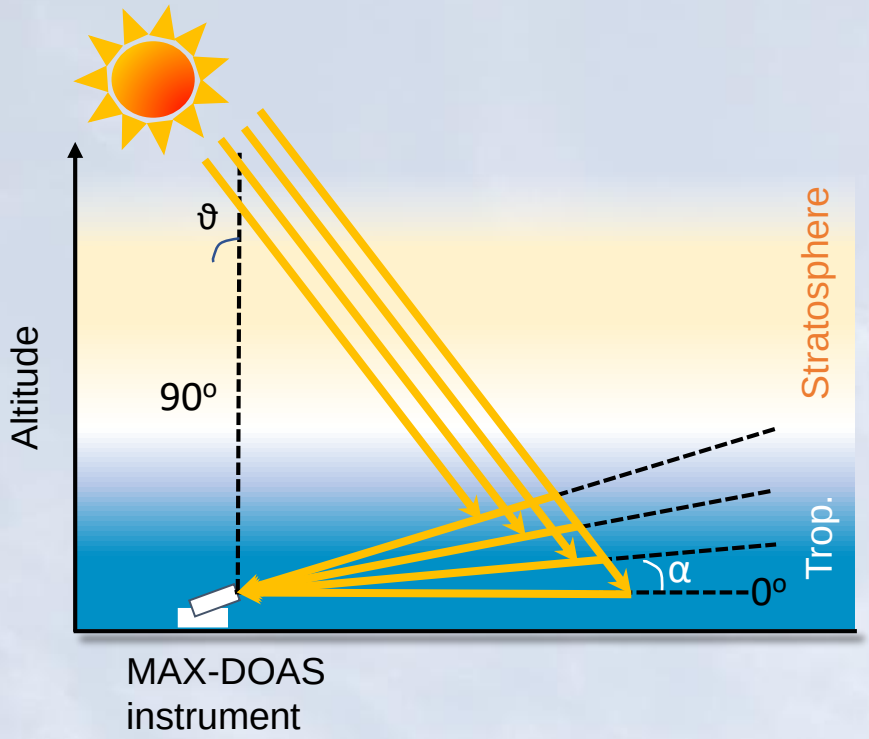
Australasian perspective

- 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

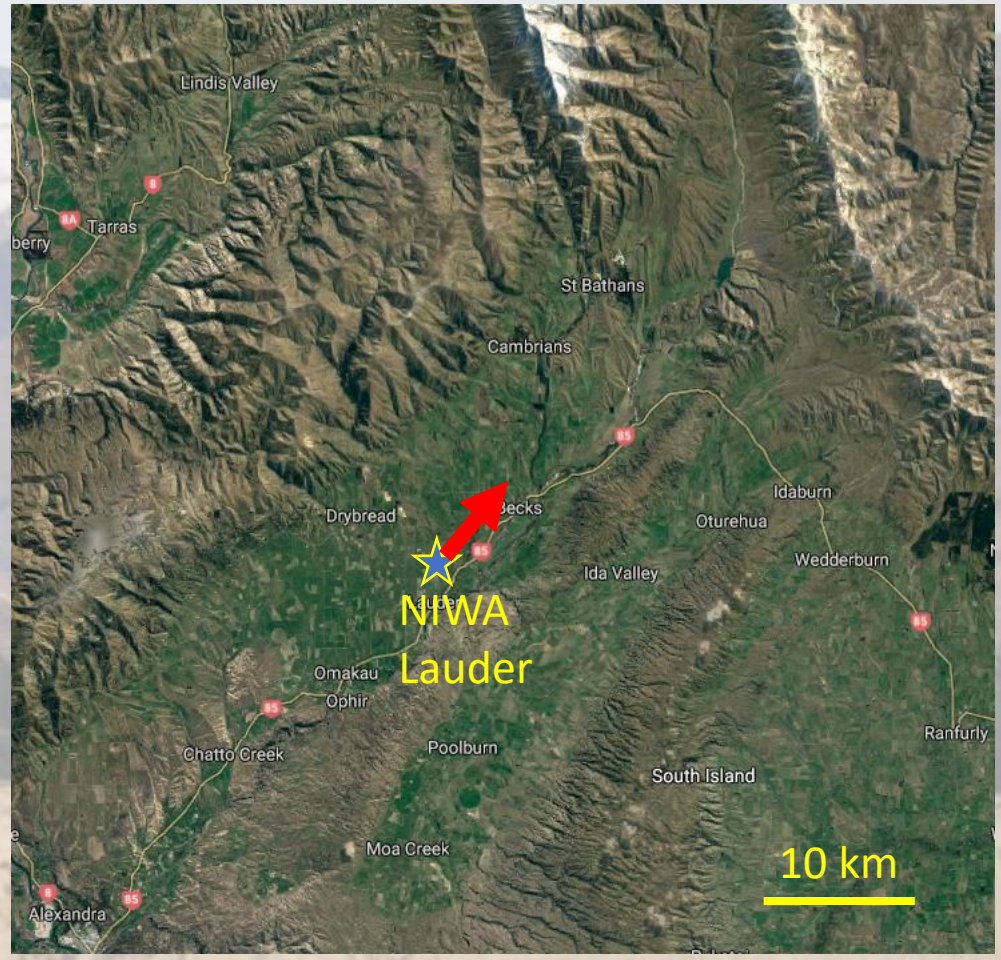
Case study 1: Lauder, New Zealand

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

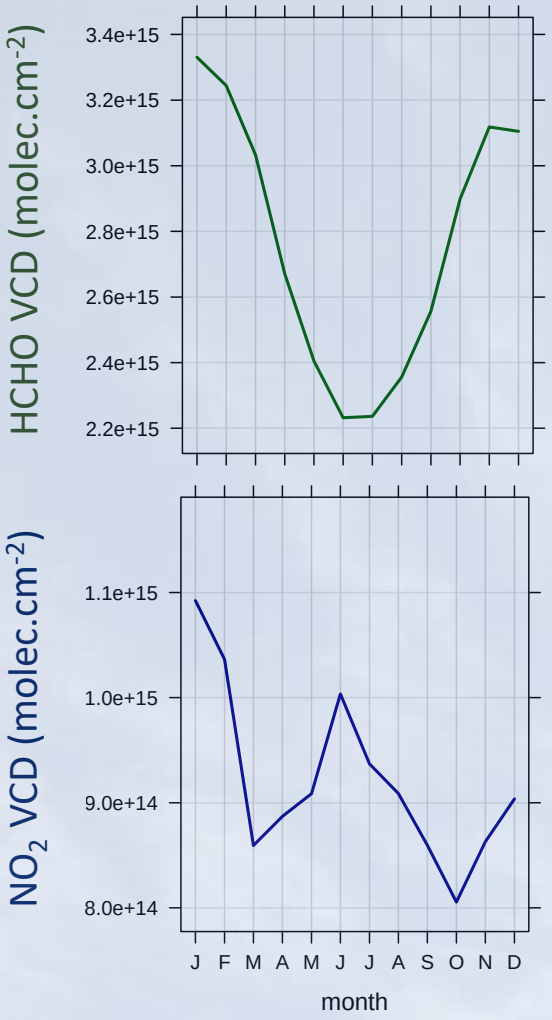
- Expected atmospheric chemistry: low aerosol optical depth, low NOx, possibly bVOCs

- MAX-DOAS measurements ongoing since mid 2016

- Validation possibilities: aerosol optical depth and HCHO column



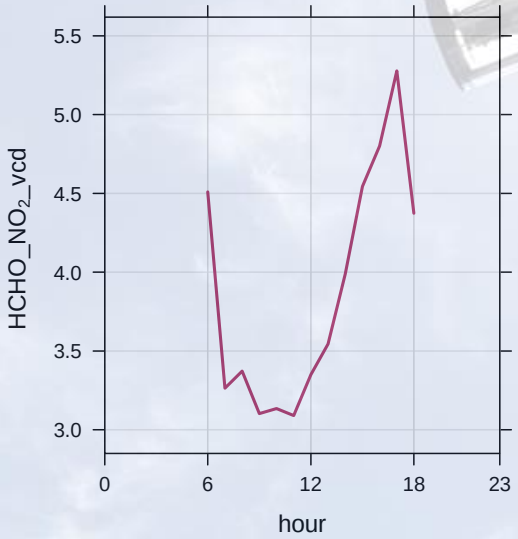
Case study 1: Lauder, New Zealand

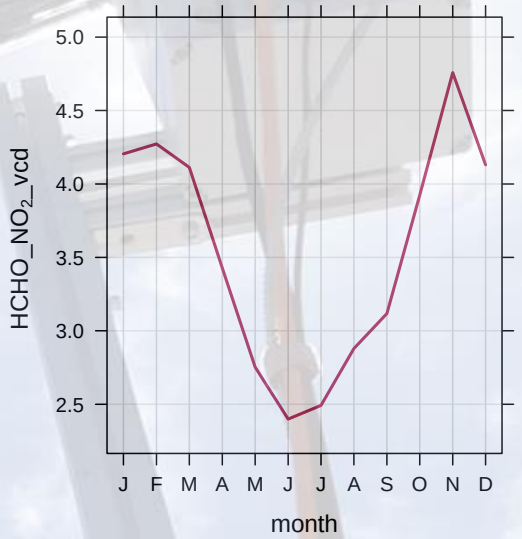


Retrieved surface vmr
0.45 – 0.60 ppb

Retrieved surface vmr
0.20 – 0.40 ppb

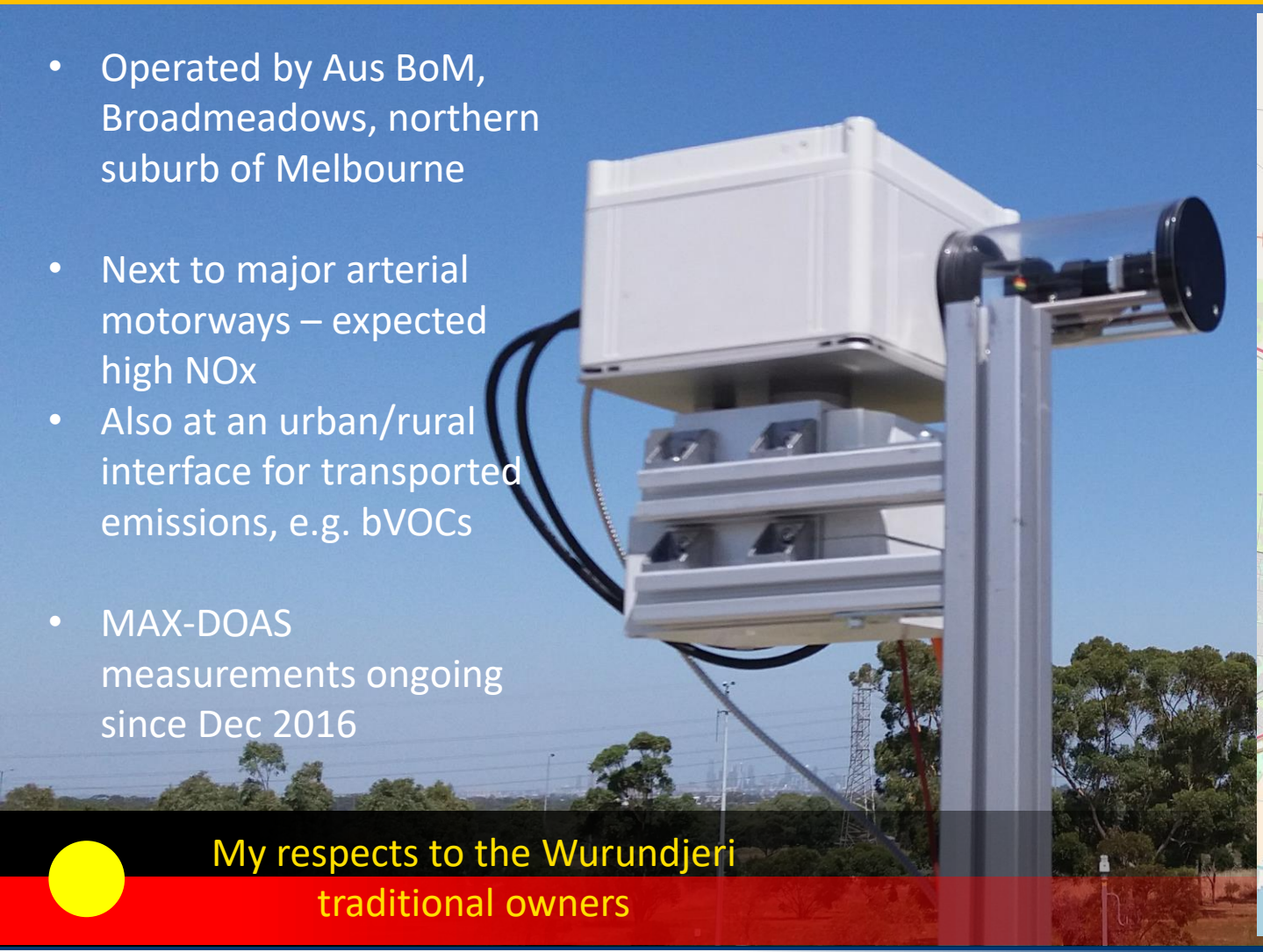
$HCHO/NO_2$ ratio (VCD/VCD)
> 2 = NO_x limited O_3 production regime
< 1 = VOC limited O_3 production regime



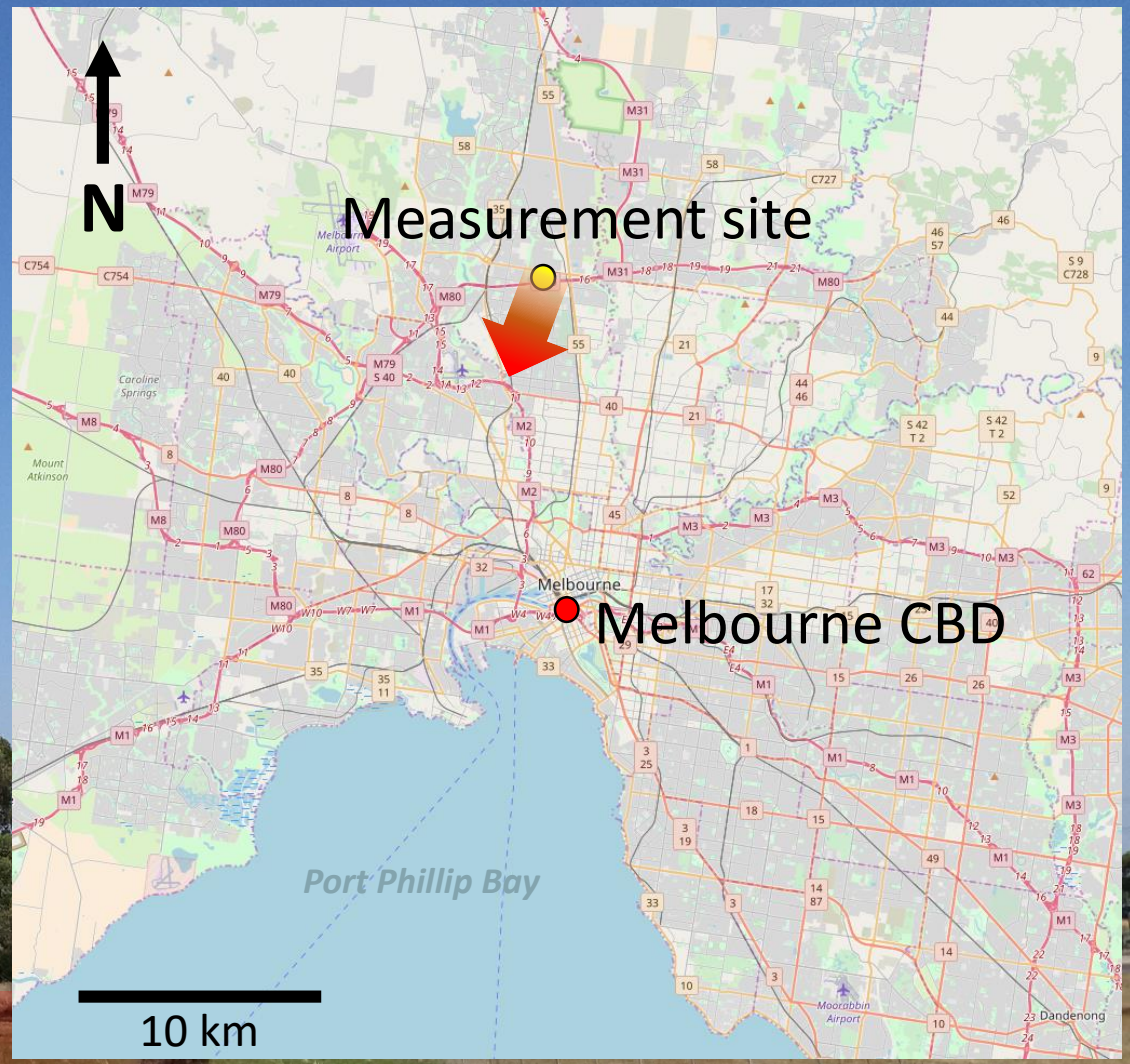


Case study 2: Broadmeadows, Australia

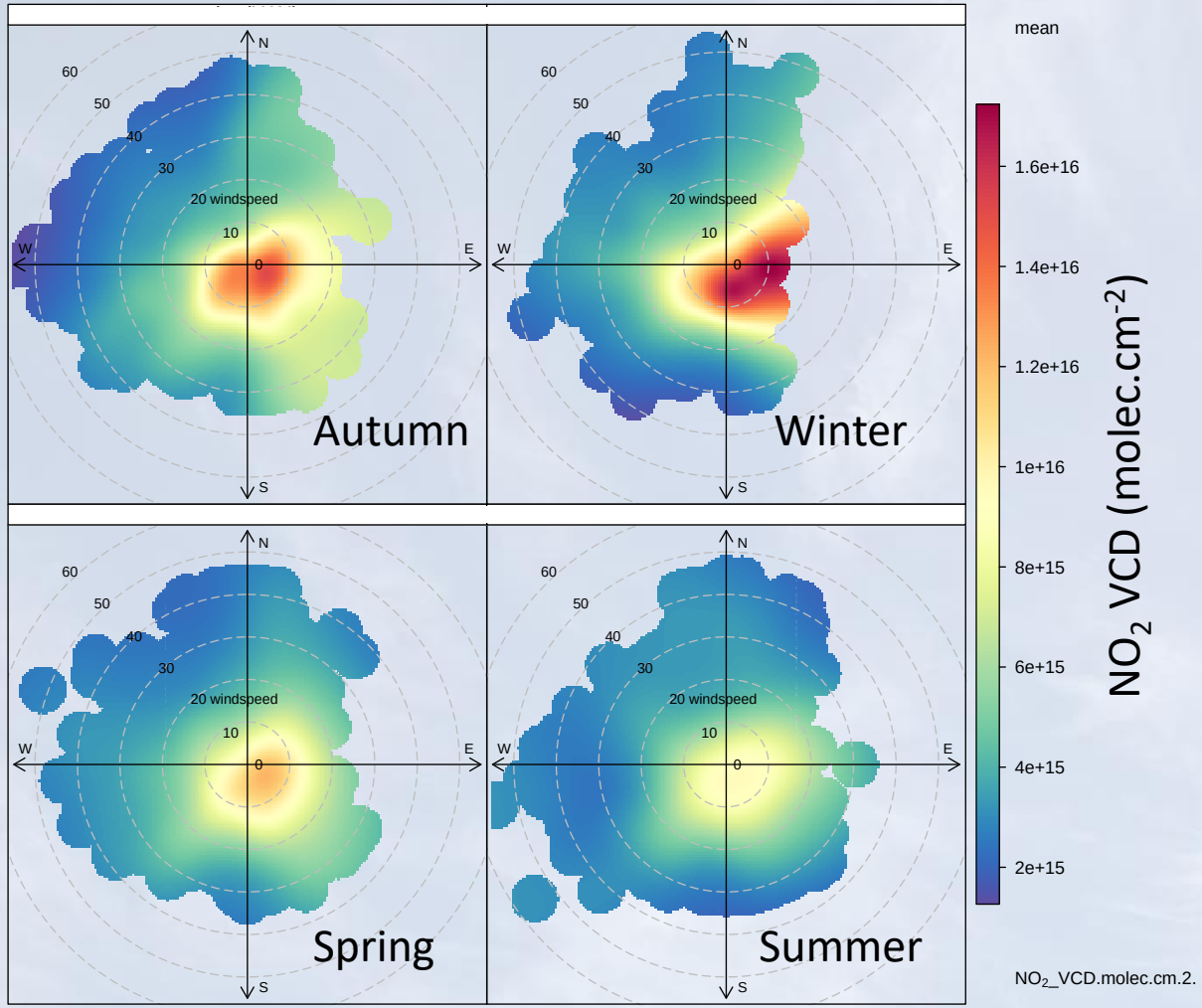
- Operated by Aus BoM, Broadmeadows, northern suburb of Melbourne
- Next to major arterial motorways – expected high NOx
- Also at an urban/rural interface for transported emissions, e.g. bVOCs
- MAX-DOAS measurements ongoing since Dec 2016



My respects to the Wurundjeri traditional owners



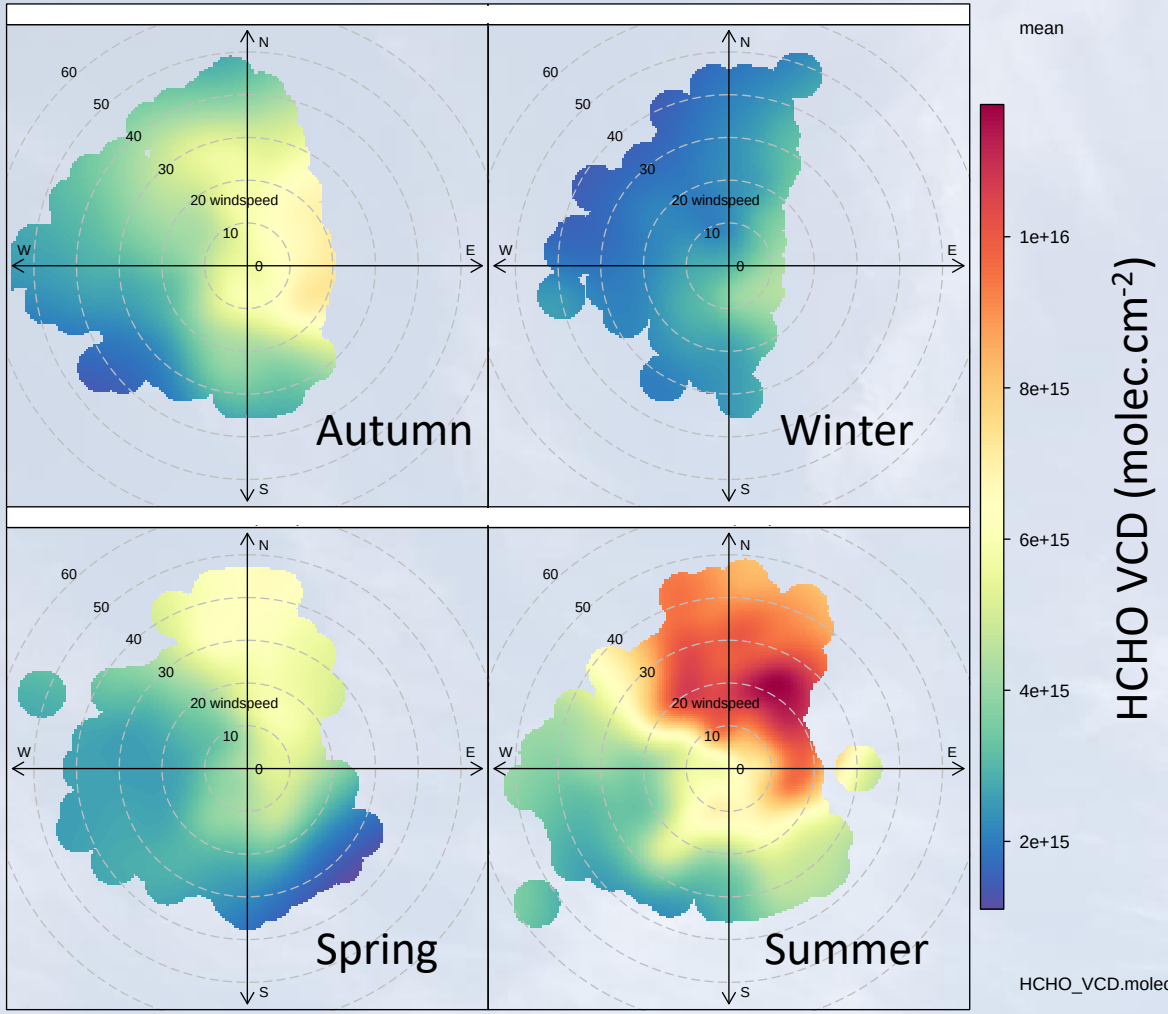
Case study 2: Broadmeadows



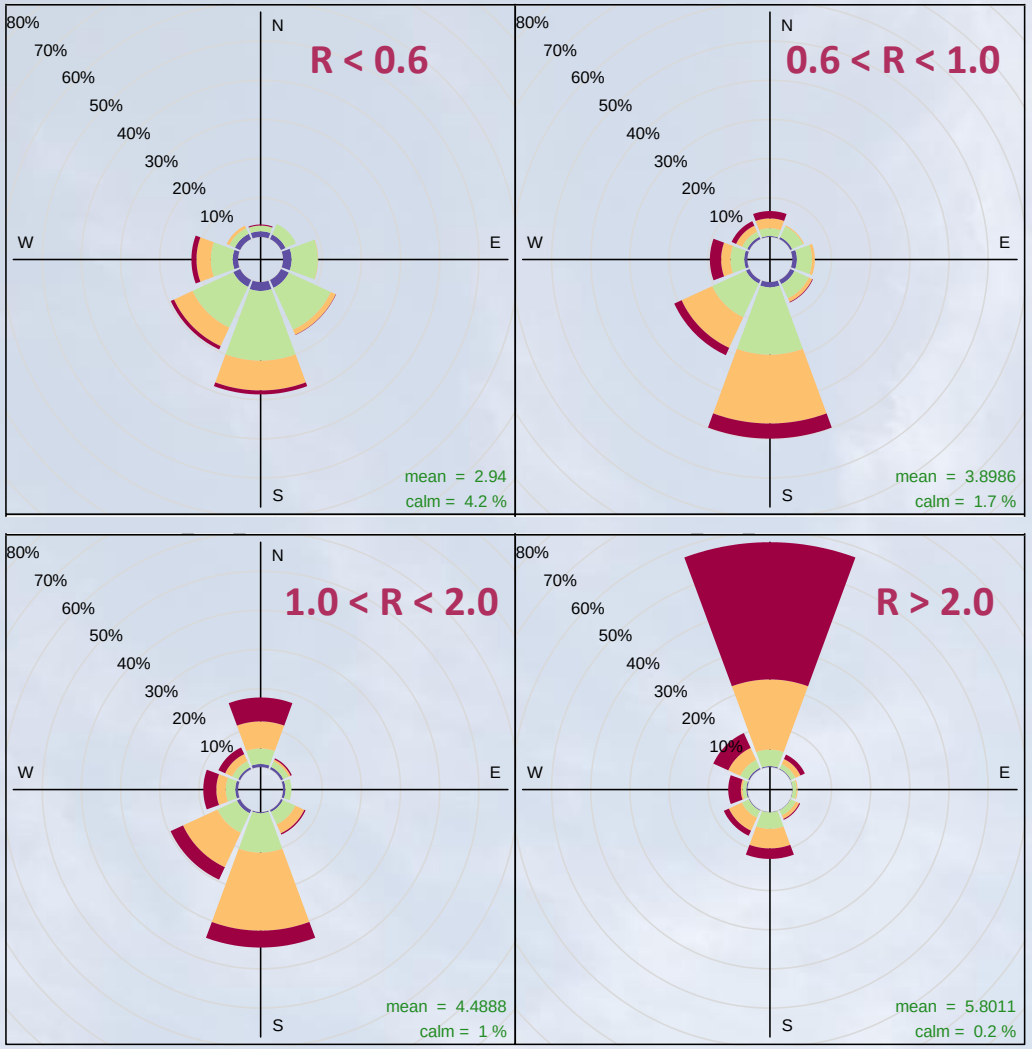
Directional distribution: NO_2

- Seasonal variation evident
- Strongest NO_2 at low wind speed indicates local production
- Consistent with adjacent road traffic

Case study 2: Broadmeadows



Controls on oxidation chemistry 1



Controls on oxidation chemistry: O_3 production regime

→ $R = HCHO_{vcd} / NO_{2\,vcd}$

- Low R means VOC-limited O_3 production rate, dominated by low wind speeds from the urban sector
- High R means NO_x-limited conditions, dominated by strong winds from the rural sector

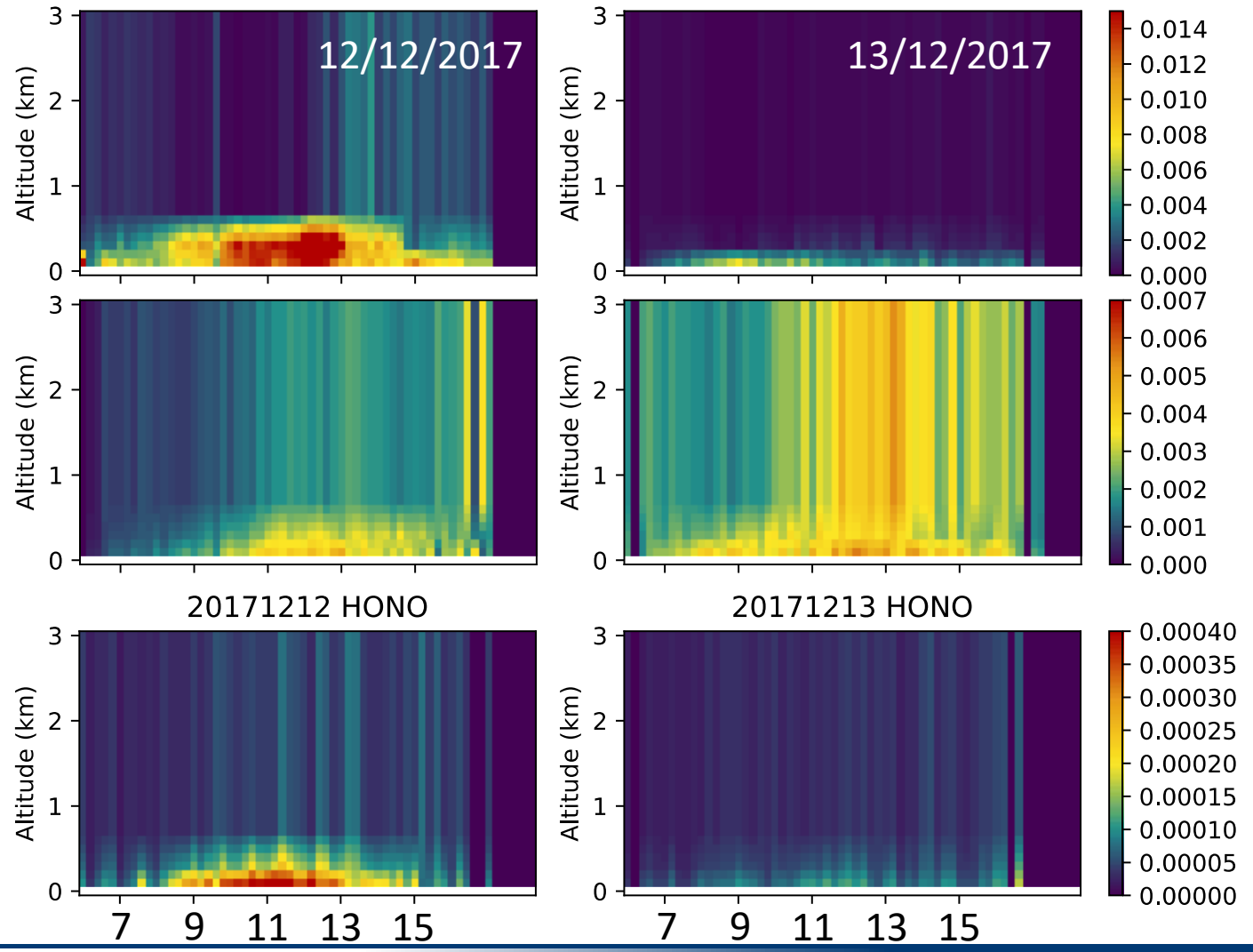
- Discernible influence of rural (bVOC) airmasses on the local atmospheric oxidation chemistry

Case study 2: Broadmeadows – Example vertical profiles

NO_2

HCHO

HONO



12/12 = Warm but calm conditions

13/12 = Hot, strong north wind

Controls on oxidation chemistry 2

Controls on oxidation chemistry: OH radical production

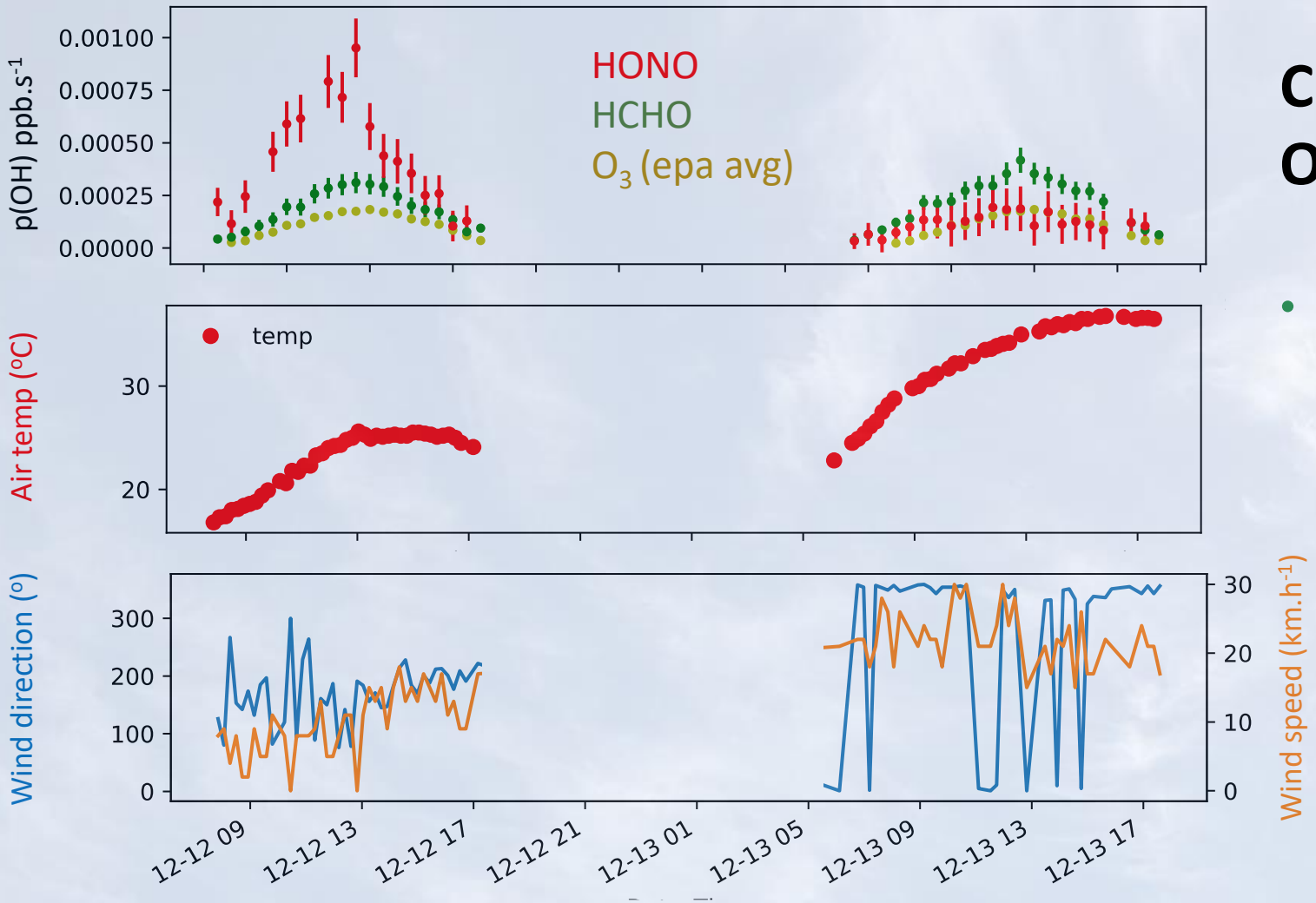
- $O_3 + h\nu \rightarrow O(^1D) + O_2$
  $O(^1D) + H_2O \rightarrow 2\ OH$
- $HONO + h\nu \rightarrow 2\ OH$
- $HCHO + hv \rightarrow H + HCO$
  $H + O_2 \rightarrow HO_2$
  $HCO + O_2 \rightarrow HO_2 + CO$
  $HO_2 + NO \rightarrow OH + NO_2$

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

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

$$P_{OH}(HCHO) = 2 \text{ x } J(HCHO) \text{ x } [HCHO]$$

Controls on oxidation chemistry



Controls on oxidation chemistry: OH radical production

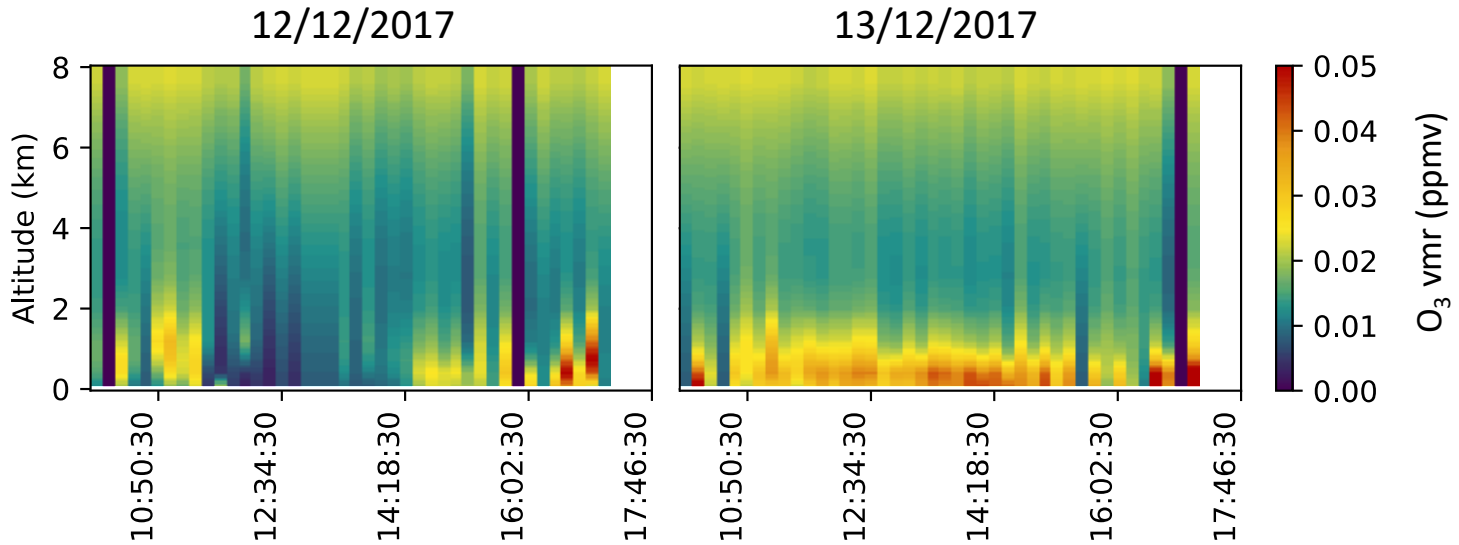
- Given strong northerly wind conditions, photolysis of HCHO can dominate the local OH radical production

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:

  SCD(O_3 trop) = SCD(O_3 total, measured) – SCD(O_3 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 NO_2, 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: O_3 and glyoxal
  - → Using these results in modelling studies – e.g. calculating absolute OH conce identifying HCHO source/s
  - → Using these results in satellite validation

Thanks for listening

rgryan@student.unimelb.edu.au

rsquared_aus

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