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Isoprene and monoterpene emissions in Australia: comparison of a multi-layer canopy model with MEGAN and with atmospheric concentration observations

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Abstract. One of the key challenges in atmospheric chemistry is to reduce the uncertainty of biogenic emission estimates from vegetation to the atmosphere. In Australia, eucalypt trees are a primary source of biogenic emissions, but their contribution to Australian air sheds is poorly quantified. CSIRO developed the Australian Biogenic Canopy and Grass Emissions Model (ABCGEM) 15 years ago to investigate this issue. Previously unpublished, ABCGEM is applied as an inline biogenic emissions inventory to model volatile organic compounds in the air shed overlaying Sydney, Australia. For comparison, biogenic emissions are calculated by the well-accepted Model of Emissions of Gases and Aerosols from Nature (MEGAN) for the same region using the same meteorological inputs. The two models use independent inputs of Leaf Area Index (LAI), Plant Functional Type (PFT) and emission factors. We find that LAI, a proxy for leaf biomass, has a small role in spatial, temporal and inter-model biogenic emission variability, particularly in urban areas for ABCGEM. After removing LAI as the source of the differences, we found large differences in the emission activity function for monoterpenes. In MEGAN monoterpenes are partially light dependent, reducing their dependence on temperature. In ABCGEM monoterpenes are not light dependent, meaning they continue to be emitted at high rates during hot summer days, and at night. Comparison with observations suggests that monoterpenes emitted from Australian vegetation may not be as light dependent as vegetation globally, as assumed in MEGAN.

The simplified ABCGEM model is comparable with the state-of-the-art MEGAN model when measured by normalised mean bias values between the models and observed atmospheric isoprene and monoterpene observations. Observed ratios of isoprene to monoterpene carbon in south east Australia are approximately unity. ABCGEM replicates this ratio for both emission rates and predicted concentrations, while MEGAN over-estimates by a factor of 4. This suggests the correct balance between isoprene and monoterpene emissions in ABCGEM, but their magnitudes need further assessment. We estimate the uncertainty in Australian BVOC emissions to be a factor of 2 for isoprene and 3 for monoterpenes.

This study identifies the uncertainties associated with the ABCGEM emission estimates, and data requirements necessary to improve isoprene and monoterpene emissions estimates for the application of both ABCGEM and MEGAN in Australia.

1 Introduction

The emission of biogenic volatile organic compounds (BVOCs) by vegetation and their impact on air quality was first noted by Went (1960), who proposed that their oxidation produced the "blue-haze" often seen over forested areas. Subsequent studies of biogenic emissions estimated the quantity and type of chemical species emitted from specific vegetation sources. The two most important BVOCs in terms of emissions are isoprene, and the group of $C_{10}H_{16}$ monoterpene species.

The high reactivity of BVOC emissions has significant impacts on tropospheric chemistry at both regional and global scales. In the presence of light and oxides of nitrogen (NO_x), BVOCs undergo a complex series of chemical reactions that can significantly affect atmospheric chemistry by increasing ground level ozone production. The interaction of BVOCs with

anthropogenic pollutants (e.g. NO_X, SO_2, NH_3 and organic carbon) can also lead to the production of low volatility organic compounds that can condense to form secondary organic aerosols (SOA) (Hallquist et al., 2009; Xu et al., 2015; Lin et al., 2013). SOA can affect the radiation budget at the surface of the earth, potentially impacting on climate. Biogenic SOA also contributes to the total atmospheric fine particle burden and exposure to these particles can have deleterious impacts on human health (Schwartz et al., 1996).

BVOC emissions have been studied extensively, however significant uncertainties remain in their estimation. These uncertainties include both variability in the vegetation types and variability in the emission rate. Emission rates depend on many parameters including sunlight, temperature and water availability. One of the most commonly used algorithms for estimating BVOC emission rates was proposed by Guenther et al. (1991; 1993; 1995; 1997) providing the basis for the Model of Emissions of Gases and Aerosols from Nature, MEGAN, (Guenther et al., 2006; Guenther et al., 2012). MEGAN has been used to estimate the BVOC emissions within many atmospheric chemistry models (Heald et al., 2008; Pfister et al., 2008; Stavrakou et al., 2009; Emmons et al., 2010; Millet et al., 2010; Situ et al., 2013; Kim et al., 2014; Stavrakou et al., 2014; Tilmes et al., 2015).

Recently, Emmerson et al. (2016) compared atmospheric BVOC observations in south-eastern Australia with predictions by MEGANv2.1 (hereafter referred to as 'MEGAN') when run inline within the CSIRO chemical transport model (C-CTM). There were considerable discrepancies, with isoprene over-estimated by a factor up to 6, and monoterpenes under-estimated by a factor of 4. There was no appropriate linear fix to correct these discrepancies that suited all examples. Emmerson et al. (2016) postulated that the discrepancies calculated by MEGAN in Australia were due to the emission factors, the majority coming from studies on eucalypt saplings under laboratory conditions. It may be that younger eucalypt trees emit more isoprene than adult trees in-situ.

The large isoprene sources from MEGAN cause large impacts on the atmospheric chemistry of Australian cities, many of which are surrounded by eucalypt forests. These uncertainties have caused us to revisit unpublished work from the early 2000s, when the Australian Biogenic Canopy and Grass Emissions Model (ABCGEM) was developed to provide a BVOC source for urban air sheds. ABCGEM is much simpler than MEGAN, using two emission factors to represent Australian native trees (isoprene and monoterpenes), and two for grasses. This paper will investigate how the ABCGEM and MEGAN emission rates and predicted concentrations compare. In comparing the two models, the original surface vegetation descriptions and emission factors used by each model have been maintained, enabling us to calculate a total uncertainty in biogenic emission rates for the Sydney Greater Metropolitan Region (GMR). We need to understand these inputs, both temporally and spatially, as they influence the model results. We also test ABCGEM using the input leaf area index (LAI) dataset used by MEGAN.

The observed isoprene to monoterpene concentration carbon ratios were approximately unity in south east Australia, a phenomenon not observed elsewhere in the world (Emmerson et al., 2016). In regions where isoprene dominates the monoterpene concentrations this could inhibit SOA formation (Kanawade et al., 2011). Emmerson et al. (2016) did not examine the carbon ratios calculated by MEGAN, and this work provides an opportunity to do so.

This paper is arranged as follows: section 2 describes the observations used in the study and includes two previously unpublished datasets in the GMR. We then introduce ABCGEM and the emission factors used. The ABCGEM algorithms are described in detail in the supplementary material. Section 3 documents how ABCGEM and MEGAN are set-up within the C-CTM. The results of the emission rate and predicted concentration comparison are presented in section 4 together with discussion on the causes of the differences. The conclusions in section 5 bring together our current experience with Australian BVOC modelling, and recommend further work to improve isoprene and monoterpene emission estimates in future.

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2 Methods

2.1 Details of campaign atmospheric VOC measurements

Five field campaigns conducted within the Sydney GMR provide atmospheric isoprene and monoterpene concentrations, spanning periods between 2007 and 2013. Each campaign used the same PTR-MS instrument and employed standard calibration gases. Three of the campaigns were documented in Emmerson et al. (2016): The Sydney Particle Studies located at Westmead, a suburban site (150.9961°E, 33.8014°S). SPS1 ran from 18 February – 7 March 2011, and SPS2 from 14 April – 14 May 2012, ((Cope et al., 2014) with data available from Keywood et al. (2016a) and Keywood et al. (2016b)); and MUMBA (Measurements of Urban Marine and Biogenic Air) at Wollongong, a coastal site (150.8995°E, 34.3972°S) from 22 December 2012 – 15 February 2013 (Paton-Walsh et al. (2017) with data from Guérette et al. (2017)). Dunne et al. (2017) have shown night time interference from wood smoke compounds in the isoprene signal taken during SPS2. Therefore the SPS2 isoprene observational dataset is restricted to daylight hours between 9am and 6pm.

A suite of meteorological data, including wind speed and direction were taken at each of the field campaign sites, with details given in the indicated literature.

2.1.1 Bringelly and Randwick

PTR-MS observations were undetaken in summer 2007 at Bringelly, a semi-rural site (150.7619°E, 33.9177°S, 24 January – 27 February 2007), and Randwick an inner Sydney urban site (151.2428°E, 33.9318°S, 28 February – 19 March 2007). Both sites are air quality management stations operated by the NSW government and take wind speed and direction, temperature and relative humidity measurements (www.environment.nsw.gov.au/AQMS/SiteSyd.htm). The inlet height for the PTR-MS instrument was approximately 4.5 m at both sites. Bringelly is located on council reserve land on the Ramsay road at 53 m elevation. The Randwick station is sited in the eastern suburbs of Sydney within army barracks at 28 m elevation.

The monoterpene observations at Bringelly and Randwick were based on the calibration and measurement of monoterpenes at mass to charge ratio m/z = 81. All campaign sites are marked on the map in Figure 1.

2.2 The Australian Biogenic Canopy and Grass Emissions Model (ABCGEM)

The ABCGEM model was developed 15 years ago at CSIRO to provide a spatially and temporally resolved interactive biogenic emission inventory for the C-CTM. ABCGEM treats the emissions of BVOCs from a 10-layer tree canopy (for which in-canopy gradients of temperature and radiation are parameterised) and from pasture and grasses. Cases which fall between these extremes (i.e. sparse canopy with an under-layer of pasture) are treated as a linear combination of the two separate approaches. The approach for trees is largely based on the light and temperature algorithms of Guenther et al. (1993) and Guenther (1997), whereas the approach for grass is based on Kirstine et al. (1998). The full equation set is documented in the supplementary material. ABCGEM uses LAI to calculate the column biomass, $B_{m,}$ and fractional area taken up by vegetation in each grid cell, and to scale the leaf level emission factors.

2.2.1 Choice of ABCGEM emission factors

The leaf level isoprene and monoterpene emission factors were selected when ABCGEM was first developed. The leaf-level isoprene emission factor for trees is 25 μg-C g^{-1} h^{-1}, equivalent to 11.3 mg m^{-2} h^{-1} areal total when B_m is 400 g m^{-2}. This represents the average isoprene emission factor for a set of measurements conducted on Eucalypt and Casuarina species (He et al., 2000; Benjamin et al., 1996; Nunes and Pio, 2001). The normalised lumped monoterpene emission rate for trees is 2.5 μg-C g^{-1} h^{-1} which is equivalent to 1.1 mg m^{-2} h^{-1} when B_m is 400 g m^{-2}, based on measurements on Eucalypt, Callistemon, and Pittosporum species (He et al., 2000; Benjamin et al., 1996; Nunes and Pio, 2001).

For grass, the emission factors are fixed at 0.02 μg-C g^{-1} h^{-1} for both isoprene and monoterpenes, measured by Kirstine et al. (1998) in tall pasture located ~100 km from Melbourne, Australia. The isoprene and monoterpene grass emission factors convert to 0.009 mg m^{-2} h^{-1} using the same B_m of 400 g m^{-2} as above. The isoprene grass emissions factor is 1250 times less than the tree emission factor assuming a similar column biomass. Accordingly, the monoterpene grass emission factor is 125 times lower.

2.2.2 Differences in the temperature and radiation activity functions

There are differences in the algorithms for the temperature and radiation activity functions between ABCGEM and MEGAN, which will impact on the processing of the emission factors. In ABCGEM, isoprene is light and temperature dependent, whereas monoterpenes are only temperature dependent. In MEGAN all species, including monoterpenes, have a light dependency (Guenther et al., 2012). For the major monoterpene, α-pinene, the light dependent function (LDF) in MEGAN is 0.6, where 1 represents complete light dependency (e.g. isoprene). For other monoterpenes in MEGAN the LDF ranges between 0.2 – 0.8. This means that a proportion of the MEGAN monoterpene emissions shut off at night, and there will be differences in the emission processing during the day. The temperature activity function is shown in Figure 2 (top), for isoprene and monoterpenes. The temperature activity function for isoprene in both emission models is similar until 303 K when MEGAN begins to plateau and ABCGEM keeps increasing. For monoterpenes, the ABCGEM temperature activity function is always higher than MEGAN for any monoterpene species. We plot both the light dependent and independent temperature functions for α-pinene, and then the range in light independent monoterpenes. At 293 K, the ABCGEM function is 64 % higher than the MEGAN α-pinene function and 29 % higher than MEGAN monoterpenes with a light independent function of 0.8. Figure 2 (bottom) also shows that the radiation activity function (RAF) in ABCGEM is capped at 1.066, the value of C_{L1} in equation 8 of the supplementary material. ABCGEM reaches a RAF of 1 at the standard photosynthetic active radiation (PAR) of 1000 μmol m^{-2} s^{-1}, whilst MEGAN achieves a RAF of 1 by 600 μmol m^{-2} s^{-1}. ABCGEM will produce more isoprene than MEGAN at very low light levels < 500 μmol m^{-2} s^{-1}, but at the standard PAR, MEGAN produces 29% more isoprene than ABCGEM. Observed noontime PAR at the MUMBA and SPS2 campaigns were ~1600 μmol m^{-2} s^{-1} and ~1200 μmol m^{-2} s^{-1} respectively (Emmerson et al., 2016).

3 The CSIRO Chemical Transport Model

The C-CTM is a coupled, three-dimensional Eulerian chemical-transport modelling framework, used to generate concentration fields of gas and aerosol phase species (Cope et al., 2004). The framework consists of modules to predict the meteorology, emissions, chemical processing and wet and dry deposition. An 80km resolution Australia wide domain houses three successively smaller modelling domains nested at 27km, 9km and 3km resolution respectively. The highest resolution inner grid is centred on each campaign site and extends for 180km north-south and east-west. The model extends up to 40km in the vertical in 35 levels. Chemical boundary conditions to the Australia domain are provided by a global ACCESS-UKCA model run (Woodhouse et al., 2015).

Meteorological fields are provided by the Conformal Cubic Atmospheric Model (CCAM, r2796 (McGregor and Dix, 2008)), which is a global stretched grid dynamical model. CCAM predicts atmospheric dynamical conditions, including wind velocity, turbulence, temperature, radiation and the water vapour mixing ratio. The cloud coverage predicted by CCAM provides an attenuation factor which is applied to the photosynthetically active radiation (PAR) calculation.

The chemistry scheme is the extended Carbon Bond 5 mechanism (CB05) (Sarwar et al., 2011; Sarwar et al., 2008), consisting of 65 gas phase species, 19 aerosol species and 172 reactions. The organic species are lumped according to their carbon–carbon bonding type. Particulate species are processed in a two-bin sectional scheme with inorganic processing via ISORROPIA_II

(Fountoukis and Nenes, 2007), and organic processing via the volatility basis set (Shrivastava et al., 2008). A 5 minute chemical timestep is used and all species are output on an hourly averaged basis.

Anthropogenic emissions come from the Sydney GMR inventory (NSW Department of Environment, Climate Change and Water (DECCW, 2007)) and includes 37 species. Anthropogenic sources include on- and off-road mobile, commercial, domestic and industrial point sources.

The C-CTM is set-up using two biogenic emission configurations; ABCGEM described in this paper, and MEGAN (Guenther et al., 2012) the set-up of which is described in Emmerson et al. (2016). The chemistry scheme and meteorological inputs are the same for both configurations, removing both as factors in possible model differences. Differences in the inputs required by each model are described below and in the supplementary material.

3.1 ABCGEM model setup

ABCGEM requires LAI datasets for the canopy and grass flux calculations used to calculate the amount of column biomass, B_m for canopy and grass, respectively. These data are from Lu et al. (2003) and based on Advanced Very High Resolution Radiometer Normalised Difference Vegetation Index data between 1981 and 1994. Native Australian trees are evergreen therefore an annual average LAI is used, with a peak of 6.1 m^2 m^{-2} (shown in the supplementary material). This yields a maximum fractional grid cell coverage of 0.95, occurring to the north west of the inner domain. The urban region of Sydney has a low tree LAI of between 1 - 2 m^2 m^{-2}. Note that the MUMBA inner domain is positioned further south than the other campaign domains, and the peak tree LAI in this grid is 4.6 m^2 m^{-2}.

The grass LAI dataset varies monthly, peaking at 3.6 m^2 m^{-2} within the inner domain during winter. In summer/early autumn when our field campaigns took place, the peak grass LAI ranges from 0.7 - 2.1 m^2 m^{-2}. This range yields B_m between 175 - 525 g m^{-2}, and a fractional area for grass between 0.30 – 0.65. However the negligible grass emission factors mean the grass LAI grid cells can be considered as 'empty'. In order to avoid skewing the results, we only use the tree LAI in the rest of the paper.

It is important to retain the original features of ABCGEM, including LAI, to provide an uncertainty estimate between two independently developed models on BVOC emissions in Australia. The total combined uncertainty of ABCGEM isoprene emissions at 95% confidence limits is approximately a factor of 2 (ccalculated in the supplementary material). However, to remove LAI as a cause of differences in the comparison, we also run ABCGEM replacing the tree LAI dataset with the LAI dataset used with MEGAN (following section). To avoid double counting, the grass LAI dataset is replaced with an array of zeros. This sensitivity test is referred to as 'AML'. Comparing MEGAN with AML ensures that the differences will only be due to each model's emission scheme. Comparing ABCGEM with AML shows how much of the emission uncertainties are due to choice of LAI dataset.

3.2 MEGAN model setup

MEGAN version 2.1 (Guenther et al., 2006; Guenther et al., 2012) is coupled to the C-CTM as an option for calculating BVOC emissions (Emmerson et al., 2016). MEGAN predicts the emission rates of 147 BVOCs. Vegetation data comes from an International Global Biosphere Product (Belward et al., 1999) split into plant functional types (PFTs) described in Emmerson et al (2016). Globally averaged emission factors are used to calculate the majority of MEGAN emission rates, but emission factor maps are also used for isoprene, myrcene, sabinene, limonene, 3-carene, ocimene, α-pinene, β-pinene, 2-methyl-3-buten-2-ol and NO at 1 km resolution. The MEGAN emission factor maps for Australia were produced by combining the mapped vegetation from Forests of Australia data (DAWR, 2003), with measurements of isoprene and monoterpene emissions from Australian native plant species, as described in Emmerson et al (2016). Regions where there is a large gradient in emission factors indicates a change in tree species or PFT. There are 41 monoterpene species in MEGAN, of which seven are mapped

species listed above. All 41 are lumped together inside the C-CTM as a single monoterpene species according to the CB05 chemistry scheme. MEGAN uses monthly LAI data provided by MODIS MCD15A2 version 4. Details of the MEGAN emission rate equations in this CSIRO set-up are repeated in the supplementary material.

Guenther et al. (2012) estimate uncertainties in MEGAN isoprene emissions of a factor of 2, and for monoterpenes a factor of 3. They note that in regions with few observations such as Australia, these uncertainties could be higher.

4 Results and Discussion

4.1 Emission factors as a function of LAI

In Emmerson et al. (2016), we concluded that high emission factors controlled the over-estimation of isoprene in MEGAN. Figure 3 shows the role of projected LAI, using it to sort the mapped MEGAN isoprene and monoterpene emission factors in the 3km domain in February. ABCGEM uses constant emission factors described in section 2.2.1, which are converted to area units ($\mu g\ m^{-2}\ h^{-1}$) using the B_m weighted by LAI, in 1 $m^2\ m^{-2}$ bins. The AML emission factors are the same as ABCGEM. The percentage of land area covered by each LAI bin is also shown. We omit rates where the land area represents less than 1% of the model domain. The equivalent plots for April (autumn) are shown in the supplementary material.

The ABCGEM emission factors are linearly dependent on LAI. The ABCGEM isoprene emission factors are generally lower than MEGAN, but within the MEGAN standard deviations. The positive standard deviations show MEGAN isoprene emission factors reaching 20 mg $m^{-2}\ h^{-1}$, whereas the equivalent in ABCGEM would require an LAI above 7 $m^2\ m^{-2}$. In MEGAN there is a distinct maximum at 3 - 4 $m^2\ m^{-2}$ after which the emission factors decrease. Eucalypts are the major tree species around Sydney occupying these 3 – 4 $m^2\ m^{-2}$ regions of MODIS LAI, and are assigned the highest emission factors up to 24 mg $m^{-2}\ h^{-1}$, causing the peak in Figure 3. The highest MODIS LAI is south of Sydney, and overlaps with regions of 'no data' in the Forests of Australia dataset surrounding a patch of temperate rainforest. These 'no data' regions are assigned low isoprene emission factors less than 3 mg $m^{-2}\ h^{-1}$, as are urban areas. This mixture of high and low emission factors for the MODIS LAI range 4 - 6 $m^2\ m^{-2}$ gives a reduced average emission factor causing the downturn. This is an illustration of the deficiencies in vegetation mapping adversely affecting BVOC emissions modelling.

The MEGAN monoterpene emission factors plotted are the sum of the mapped species (myrcene, sabinene, limonene, 3-carene, ocimene, α-pinene and β-pinene) and represent most of the total monoterpene mass. The monoterpene emission factors for ABCGEM and MEGAN are similar below 3 $m^2\ m^{-2}$ LAI, after which ABCGEM diverges, and is 39 % higher than MEGAN at an LAI between 4 - 5 $m^2\ m^{-2}$. However the influence of the highest ABCGEM emission factors is reduced as the percentage of grid cells occupied by LAI 4 – 5 $m^2\ m^{-2}$ is 7 %. (Figure 3, right). There is the same downturn in MEGAN monoterpene emission factors at high LAI as for isoprene, for the same reasons given above. The standard deviations in MEGAN monoterpenes are much less than for isoprene. As the bulk of the land area is occupied by LAI less than 4 $m^2\ m^{-2}$, the ABCGEM and MEGAN monoterpene emission factors are similar.

LAI is a key input factor to both models, but has more influence on BVOC emission factors in ABCGEM as the fractional areas covered by vegetation are controlled by the LAI. In MEGAN these fractional areas are controlled by the PFT maps. Broadleaf evergreen trees (Eucalypts) occupy up to 95% of the non-urban region of the Sydney model domain (Emmerson et al., 2016). These emission factors are processed by emission activity functions incorporating radiation, temperature, LAI and PFT datasets, with both spatial and temporal differences, to calculate the emission rates.

4.2 Emission rates as a function of LAI

Figure 4 presents the calculated average emission rates (including AML) from the 3km domains sorted by the LAI parameter. The MEGAN monoterpene emission rates and concentrations used in the rest of this paper are the sum of 41 monoterpene species, and not just the 7 mapped species used in the previous section. Figure 4 shows each model's average emission rates with binned LAI, omitting rates where the land area represents less than 1% of the model domain. The plots are arranged by time of year, with MUMBA first (January, Southern Hemisphere summer) to SPS2 (April). The standard deviation in emission rates are shown as error bars.

Figure 4 shows the MEGAN isoprene emission rates have a greater relative variability than ABCGEM or AML. MEGAN has a more enhanced curve to the isoprene emission rates versus LAI, with a peak at 3 - 4 m^2 m^{-2}, decreasing with denser canopies for the reasons in the previous section. The ABCGEM isoprene emission rates increase with LAI, but are not linear, indicating the processing of the emission factors. In summer the isoprene emission estimates from MEGAN are distinctly higher than ABCGEM or AML, whereas there was some overlap in their emission factors from Figure 3. This demonstrates the impacts of the lower radiation activity function in ABCGEM across the main part of the day. Reduced temperatures and light levels in autumn cause substantial overlap in the SPS2 isoprene emission rates for all models.

The AML domain average isoprene and monoterpene emission rates are 10% and 20% respectively different from ABCGEM and suggests that the choice (and age) of the LAI dataset is not critical to the BVOC emission estimates.

The ABCGEM and AML monoterpene emission rates are almost linear with LAI only overlapping with MEGAN below 2 m^2 m^{-2}. When the LAI is more than 4 m^2 m^{-2} the ABCGEM and AML monoterpene emission rates are 2 - 3 times greater than MEGAN and the separation increases at high LAI, similar to Figure 3. Whilst the monoterpene emission factors are similar between ABCGEM and MEGAN, and the influence of LAI is removed in AML, the lower MEGAN monoterpenes are impacted by the temperature activity function. To demonstrate the day/night differences, the SPS1 monoterpene emission rates are split into daytime and night-time hours (shown in the supplementary material). By reducing the impact temperature has on monoterpene emission rates, the MEGAN gradients in monoterpene emission rates are approximately 3 times lower than ABCGEM and AML during the day and night.

Overall the isoprene and monoterpene emissions rates show a greater divergence between ABCGEM and MEGAN than the emission factors. This arises because of differences in the emission activity algorithms and parameters within the two models.

4.4 Spatial distribution of emission rates

The spatial distribution in the emission rates are now examined using the SPS1 campaign as an example. Figure 5 shows maps of the grid cell average emission rates for ABCGEM, AML and MEGAN, followed by the differences between them. The difference plots subtract the ABCGEM or AML emission rates from MEGAN, where red shows positive differences (MEGAN higher) and blue shows negative differences (MEGAN lower). Equivalent maps for SPS2 are shown in the supplementary material to demonstrate the seasonal differences.

The SPS1 peak isoprene emission rate of 6473 g km^{-2} h^{-1} for MEGAN occurs to the north west of Westmead in the Blue Mountain ranges, matching with the location of the highest emission factors. The peak ABCGEM isoprene emission rate of 2441 g km^{-2} h^{-1} occurs to the north east of Westmead (near Wyong), at the location of the highest projected LAI. The AML peak isoprene emission rate occurs in the same location as ABCGEM due to high LAI here, but is slightly lower at 2391 g km^{-2} h^{-1}. Where MEGAN shows inland patches with no emissions, these are due to zero emission factors at these locations, e.g. Lake Burragorang, west of Bringelly. ABCGEM relies entirely on the LAI distribution to place the emissions, and neither the

ABCGEM nor MODIS LAI distribution recognise these lake features. Again this is an illustration of the deficiencies in vegetation mapping adversely affecting BVOC emissions modelling.

In the isoprene difference plots, MEGAN predicts 1000 – 4000 g km^{-2} h^{-1} more isoprene to the west and north of Sydney than ABCGEM/AML. However MEGAN predicts 100 – 1000 g km^{-2} h^{-1} less isoprene than ABCGEM/AML in the urban regions where the field campaigns took place, contrary to the domain averages. In this urban zone, MEGAN has a low fraction of plant coverage (30%) and an isoprene emission factor less than 3 mg m^{-2} h^{-1}. In ABCGEM (and AML) the urban fraction of plant coverage and emission factors are dependent on the projected LAI which is 1 - 2 m^2 m^{-2} here. Thus ABCGEM vegetation covers a larger area of the urban grid cells (39 - 63%), and the corresponding emission factor is also larger (2.8 - 5.7 mg m^{-2} h^{-1}) than MEGAN. These spatial patterns reiterate that a key difference between the two isoprene emission models is the input vegetation coverage.

The peak ABCGEM monoterpene emission rate of 1701 g km^{-2} h^{-1} also occurs in the north east of the domain (near Wyong), and is more than three times the peak monoterpene emission rate at the same location in MEGAN. ABCGEM and AML predict between 0 - 300 g km^{-2} h^{-1} more than MEGAN over most of the domain. The only location where MEGAN predicts higher monoterpene emission rates than ABCGEM, occurs about 30 km southwest of Sydney (shown in red, Figure 5d). MEGAN predicts 0 – 300 g km^{-2} h^{-1} more monoterpenes than ABCGEM, but this difference is not observed between MEGAN and AML and must result from a difference in the LAI dataset. At this location, the ABCGEM LAI is 0.6 m^2 m^{-2} and is considered to be 'urban'. The MODIS LAI is 3 m^2 m^{-2} and corresponds with a region of "Eucalypt medium woodland" when overlaid on the Forests of Australia inventory (on which the MEGAN emission factors are based). This same feature is present for isoprene, though is less visible in Figure 5c because differences elsewhere in the domain are also large. These differences are due to the spatial distribution of the LAI dataset.

Geometric mean emission rates are calculated for each of the models and presented in Table 1. The MEGAN isoprene emission rates are a factor of 1.7 larger (range 1.4 – 2.1) than ABCGEM across the five field campaigns, with the higher values occurring in summer. As the AML isoprene emission rates are a factor of 0.9 times lower than ABCGEM, MEGAN is a factor of 1.9 higher (range 1.5 - 2.5) than AML. For monoterpenes, the ABCGEM emission rates are larger than MEGAN by a factor of 2.1 (range 2.0 – 2.4), with the larger values tending towards autumn. AML monoterpenes are a factor of 1.7 higher (range 1.5 -1.9) than MEGAN, and a factor of 0.8 lower than ABCGEM.

Table 1 presents the ratio of isoprene to monoterpene carbon for these geometric mean emission rates. This carbon ratio must be controlled by metabolic processes within the plants and as such is a valid test of the models. The average carbon ratio for ABCGEM is 1.3 (range 0.8 – 1.5), AML is also 1.3 (range 0.9 – 1.6), whilst the MEGAN ratio is higher at 4.4 (range 2.7 – 5.3). Whilst these ranges demonstrate the substantial uncertainties in the estimated emission rates, the ABCGEM and AML ratios are more in line with Australian observed ratios.

4.5 Predicted versus observed atmospheric concentrations

Concentrations of isoprene and monoterpenes from the time periods and locations of each field campaign have been extracted from the models to compare with the PTR-MS observations. The transport and chemical schemes are the same in each model therefore for any particular campaign, the concentration differences between the ABCGEM, AML and MEGAN models should directly scale to the differences in emission rates between the models. Campaign average diurnal cycles are shown in Figure 6, with the percentage of points within a factor of 2 of the observations.

ABCGEM predicts isoprene and monoterpene concentrations closer to those observed compared to MEGAN. In all of the 10 cases ABCGEM predicts an equal or higher number of points within a factor of two of the observations than MEGAN. AML

generally predicts higher isoprene and monoterpene concentrations for all campaigns than ABCGEM because the campaign sites are within the urban zone where the MODIS LAI is higher than the ABCGEM LAI.

As the MODIS LAI is the more modern of the two datasets, it makes sense to upgrade ABCGEM with it, despite causing the urban BVOC emission factors to be overestimated due to ABCGEM's one tree species approach. The urban areas in the Sydney GMR have a substantial proportion of imported deciduous tree species. ABCGEM could be improved by introducing another tree species to the model and by revisiting the negligible impact of the grass emissions model.

Usually isoprene peaks with solar noon, but the modelled and observed isoprene at Randwick peaks at 9 am, decreasing afterwards (Figure 6). All models show isoprene increasing after 7pm which suggests the phenomena is not a function of the emission model, but the meteorology. A stable nocturnal boundary layer develops post 7 pm. The isoprene decrease after 9am is due to a change in wind direction, bringing marine air with low BVOCs to the Randwick site. Randwick is close to the coast, therefore local isoprene emissions do not build up with easterly winds. Peak monoterpene concentrations occur at night, so are not affected by the daytime onshore breezes. The MUMBA campaign site is also coastal. The wind direction at MUMBA switches from south west to north east later in the day, travelling over land regions and allowing isoprene to be present during the day. Wind roses have been plotted for each of the campaigns and are shown in the supplementary material, along with a detailed hourly analysis for MUMBA and Randwick. These support the above analysis.

The daytime ABCGEM and AML isoprene atmospheric concentrations estimated for SPS2 are greater than those predicted by MEGAN. Whilst the domain average isoprene emission rates in ABCGEM are lower than MEGAN for SPS2, the ABCGEM isoprene emission rates in urban areas are higher than MEGAN. This is a combination of the ABCGEM emission factors being directly scaled by the LAI, and low wind speeds (less than 2 m s^{-1}), allowing isoprene to build up.

At all sites except Bringelly, ABCGEM represents the shape and magnitude of the observed monoterpene diurnal cycles well, whilst MEGAN under-predicts. This suggests that the light independent method of processing monoterpenes is more in line with these observations. Monoterpene emissions from boreal pine forests are also described well using a temperature dependent function (Tarvainen et al., 2005). Monoterpene storage pools in Australian native vegetation may behave differently to the average global conditions represented in MEGAN, and in-situ observations in Australia are necessary to determine the process correctly.

Average monoterpene emission rates for SPS1 are of a similar magnitude at Bringelly, yet the observed concentrations at Bringelly are half those observed for SPS1, resulting in a large over-prediction at Bringelly by all models. These observations suggest that biomass present during the Bringelly campaign was less than SPS1, highlighting the need for time-specific LAI and PFT data, rather than using static monthly data for all years.

Table 2 gives the campaign average atmospheric concentrations from the models and the observations. We also include the observed isoprene to monoterpene carbon ratios, which were presented in Emmerson et al. (2016) for SPS1, SPS2 and MUMBA. The observed carbon ratios for Bringelly (1.5) and Randwick (1.0) datasets roughly conform to the unity phenomena in SE Australia with all the measurements giving an average of 1.2 (range 0.9 – 1.5). In the models the average carbon ratio across all campaigns is 1.2 (range 0.7 – 1.7) for ABCGEM, 1.0 (range 0.6 – 1.4) for AML and 4.1 (range 1.7 – 7.3) for MEGAN, similar to the emission rate results. Whilst the carbon ratios for ABCGEM and AML are more within the observed range, suggesting the balance between isoprene and monoterpene emissions are about right, there is still work to be done on the magnitudes of these emissions.

Figure 7 shows a quantile-quantile (q-q) plot, where all modelled and observed data from all five field campaigns are paired in time and ranked from low to high concentrations, forming one line per emission model. Logarithmic axes are chosen as the region below 1 ppb represents 93% of the observed data points (for observed isoprene 24% are between 0.01 - 0.1 ppb, 69% are between 0.1 - 1 ppb with only 7% above 1 ppb). For ease of comparison, a 1:1 line is plotted. All models predict isoprene concentrations that are too low at observations < 0.3 ppb, after which all models over-predict.

Normalised mean biases (NMB) have been calculated comparing each emission model to the ranked observations (equation 1), where P are the predicted concentrations and O are the observed concentrations. An NMB closer to zero is regarded as the better comparison.

$$\mathrm{NMB} = \frac{\sum(\mathrm{P}-\mathrm{O})}{\sum \mathrm{O}} \quad (1)$$

MEGAN has least bias for the lowest 50% of the isoprene data points from 0.01 to 0.28 ppb of observed isoprene, whilst AML is most biased. ABCGEM is less biased for the upper 50% of data points from 0.28 – 7.1 ppb of observed isoprene, and MEGAN is most biased. With the inputs used in this study, the overall NMB for isoprene is 0.45 for ABCGEM, compared to 0.67 for AML and 1.39 for MEGAN.

The monoterpene q-q plot has been clipped to observations > 0.04 ppb, which was the limit of detection at Bringelly and Randwick. ABCGEM is less biased for the first 90% of data points from 0.04 – 2.7 ppb of observed monoterpene; MEGAN least biased for the last 10%. AML is more biased than ABCGEM and tends to over-predict at all observed concentrations, whilst MEGAN mainly under-predicts. Overall, the monoterpene NMB for ABCGEM is 0.33, 0.56 for AML and -0.28 for MEGAN. NMB calculations for each field campaign considered individually are shown in Table 2.

One goal in this work is to calculate a total uncertainty in BVOC emissions rates for the Sydney GMR. Taking the NMB between the models and observations, Table 2 provides one approach where the scatter from model to model and campaign to campaign are identified as a measure of uncertainty. The 95% confidence limits from the NMBs in Table 2 are equivalent to uncertainties of factors of ~2 for isoprene and ~3 for monoterpenes. This is consistent with the factors of 4 difference in the modelled carbon rations between ABCGEM and MEGAN.

5 Conclusions

This work demonstrates the differences that are obtained from two relatively independent approaches to isoprene and monoterpene emissions modelling. We present ABCGEM, a tree canopy and grass model for dynamically estimating isoprene and monoterpene emissions from vegetation in Australia. ABCGEM is compared with the well-established MEGAN model both in terms of estimated emission rates and also via simulated and observed atmospheric concentrations of isoprene and monoterpenes. Both models are run within the C-CTM, for five field studies within the Sydney GMR, in New South Wales, Australia. Both models use the same meteorology and chemistry scheme from the C-CTM but each have independent inputs for LAI and BVOC emission factors. We examined the differences in the LAI input by running ABCGEM with MODIS LAI, (AML), resulting in small differences of 10% and 20% in isoprene and monoterpene emission rates, respectively.

The isoprene emission factors used in MEGAN are in a similar range to the LAI-weighted ABCGEM emission factors, but the MEGAN standard deviations extend much higher than ABCGEM. The eucalypt trees surrounding Sydney have a projected LAI in the 3 - 4 m^2 m^{-2} region, where MEGAN isoprene emission factors are about 50% higher than ABCGEM. For monoterpenes, the ABCGEM emission factors increase linearly, whilst the MEGAN emission factors peak at 3 m^2 m^{-2}

thereafter decreasing due to averaging of high and low emission factors at high LAI. As the bulk of the LAI in the 3km domain is less than 4 $m^2 m^{-2}$, the ABCGEM monoterpene emission factors are similar to MEGAN.

There are differences in the temperature and radiation activity functions between ABCGEM and MEGAN, causing MEGAN to produce more isoprene and less monoterpenes than ABCGEM on an Australian summer's day, if all other inputs are equal. Isoprene emission rates determined via the radiation activity function are higher in MEGAN than ABCGEM at light levels above 600 μmol m^{-2} s^{-1}. Using the geometric mean emission rates, the MEGAN isoprene emission rates across the five field campaigns are a factor of 1.7 larger (range 1.4 – 2.1) than ABCGEM and a factor 1.9 larger (range 1.5 - 2.5) than AML.

The monoterpene emission factors are similar between the models, but the resulting emission rates are very different because MEGAN has a light dependence whereas ABCGEM does not. MEGAN emission rates are lower than ABCGEM by a factor of 2.1 (range 2.0 – 2.4), and lower than AML by a factor of 1.7 (range 1.5 -1.8). During summer, the temperature activity function plays a significant role in monoterpene production, with 64% higher rates at 293 K in ABCGEM than for α-pinene in MEGAN, the largest monoterpene compound by mass.

The distribution of ABCGEM, AML and MEGAN emission rates are spatially different, with ABCGEM and AML predicting peak isoprene to the north east of Sydney, and MEGAN predicting peak isoprene to the north west of Sydney. In ABCGEM and AML the emission rate distributions are dependent on the LAI dataset, whereas in MEGAN the impact of LAI is less dominant than the emission factors maps. ABCGEM and AML predict more isoprene in urban regions than MEGAN. Here the MEGAN isoprene emission factor is less than 3 mg m^{-2} h^{-1}, whereas ABCGEM scales the emission factors by LAI, leading to urban isoprene emissions in the 2.8 – 5.7 mg m^{-2} h^{-1} region. For monoterpene emission rates, ABCGEM and AML are a factor of 2 -3 higher than MEGAN everywhere in the domain, apart from a small region south of Sydney where the LAI datasets disagree on the extent of the urban area.

The concentrations of isoprene and monoterpenes from the model runs were compared to PTR-MS observations made at each field campaign site. As the transport and chemical processing were the same in each model, the differences in modelled concentrations were due to the differences in calculated emission rates. For four of the five campaigns the ABCGEM model predicts lower isoprene concentrations and higher monoterpene concentrations than the MEGAN model. ABCGEM had a higher number of modelled concentrations within a factor of 2 of the observations than MEGAN or AML for both isoprene and monoterpene comparisons. MEGAN tends to under-predict concentrations of Australian monoterpenes by a factor of 3, which could be due to the application of light dependence to monoterpene species, rather than the raw emission factors being too low. Monoterpenes from Australian vegetation may not be as light dependent as vegetation globally, and this can only be ascertained though in-situ measurements.

In south east Australia we are starting to see a trend of unity for campaign average observed ratios of isoprene to monoterpene carbon, not observed in other parts of the world. In this study we present two additional observed datasets conforming to this phenomena. The ABCGEM model predicts isoprene and monoterpene concentrations producing an average carbon ratio of 1.2, and 1.0 for AML. MEGAN over-predicts isoprene and under-predicts monoterpene concentrations to the extent that the average carbon ratio is 4.1. These ratios are also calculated for the geometric mean emission rates for each model, with ABCGEM and AML at 1.3 and MEGAN at 4.4. In ABCGEM this suggests the balance between isoprene and monoterpene emissions are about right, but there is still work to be done on the magnitudes of these emissions.

We calculate a total uncertainty for Australian BVOC emissions of a factor of 2 for isoprene and a factor of 3 for monoterpenes, based on a combination of modelling and observations. This provides a guide to the uncertainty that might be expected in applying an emission model to a region where the VOC emissions have not been observed or modelled previously.

These comparisons are undertaken to strengthen understanding and to identify ways to reduce uncertainty in emissions of isoprene and monoterpenes in Australia. Whilst more work is needed to uncover the underlying causes of the reported differences, the simplified ABCGEM model is a fair predictor of observed isoprene and monoterpene concentrations for these simulations of the Sydney air shed, compared with the state-of-the-art MEGAN model. We have highlighted the roles of the spatial and temporal distributions of LAI and the correct mapping of plant species or plant functional types in this modelling. Improvements to ABCGEM will concentrate on BVOC emission factors in urban areas, by introducing another tree species and revisiting the assumptions made in the grass model. For MEGAN, we propose that the light dependence of monoterpenes from Australian vegetation is examined in detail through targeted measurements.

Data Provision

Observed PTR-MS data is available for SPS1 (http://doi.org/10.4225/08/57903B83D6A5D), SPS2 (http://doi.org/10.4225/08/5791B5528BD63) and MUMBA (https://doi.pangaea.de/10.1594/PANGAEA.871982). The Bringelly and Randwick PTR-MS data are available from the author.

The MODIS LAI data product was retrieved from MCD15A2 version 4 from the online Data Pool, courtesy of the NASA Land Processes Distributed Active Archive Center (LP DAAC), USGS/Earth Resources Observation and Science (EROS) Center, Sioux Falls, South Dakota, https://lpdaac.usgs.gov/data_access/data_pool.

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Table 1 Geometric mean emission rates, g km^{-2} h^{-1} for isoprene and monoterpenes across the five field campaigns. The difference between the geometric means is also given as a factor, using MEGAN/ABCGEM for isoprene and ABCGEM/MEGAN for monoterpenes. Result for AML given in brackets.

	Isoprene			Monoterpenes			Ratio isoprene to monoterpene carbon	
	ABCGEM (AML)	MEGAN	Difference M/A	ABCGEM (AML)	MEGAN	Difference A/M	ABCGEM (AML)	MEGAN
MUMBA	1489 (1238)	3123	2.1 (2.5)	598 (435)	297	2.0 (1.5)	1.2 (1.4)	5.3
Bringelly	1738 (1487)	2849	1.6 (1.9)	574 (474)	283	2.0 (1.7)	1.5 (1.6)	5.0
SPS1	1562 (1467)	2767	1.8 (1.9)	608 (534)	295	2.1 (1.8)	1.3 (1.4)	4.7
Randwick	1385 (1159)	2039	1.5 (1.8)	486 (410)	228	2.1 (1.8)	1.4 (1.4)	4.5
SPS2	372 (339)	516	1.4 (1.5)	229 (180)	96	2.4 (1.9)	0.8 (0.9)	2.7

Table 2 Comparison of the observed atmospheric concentrations of isoprene and monoterpenes to model estimates from ABCGEM and MEGAN. NMB= normalised mean bias.

		Isoprene		**Monoterpenes**		**Ratio isoprene to monoterpene carbon**
		Average Concentration, ppb	NMB	Average Concentration, ppb	NMB	
MUMBA	Observed	0.28		0.12		1.2
	ABCGEM	0.34	0.18	0.14	0.12	1.2
	AML	0.28	0.01	0.17	0.37	0.8
	MEGAN	0.88	1.96	0.06	-0.50	7.3
Bringelly	Observed	0.48		0.16		1.5
	ABCGEM	0.83	0.69	0.62	2.80	0.7
	AML	0.97	1.18	0.75	3.10	0.6
	MEGAN	1.47	1.55	0.43	1.32	1.7
SPS1	Observed	0.76		0.44		0.9
	ABCGEM	1.00	0.37	0.36	-0.17	1.4
	AML	1.23	0.61	0.45	0.00	1.4
	MEGAN	1.35	0.89	0.21	-0.53	3.2
Randwick	Observed	0.28		0.14		1.0
	ABCGEM	0.37	-0.22	0.11	-0.50	1.7
	AML	0.38	-0.26	0.13	-0.52	1.5
	MEGAN	1.11	-0.58	0.09	-0.61	6.2
SPS2	Observed	0.54*		0.46		N/A*
	ABCGEM	0.72	1.02	0.37	-0.16	1.0
	AML	0.85	1.61	0.48	0.09	0.9
	MEGAN	0.70	0.75	0.17	-0.61	2.1

* SPS2 average observed concentration of isoprene is different from Emmerson et al. (2016) because evening/night data has been removed due to wood smoke contamination.

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Figure 1 Physical map of the Sydney Greater Metropolitan Region, showing the position of the field campaign sites in relation to the surrounding forested regions. Map produced by QGIS using Google physical layer.

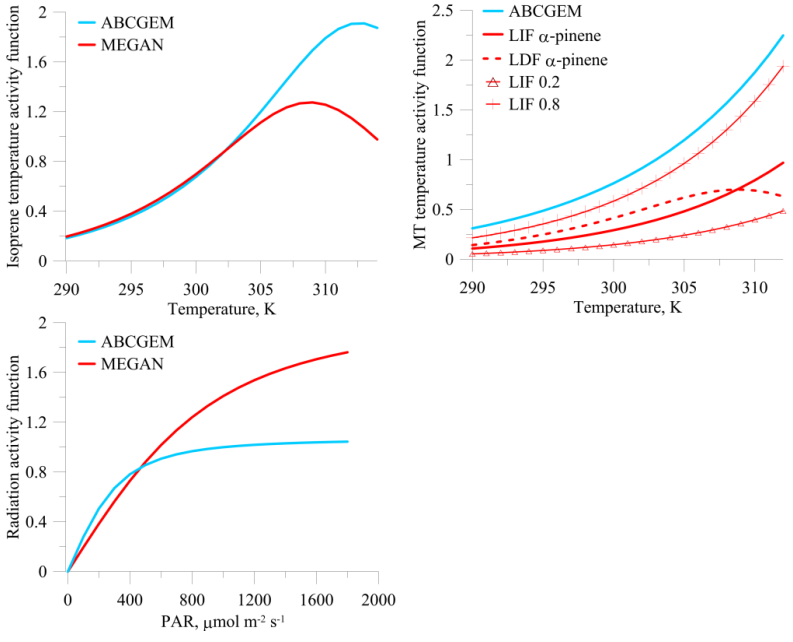

Figure 2 (top) Temperature activity functions in ABCGEM (blue) and MEGAN (red) for isoprene (left) and monoterpenes (MT, right). LIF is light independent fraction, LDF is light dependent fraction. (bottom) Radiation activity function, demonstrated for non-shaded leaves.

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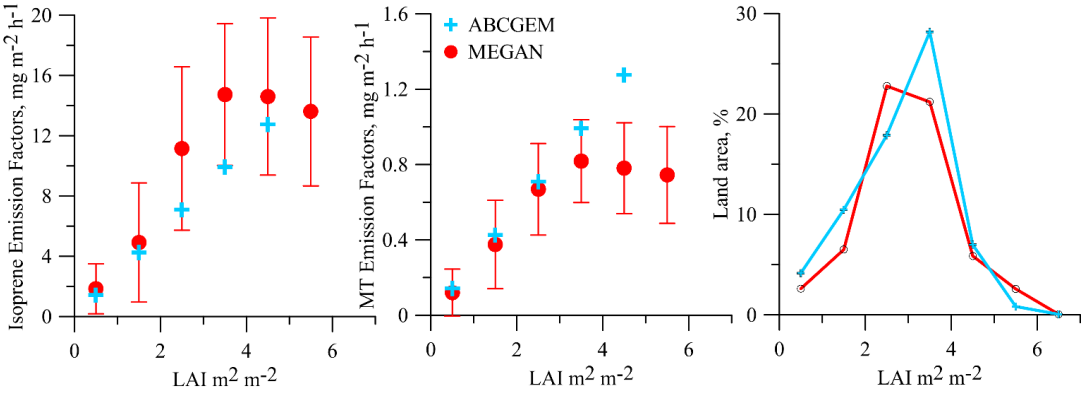

Figure 3 Scatter plot of the canopy isoprene (left) and monoterpene (MT, middle) emission factors across the Sydney domain with LAI for ABCGEM and MEGAN during February. Note y-axes are not the same. (Right) percentage of land area within each LAI bin in February. Error bars represent ± 1 standard deviation.

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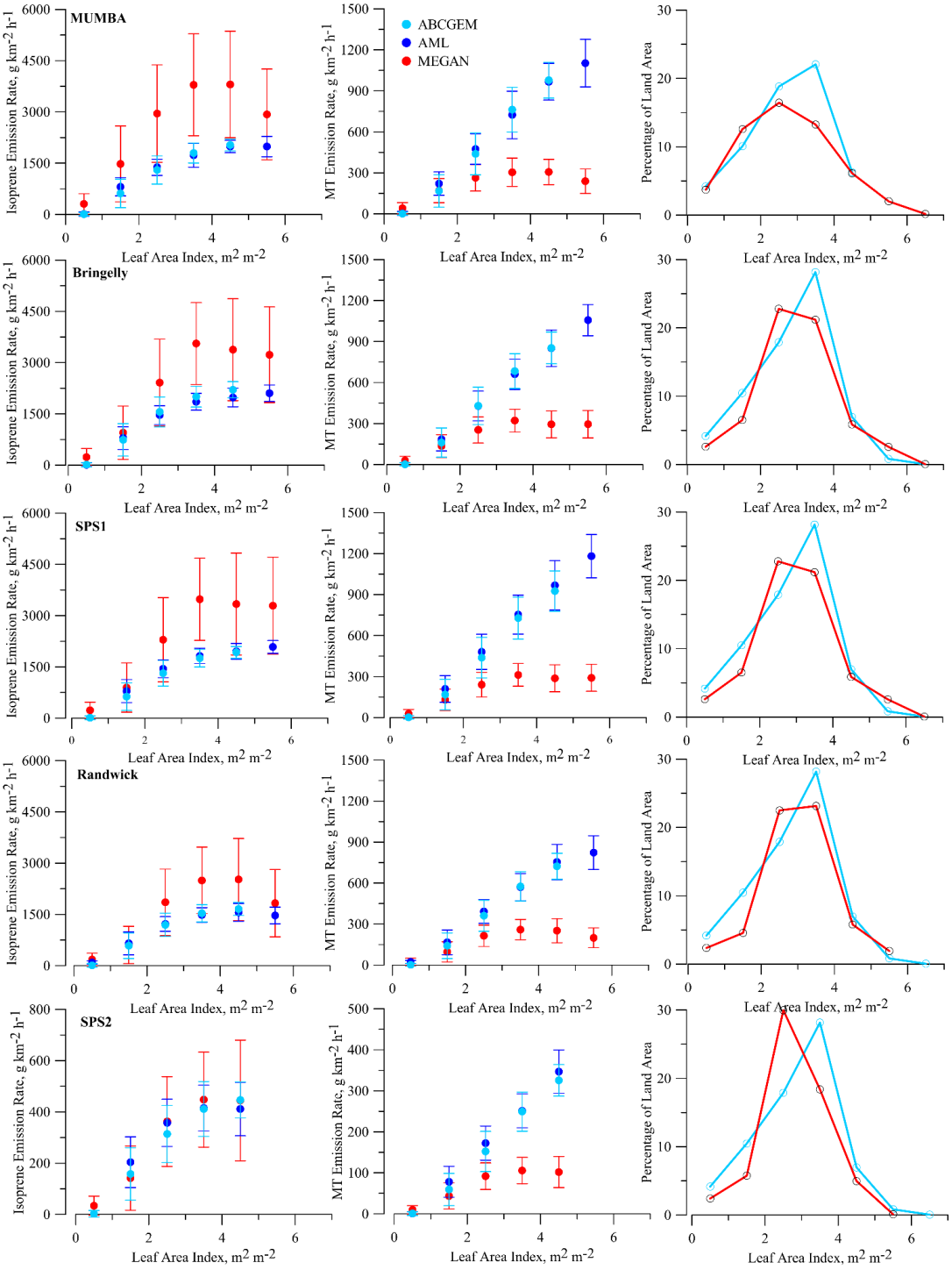

Figure 4 Distribution of grid cell average emission rates with leaf area index for ABCGEM, AML and MEGAN (left) isoprene and (middle) monoterpenes (MT). Error bars are ±1 standard deviation. (Right) Percentage of land area within each LAI bin for the ABCGEM and MEGAN MODIS LAI datasets.

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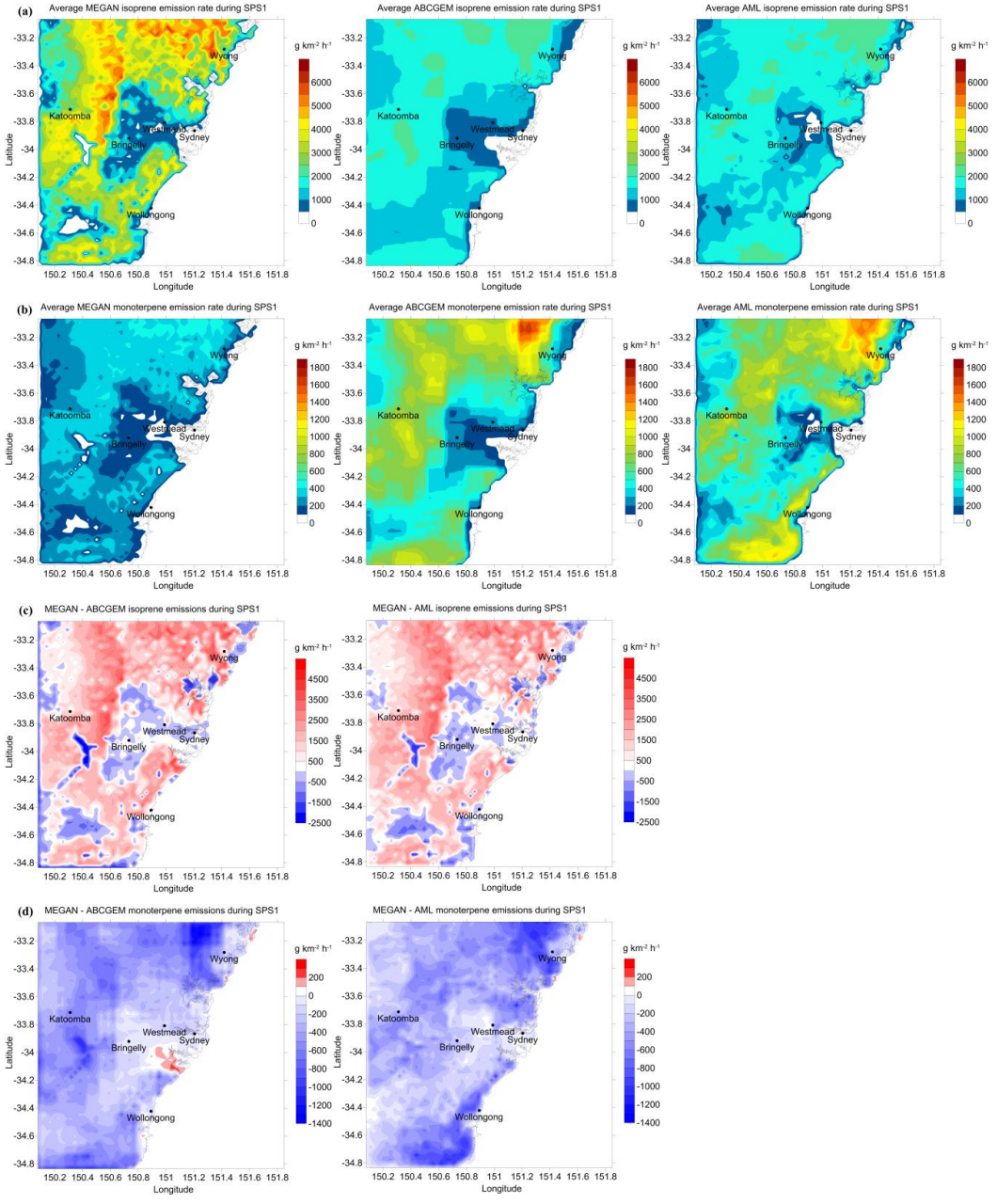

Figure 5 Spatial distributions of grid cell average emission rates for (a) isoprene (b) monoterpenes, and the differences between MEGAN with ABCGEM or AML emission rates for (c) isoprene and (d) monoterpenes for the SPS1 campaign. Note: scales are unalike for isoprene and monoterpenes.

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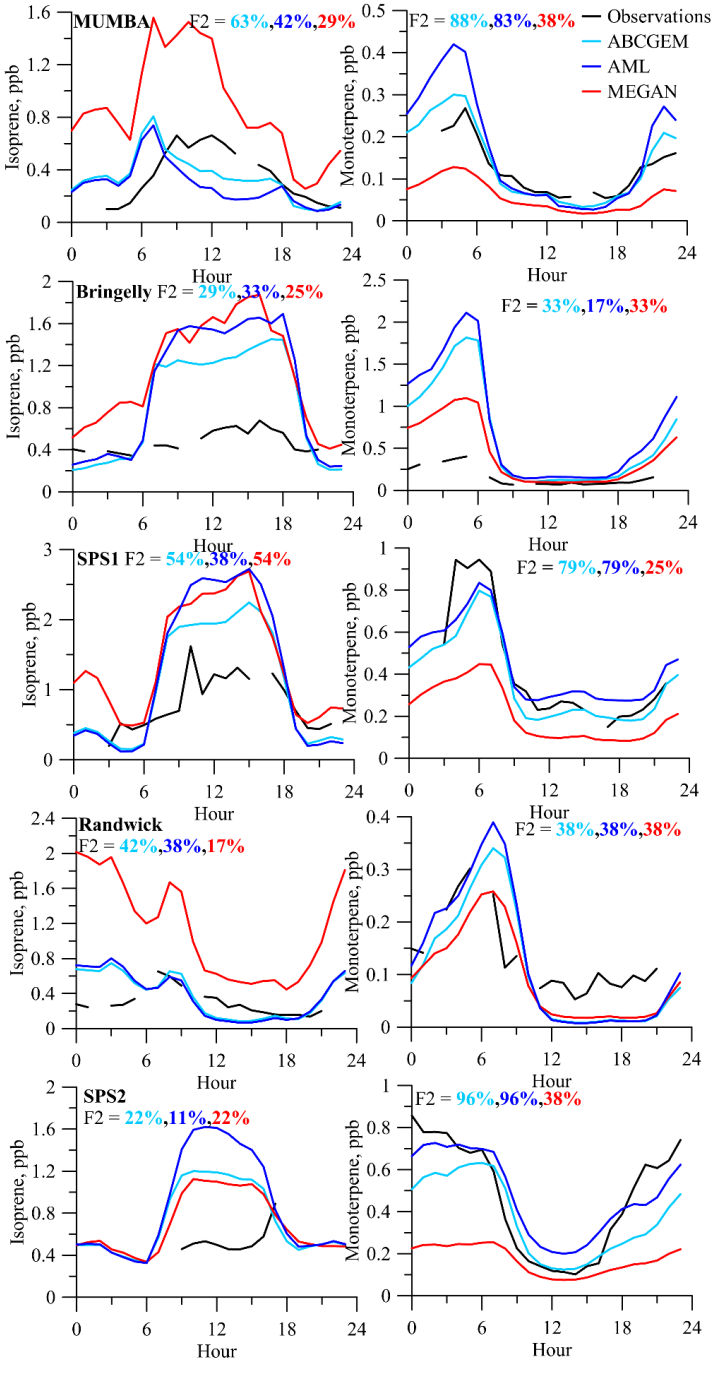

Figure 6 Diurnal time series of modelled and observed isoprene (left) and monoterpenes (right) at MUMBA, Bringelly, SPS1, Randwick and SPS2. F2 is the percentage of points within a factor of 2 of the observations.

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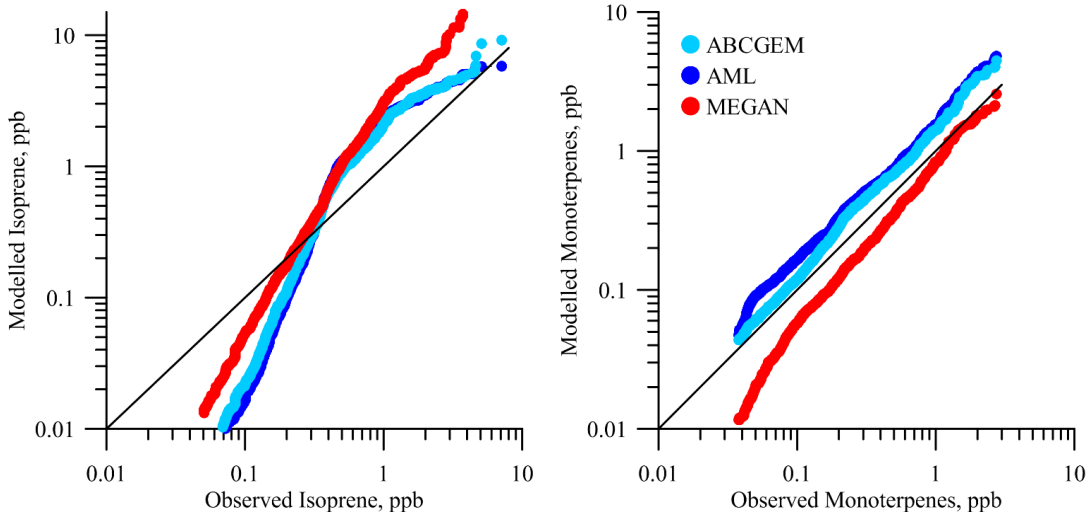

Figure 7 Quantile-quantile plots comparing all observed data to the coincident modelled data for (left) isoprene and (right) monoterpenes. The solid line represents the 1:1 ratio. The y-axis in the isoprene plot is restricted to 15 ppb, as peak MUMBA modelled isoprene reaches 30 ppb.