



Clean Air and
Urban Landscapes
Hub

National Environmental Science Programme

CAUL Project 1, Milestone 7.1.10 Report on Atmospheric VOC Measurements

Clean Air and Urban Landscapes Hub

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About the Clean Air and Urban Landscapes Hub

The Clean Air and Urban Landscapes Hub (CAUL) is a consortium of four universities: the University of Melbourne, RMIT University, the University of Western Australia and the University of Wollongong. The CAUL Hub is funded under the National Environmental Science Programme of the Australian Government's Department of ^[1]_[SEP]the Environment. The task of the CAUL Hub is to undertake research to support environmental quality in our urban areas, especially in the areas of air quality, urban greening, liveability and biodiversity, and with a focus on applying research to develop practical solutions.

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CAUL Project 7 Report for completion of Milestone 7.1.10

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Introduction

As part of CAUL Project 7 a study of spatial and temporal variability of ambient atmospheric concentrations of volatile organic compounds (VOCs) air quality variability has been undertaken at ANSTO at Lucas Heights.

The measurements have used the Biogenic Ambient Air Sampling System (BAASS), which was partially funded by CAUL as is illustrated below with a photograph taken from the ANSTO sampling location. This system is new and a significant part of the research effort has been in characterising the system and establishing the measurement protocols for anthropogenic sources and biogenic sources (Milestone 7.1.8). The data from the Lucas Heights measurement campaign has been made publically available through the AURIN database (Milestone 7.1.9). The data available via the [AURIN Portal](#). The data can be found through selecting University of Wollongong - Centre for Atmospheric Chemistry (UoW_CAC) as the Organisation within the data browser of the Portal.

The observed atmospheric concentrations of biogenic and anthropogenic VOCs will form the basis of a future scientific paper. This report outlines the basic methods and results in fulfilment of milestone 7.1.10., including the time-series of the biogenic VOCs (see Figure 1) and the anthropogenic VOCs (see Figure 2).

Biogenic Ambient Air Sampling System



Timeseries Volatile Organic Compound Measurements

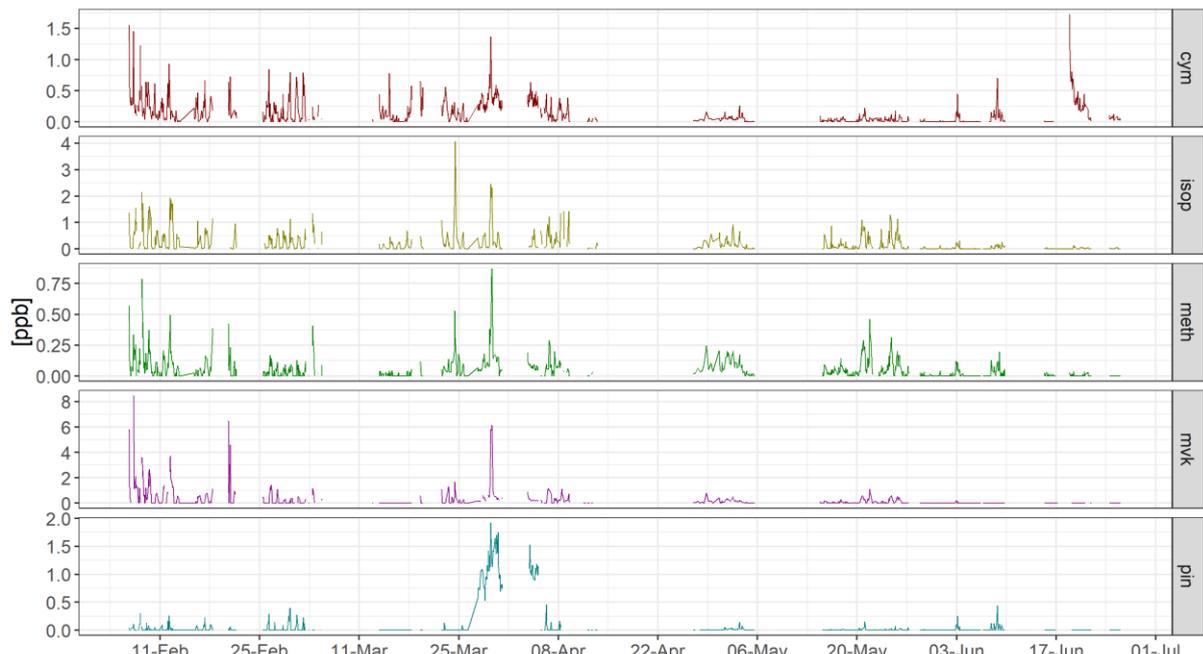


Figure 1: Biogenic VOC concentration time series for the ANSTO campaign during 2019. *cym*: p-cymene, *isop*: isoprene, *meth*: methacrolein, *mvk*: methyl-vinyl-ketone, *pin*: α -pinene

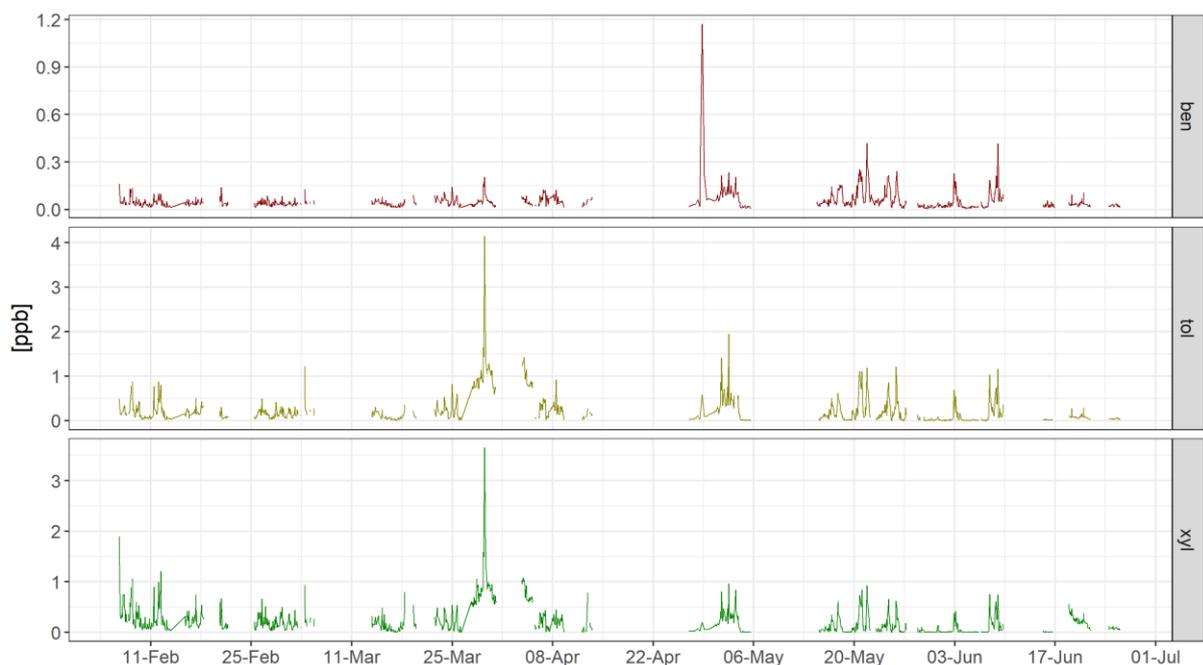


Figure 2: Anthropogenic VOC concentration time series for the ANSTO campaign during 2019. *ben*: Benzene, *tol*: toluene, *xyl*: xylene

Start: February 6th, 2019

End: June 26th, 2019

Location: -34.05°, 150.98°

Release date: 2019

Study type: long term measurement

Research topic: biogenic VOCs, ambient VOC monitoring

Keywords: VOC, biogenic, GC-MS

Abstract:

Ambient measurements of some volatile organic compounds made by continuous thermal desorption-gas chromatography-mass spectrometry in south east Australia are presented below. Measurements were made on the campus of the Australian Nuclear Science and Technology Organisation (ANSTO, Lucas Heights, NSW, Australia) on the edge of the Sydney Basin. Measurements were made on a quasi-hourly basis. Significant gaps in the measurements exist.

Methods:

a. Sampling Location

The BAASS was located at the Australian Nuclear Science and Technology Organisation (ANSTO), Lucas Heights, 2234, NSW (34°03'S 150°59'E). The site was selected as the vicinity is free of confounding sources of volatile organic compounds and its proximity to large areas of native forest, particularly to the north-northwest and southwest (Figure x). Lucas Heights is located on the edge of the Sydney Basin, 30 km southwest the centre of Sydney.

b. Sampling System

The sampling inlet was installed on a mast of the second-floor balcony of a three-storey building, 7.5 metres above ground level and 2 metres above the balcony. The inlet consisted of 3/8" ID PTFE tubing, fitted with an upside-down PTFE beaker as a rain cap. The inlet line was 25 m long. Line exposed to direct sunlight was covered in garden hose in an attempt to minimise photochemistry inline. The sample was drawn through the line at by a PTFE-coated diaphragm vacuum pump (N810 LABOPORT, KNF Neuberger, Freiburg, Germany. A 5 µm paper filter in a PTFE cartridge was installed inline to protect the pump from atmospheric particulates. The filter was changed on a quasi-monthly basis. A check valve was installed downstream of the pump. A short (~1 m) length of 1/8" ID PTFE tubing carried sample to the instrument.

c. Thermal desorption

VOC samples were analysed using a thermal desorption-gas chromatography-mass spectrometry system (TD-GC-MS). The thermal desorption system consisted of three parts. An inlet manifold (Air Server-xr, Markes International, Llantrisant, UK) with eight inlet ports. The manifold allowed sampling from the inlet, of calibration gas or laboratory air. From the Air Server, samples passed through a Peltier-cooled glass trap (Kori-xr, Markes International). This trap, held at -20°C during sampling, removed water from humid ambient samples by freezing. The trap was heated to 300°C and flushed with 50 mLmin⁻¹ UHP nitrogen between samples to vent accumulated ice. Finally, targeted analytes were collected onto a focusing trap (Unity-xr, Markes International, with General Purpose trap, U-T11GPC-2S). This trap was held at -20°C for all measurements. Following sampling completion, this trap was purged with 20 mLmin⁻¹ dry carrier gas for 2 min. The trap was then heated to 300°C to purge analytes to the GC. The VOC focussing trap was heated at

40°Csec⁻¹ and purged for 5 minutes. A split of 20 mLmin⁻¹ was used and a column flow of 1mLmin⁻¹, giving a split ratio of 20:1. Following sampling, the sampling manifold and water trap were flushed with UHP nitrogen for 5 minutes minimum at 100 mLmin⁻¹.

Ambient samples were collected at 100 mLmin⁻¹ for 30 minutes, giving a total sampled volume of 3000mL. Calibration samples of a mixture of ten targeted species (Air Liquide, Paris, France, detailed in Supplementary Table 1) were collected at 3 mLmin⁻¹ to a total sampled volume of 5 mL.

d. Gas Chromatography-Mass Spectrometry

Analytes were separated using a gas chromatograph (7890B, Agilent Technologies, Santa Clara, CA, USA) with a HP-5 MS column installed (30 m x 0.25mm ID x 0.25 µm film thickness, Agilent Technologies). The temperature program was held at 35°C for 5 minutes before ramping at 7°Cmin⁻¹ to 100°C. The ramp was then increased to 20°Cmin⁻¹ to 250°C with a final hold time of 1 minute. The program time was 28 minutes, allowing for samples to be collected on a quasi-hourly basis.

The eluent was detected using a single quadrupole electron ionisation mass spectrometer (Agilent 5977B with Xtr EI source, Agilent Technologies). The mass spectrum detector was operated in selected ion mode (SIM). Details of SIM windows are presented in Supplementary Table 2.

e. Sampling regime

Measurements were taken on a quasi-hourly basis. Sampling was near-continuous for the duration of the experiment, though large gaps exist in the measurement time-series. These gaps are associated with system maintenance and characterisation, or exhaustion of supply gases.

The sampling schedule varied throughout the campaign. Most frequently, samples were taken on a quasi-hourly basis. A calibration measurement was taken every six-to-twelve hours. The mass spectrum detector was tuned approximately every two weeks. Irregularities in sampling procedures have resulted in uneven measurement distributions across diurnal and seasonal cycles.

f. Chromatogram processing

A quality check process was applied to the results. Each chromatogram was inspected looking for the targeted ions in air samples, calibrations and blanks using the Agilent Data Navigator software. Peak height ratios between calibrations samples and blanks were used as an input to check and correct mislabelling from the software. The chromatograms were imported to the software GC-werks where the integration was made again using the clean chromatogram dataset. The final concentrations were estimated in GC-werks using the ratios between the samples and the calibration signal. Finally, the data was analysed using R to remove outliers of more than three standard deviations of the dataset.

Detailed Metadata

1. date: datetime of the measurement.
2. ben: concentration of benzene (ppb) calculated from process described in (f.).
3. cym: concentration of p-cymene (ppb) calculated from process described in (f.).
4. isop: concentration of isoprene (ppb) calculated from process described in (f.).
5. meth: concentration of methacrolein (ppb) calculated from process described in (f.).
6. pin: concentration of alpha-pinene (ppb) calculated from process described in (f.).
7. tol: concentration of toluene (ppb) calculated from process described in (f.).
8. xyl: concentration of p-xylene (ppb) calculated from process described in (f.).
9. mvk: concentration of methyl vinyl ketone (ppb) calculated from process described in (f.).

Supplementary information

Table 1: Details of calibration cylinder CC511971 used in the present measurements.

| Species | Concentration (ppb) | Uncertainty (%) |
|-------------------------------|---------------------|-----------------|
| 1,2,4-trimethylbenzene | 1110 | +/- 5 |
| 1,8-cineole (eucalyptol) | 1030 | +/- 5 |
| alpha-pinene | 1070 | +/- 5 |
| benzene | 1100 | +/- 5 |
| isoprene | 1090 | +/- 5 |
| methacrolein | 1110 | +/- 5 |
| methyl vinyl ketone | 1080 | +/- 5 |
| p-isopropyltoluene (p-cymene) | 1080 | +/- 5 |
| p-xylene | 1080 | +/- 5 |
| toluene | 1100 | +/- 5 |
| nitrogen | balance | +/- 2 |

Table 2: Details of SIM mass spectrometry detection method used in the present measurements.

| SIM time window (sec) | Ions selected (m/z) | Analytes detected (primary ion, qualifying ion) |
|-----------------------|--------------------------------------|---|
| 0-225 | 39, 53, 67, 68 | isoprene (68,67) |
| 225-300 | 41, 55, 70 | methacrolein (70,39), mvk (70,55) |
| 300-450 | 77, 78 | benzene (78,77) |
| 450-600 | 91, 92, 93 | toluene (92, 91) |
| 600-780 | 68, 91, 93, 106, 121, 136 | p-xylene (106, -) |
| 780-960 | 93, 105, 120, 121, 136 | a-pinene (136, 93), 1,2,4-trimethylbenzene (120, -) |
| 960-1800 | 81, 93, 108, 119, 121, 134, 136, 154 | p-cymene (119, 134), eucalyptol (108, 81) |