Supplementary Materials: Seasonal variation of biogenic and anthropogenic VOCs in a semi-urban area near Sydney Australia.

System description



Supplementary Figure S1. A. Instrument inlet along with a secondary meteorological station located at the roof of ANSTO facilities. B. Picture of the system including the different cylinders used during the campaign. C. General diagram of the system going from the inlet to the Mass Spectrometer.

Supplementary Table S1. Composition of the calibration cylinder used during the sampling campaign. Cylinder number CC511971 manufactured by Air Liquide, Houston, TX, USA analysed 06/12/2018.

Component	Concentration [ppb]	Accuracy
Isoprene	1090	+/-5%
Methacrolein	1110	+/-5%
MVK	1080	+/-5%
Benzene	1100	+/-5%
Toluene	1100	+/-5%
p-xylene	1080	+/-5%
α-pinene	1070	+/-5%

Component	Concentration [ppb]	Accuracy
TMB-1,2,4	1110	+/-5%
p-cymene	1080	+/-5%
Eucalyptol	1030	+/-5%

Inlet losses

Inlet VOC losses depend on two variables: the time spent in the line and the line material. We used a PTFE inlet with a 3/8" OD and 25 m length. To avoid accumulation of compounds inline, the sampling line kept a continuous flow even when the instrument was malfunctioning [68,69]. With an average sampling flow of 12 L/s the retention time in the line is less than 4 seconds. This retention time is sufficiently short to ensure losses from reactions are negligible. PTFE was selected as it is a highly inert material and therefore limits sample-surface interactions inline.

Water influence in the sampling

Ambient humidity is one of the major problems when sampling ambient air VOCs. The KORI-xr water trap used in the study is among the best method available to reduce sample humidity without disturbing the VOC in the matrix. If sampled air is too humid, damage to the trap, the sampling system or shifts in compound elution times can occur. The influence of the difference in humidity between calibration gas (dry) and ambient air was evaluated comparing neat calibration results to calibration gas diluted in ambient air (first cleaned of VOCs using the platinum-coated glass wool catalyst). From the mass spectrometer tune results, it was determined that relatively low water content was introduced with the sample so no damage to the system or the trap was expected. The changes in the elution time were evaluated graphically as shown in Supplementary Figure 2. For compounds with an elution time less than 550 s there is no change but as the temperature ramp increases, the elution time shifted by 1-5 seconds.



Supplementary Figure S2. Chromatogram comparing a dry calibration sample (blue) to a calibration sample diluted with moist ambient air. The peaks in order from top to bottom and left to right are: 1. isoprene, 2. methacrolein, 3. methyl-vinyl-ketone, 4. benzene, 5. toluene, 6. p-xylene, 7. a-pinene, 8. 1-2-4 trimethylbenzene 9. p-cymene, 10. eucalyptol. The difference in peak height is caused by the difference in mass used for the samples when using the calibration gas and the diluted mix.

Trapping efficiency and contamination

The VOC trap U-T11GPC-2S (Markes International) used in this study is designed as a general-purpose trap. The adsorbents in the trap are classified as weak and medium relative to the trapping capacity of the strongest adsorbents available. The adsorbents have a demonstrated trapping efficiency of \geq 99% for benzene, toluene, p-xylene and trimethyl-benzene [70,71] and >96% for isoprene, p-cymene, a-pinene [72,73]. Despite this, the manufacturer alerted the users of this trap to the possibility of monoterpene isomerization. Other peaks in the monoterpene range were not observed in calibration measurements during most of the sampling period.

Due to the possibility of carryover and sample contamination by the magnitude difference between the calibration gas concentration and the expected VOC in ambient air, a test was made comparing two calibration samples of ~1 ppm (5 mL sampled volume) against two diluted calibration samples of ~20 ppb (250 mL sampled volume). There was no significant difference between the measurements for any species. This implies the trap is not being saturated during high concentration calibration measurements and is able to trap as much analyte sampling a low volume with high concentrations than at a larger volume with lower concentrations.

We used a zero-volume trap fire test to check if artefacts from the trap were impacting our observations. The test was repeated three times with no significant peaks observed.

Instrument Linearity

A multipoint calibration was used to evaluate the linearity of the instrument response to each analyte. 0, 50, 100 and 400 mL of ~20 ppb diluted standard were used during this test. A final span point of a regular calibration (5 mL at 1 ppm) was also included. This test was made after the reported sampling period so TMB-1,2,4 is not included in the results. Eucalyptol is also not included due to an error during the method edition. Despite this, the total ion count for the eucalyptol peak shows similar behaviour when compared to other compounds. The results of the test are presented in Figure S3. All reported compounds showed an r^2 of ≥ 0.99 excepting a-pinene, in which no response was observed with the 50 mL sample. This is expected as the adsorbents in the trap may isomerize or not trap all monoterpenes given their weak and medium capacity to trap VOCs.



Supplementary Figure S3. Result of the linearity test of the BAASS system to multiple volumes of analyte. Where isop=isoprene, macr= methacrolein, mvk= methyl vinyl ketone, cym= p-cymene, pin= α -pinene, ben= benzene, xyl= p-xylene and tol= toluene.

Precision and repeatability

To evaluate precision and repeatability of the sampling system, multiple calibrations in sequence were sampled. Three calibrations in sequence were used and this test was repeated 8 times under different conditions. Between calibrations in the same short period of time the changes in response from the system for most of the gases is less than 5%, except for monoterpenes where the difference can be up to 15%.

Data processing and concentration estimation

The data collected during the sampling period was imported to the GCWerks software for chromatogram integration. Next a manual relabelling of some samples was applied to correct mislabels from the Agilent software. The sampling sequence usually followed a pattern of Blank-Calibration-Blank and six samples. The post-calibration blank samples were removed from the analysis due to contamination with calibration gas in the system. It was confirmed that a one-sample flush of UHP nitrogen will remove most of the calibration gas left in the system after a calibration. No contamination was observed in subsequent samples after the post calibration blank. The total carryover observed in the instrument is less than 1% of the signal in calibration samples for all ten compounds analysed in this study. When the starting column temperature was changed from 35°C to 30°C the MS SIM method was not modified. This change increased the elution times of the compounds moving TMB out of the SIM window. This error was overlooked and TMB data was not recorded after mid-April.

To clean the calibration record a "7-point rolling mean" was applied, averaging seven continuous calibration samples during the same sampling conditions. We considered that sampling conditions for the system changed when a nitrogen or zero-air tank ran out or was changed, the ion source was replaced or the instrument was malfunctioning. Each time the conditions changed, the rolling mean was stopped and restarted. Using the difference between the rolling mean and each single calibration observation, outliers where removed from the dataset. The data with a difference of more than 10% with respect to the rolling mean were removed from the subsequent analysis. The compounds with the highest variation within calibrations were the monoterpenes eucalyptol and a-pinene (Supplementary Table 2). This is attributed to the adsorbents in the VOC trap used in the system during this period.

Compound	# cals	#samples within 10%	% samples
Isoprene	320	287	90%
Methacrolein	320	287	90%
MVK	316	238	75%
Benzene	320	308	96%
Toluene	320	285	89%
p-xylene	320	282	88%
α-pinene	320	242	76%
TMB-1,2,4	318	283	89%
p-cymene	317	261	82%
Eucalyptol	320	213	67%

Supplementary Table S2. Carryover percentage to calibration. Total number of calibrations during the sampling period and results from the data filtering applied to the calibration record per compound.

Uncertainty estimation

Under normal conditions the response of an FID/MS detector is given by

$$R = \frac{S-B}{Tr_{Inlet}*Tr_{H2O} trap*Tr_{Trap}*Tr_{Desorp}*\mu*M}$$

(1)

Where *R* is the response function of the detector, the output signal per unit of analyte, *S* is the signal from the detector (peak area), *B* is the factor for contamination coming from the trap, $Tr_{H20 trap}$ is the influence of water in the trap (the transmission of VOCs through the water trap), Tr_{Trap} is the trapping efficiency of the trap for each particular analyte, Tr_{Desorp} is thermal desorption efficiency (releasing the analyte), μ is the mole fraction of the analyte and M is the number of moles of the gas sampled.

For an ambient sample:

$$R = \frac{S_{amb} - B_{amb}}{Tr_{Inlet} * Tr_{H20} trap * Tr_{Trap} amb} * Tr_{Desorp} * \mu_{amb} * M_{amb}}$$
(2)

The relationship between the mole fraction and the signal in an ambient sample is:

$$\mu_{amb} = \frac{S_{amb} - B_{amb}}{R^* Tr_{Inlet} * Tr_{H20} \operatorname{trap} * Tr_{Trap_{amb}} * Tr_{Desorp_{amb}} * M_{amb}}$$
(3)

If Tr_{Trap} and Tr_{Desorp} are the same for calibrations and air samples, a simplification is possible:

$$\mu_{amb} = \frac{(S_{amb} - B_{amb})*\mu_{cal}*M_{cal}}{Tr_{Inlet}*Tr_{H20} trap*(S_{cal} - B_{cal})*M_{amb}}$$
(4)

The uncertainty due to $\frac{\mu_{cal}*M_{cal}}{(S_{cal}-B_{cal})}$ is the uncertainty in the measured calibrations, R, to which the uncertainty in the calibration standard must be added. Then the uncertainty in $\frac{(S_{amb}-B_{amb})}{M_{amb}}$, described here as K_{amb} , is unknown. However, a reasonable assumption, comparing the variables in each, is that the uncertainty in this term is greater than the observed uncertainties in the calibrations as expressed as R, particularly because the blank term becomes more significant at lower signal values. Then the uncertainty will be

$$\left(\frac{\sigma\mu_{amb}}{\mu_{amb}}\right)^2 = \left(\frac{\sigma K_{amb}}{K_{amb}}\right)^2 + \left(\frac{\sigma R_{cal}}{R_{cal}}\right)^2 + \left(\frac{\sigma\mu_{cal}}{\mu_{cal}}\right)^2 + \left(\frac{\sigma Tr_{Inlet}}{Tr_{Inlet}}\right)^2 + \left(\frac{\sigma Tr_{H20}}{Tr_{H20}}\right)^2 \tag{5}$$

The uncertainty in R_{cal} is a lower limit for the uncertainty of the ambient uncertainty analysis. After a review of the data, a value of three times the R_{cal} is assumed. As mentioned before the losses in the inlet and the water trap are negligible. Therefore the final uncertainty in the measurements can be calculated using

$$\left(\frac{\sigma\mu_{amb}}{\mu_{amb}}\right)^2 = 4 * \left(\frac{\sigma R_{cal}}{R_{cal}}\right)^2 + \left(\frac{\sigma\mu_{cal}}{\mu_{cal}}\right)^2 \tag{6}$$

Supplementary plots



Supplementary Figure S4. Polar plot using mean concentrations of the sum of BVOCs during the sampling period separated by month. Concentrations are reported in ppb.



Supplementary Figure S5. Isoprene to isoprene + MACR + MVK ratios. Left plot is day-time data, right plot is night-time data. The black line represents a ratio of 1, representing fresh emissions. The red dotted line represents a ratio of 0.25, where the total concentrations are mostly oxidated products. There is a clear trend showing the fresher emissions coming from the south (yellow) during day time. There are higher total concentrations (Isop+ox) coming from the north (purple) but a considerable part of this mass is oxidized isoprene (lower isop-ratio).



Supplementary Figure S6. Wind roses by month during the first half of 2019 at the sampling site. The N-NE components influencing the site decrease with each passing month, hence the influence of metropolitan Sydney emissions over the site decreases from summer to winter.



Supplementary Figure S7. Data filtered to keep the stable nights to reduce variability caused by changes in meteorology. Only the moderate stable and mostly stable data (as determined by the radon analysis) was used for this analysis. A. Box plot showing the variation of the total daily mean targeted BVOC

concentration per month, along with the mean temperature of the sampling period (24 hrs) in red. The black line represents the median, the line on the box is the 95% of the distribution range and outliers are shown as black dots. The number on top of the box plots represents the number of samples per month in the analysis. The blue dot represents the overall mean concentration B. Box plot showing the total daily mean concentration of targeted AVOCs per month along with the monthly mean temperature in red. C. Daily mean concentration box plot of the monoterpenes (orange) and the sum of isoprene and its oxidation products (blue). D. Relative contribution of BVOC groups estimated from the average concentration of each group divided by the sum of both groups per month.



Supplementary Figure S8. Composite mean concentration of monoterpenes and isoprene groups by hour between February and May. On the right y-axis is the hourly average PAR for the analysed period.



Supplementary Figure S9. The concentration of the sum of isoprene and its oxidation products plotted against PAR. Data points are coloured using temperature. The high scatter in the data can be explained by the influence of days with temperatures over 30 °C. During these days the isoprene emission and the MACR and MVK formation is higher compared to days with lower temperatures, promoting transport of isoprene and its oxidation products.



Supplementary Figure S10. Wind speed frequency distribution per month during the COALA-JOEYS divided in day and night time. Only the wind speed data of the sampling period was included.