A BIOGENIC VOLATILE ORGANIC COMPOUNDS EMISSION INVENTORY FOR THE METROPOLITAN AIR QUALITY STUDY (MAQS) REGION OF NSW

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Abstract

An emission inventory for volatile organic compounds (VOCs) emitted from biogenic sources has been developed for the Metropolitan Air Quality Study region (MAQSR) of NSW Australia (Fig. 1). The spatially and temporally varying inventory was developed based on a Geographic Information System (GIS), remote sensing data and field measurement data. The inventory has a spatial resolution of 1x1 km^2 and a time resolution of 1 hour. Urban, agricultural and natural land-use distributions in the MAQS region were combined with biomass factors for each land-use category to produce a spatially resolved biomass inventory. A biogenic emission inventory was then developed by combining the biomass inventory with hourly emission rates for trees, shrubs and cut and uncut grass species. Biogenic emission rates were measured for 19 native tree species representative of the region and 6 types of grass using an enclosure method. Real time measurements of isoprene and its oxidation products were made in several forested areas within the study region and compared to model predictions. Canopy and grass models, which take into account radiation, shading, temperature, biomass and leaf area index were developed based on the experimental results and recent literature values.

Keywords: Biogenic VOC; Isoprene, Monoterpene, Emission Inventory, MAQS region

1. Introduction

Biogenic emissions are defined as all pollutants emitted from non-anthropogenic sources. These emissions can significantly change the total emission fluxes of volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) estimated for a given airshed and for the global atmosphere. To assess the impact of reactive VOCs on local, regional and global ozone formation accurate estimates of the magnitude of VOCs and NO_x emissions from natural sources are necessary and a reliable emission inventory is required.

It is well known that biogenic VOCs emitted from vegetation play a key role in atmospheric chemical processes within the planetary boundary layer and have a significant impact on photochemical processes which result in the formation of oxidants such as O_3 and secondary organic aerosols. During the atmospheric oxidation of biogenic VOCs, short-lived intermediate reaction products such as radicals, peroxides and aldehydes are produced. These intermediate species undergo complex chemical reactions where nitrogen oxide (NO) is converted to nitrogen dioxide (NO_2), which is a precursor reaction for ozone formation. Because the interaction between NO_x and VOCs affect atmospheric ozone levels, biogenic emissions should be included in any inventory which will be used to predict or to monitor atmospheric ozone levels. Accurate estimates of biogenic emissions are critical for regional photochemical modelling where biogenic VOCs may comprise a significant fraction of the total VOCs inventory of a given airshed.

Concern about the critical role of biogenic VOCs emissions is reinforced by the fact that isoprene, one of the major constituents of biogenic VOCs emissions, is very photo-reactive (Went, 1960, Guenther et al., 1995, 2000), making biogenic emissions an even more important source of VOCs. Isoprene was found to be approximately 3 times more photochemically reactive than a weighted

average of VOCs emitted in vehicle exhaust (Carter, 1994).
Biogenic VOCs emissions are influenced primarily by five factors namely ambient temperature, vegetation type and density, solar radiation and cloud cover. Valid inputs for air quality models depend on correct spatial allocation of both plant species and coverage areas.
For NSW, the biogenic component of the current Greater Metropolitan Air Quality Study (GMAQS) inventory (Carnovale et al., 1996) was developed using limited databases of vegetation distributions and emission factors that may not be adequate for the NSW environment. In addition the models used to construct the existing biogenic emission inventory were based on US studies, which concentrated on deciduous and coniferous species. The GMAQS inventory adopted eucalyptus as the surrogate emitter for all vegetation in GMAQS region. Biogenic VOCs emissions in the GMAQS region were assumed to consist of 40 percent isoprene, 40 percent cineole and 20 percent monoterpenes (by carbon) during the day, with isoprene set to zero at night (Carnovale et al., 1996). In addition, the calculation of isoprene emission was estimated to become light saturated within one hour of sunrise and remain so until one hour before sunset.

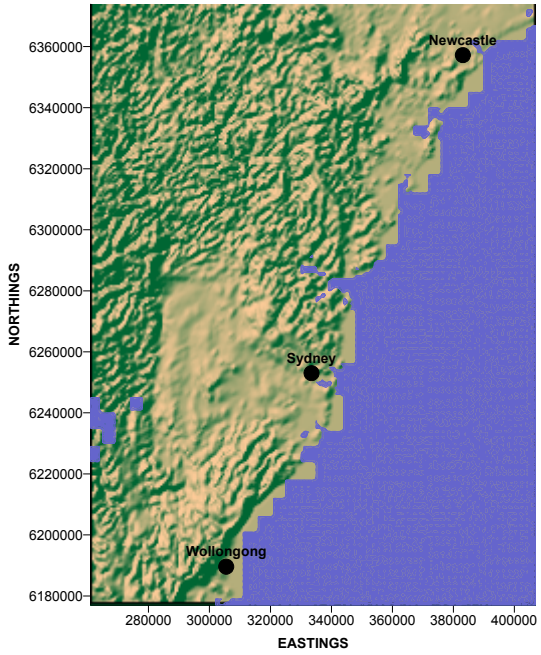

Figure 1. Extent of the Greater Metropolitan Air Quality Study (MAQS) region of NSW

The Environmental Research Program of the Environment Trust of NSW funded CSIRO to conduct a study of biogenic emissions from trees and grasses representative of those found in the Sydney region (Nelson et al., 2004).
The objectives of the study were to:

- measure emission fluxes from a range of Australian species;
- determine the effects of temperature and photosynthetically active radiation (PAR) on emission rates;
- compare the measurements of emission rates with the empirical relationships developed by Guenther et al., (1993);
- measure emissions from common grasses found in the Sydney region;
- review the available information on emissions from eucalypt and other species, and develop an Australian database of emissions;
- develop and use a Graphical Information System (GIS) to combine the emissions database with information on land use, biomass distribution, seasonal land-use emission rate factors, seasonal temperature and light intensity, to produce a spatially and temporally resolved biogenic emissions inventory for the Greater Sydney Region;
- produce the emissions inventory in a format most suitable for airshed modelling purposes.

2. METHODOLOGY

2.1. Plant Species Selection

The vegetation mix of Sydney and environs is very diverse and contains a large assemblage of plant communities. In the highly urbanised parts of the region, significant clearing and alteration of the original native vegetation cover has occurred. However, the Sydney region is bounded by a series of national parks and reserves where the native vegetation remains relatively intact. There are also numerous pockets of remnant bush and parkland within the metropolitan area which contribute significantly to the total vegetation cover. Within this range of plant communities are hundreds of individual species. It was not practical within the scope of this project to measure emissions from every species of plant within the Sydney region, so it was important that the plants selected for measurement were representative of the vegetation of the region. In developing an inventory of biogenic emissions, it was also necessary to have some information on the relative abundance of the plants within each community. Given the relative lack of vegetation surveys of the Sydney region which provide information on the abundance of the main canopy species, plant selections for this project

were made by assuming that the Smith and Smith (1990) survey was representative of the rest of Sydney's bushland. A total nineteen species of plant were selected for the characterisation of VOC emissions (Nelson et al., 2004).

2.2. Measurement of Tree Species Emissions

Biogenic VOCs are often separated into three classes: isoprene, monoterpenes and other reactive VOCs. In this work, we have focused on isoprene and monoterpenes. Measured isoprene fluxes were found to vary between 0 and 5.9 mg m^{-2} hr^{-1}. The data collected from the laboratory experiments (Nelson et al. 2004) showed that isoprene emissions from the selected plant categories were found to vary by a factor of more than 20 from about 0.1 to 2.2 mg m^{-2} hr^{-1}. The minimum and maximum fluxes measured for E. *saligna* and E. *haemastoma* also varied by factors of more than ten. For most of the other plants the difference was usually less than a factor of five. However, terpenes were present at lower levels than isoprene and were typically less than 10% of the total biogenic emissions

Field sampling for isoprene and its photochemically-derived oxidation products was performed at a number of forested locations in the greater Sydney region. The results showed that isoprene emissions correlated with ambient temperature and the measured concentrations varied between 0.12 to 4.5 ppbv (Fig 2). In addition, the isoprene oxidation products MVK and methacrolein in the samples were measured at concentrations in the range 0.05-0.69 ppbv and 0.03-0.38 ppbv, respectively.

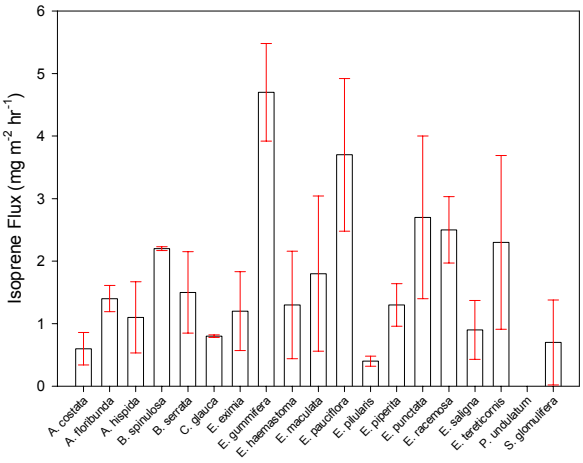

Figure 2: Graphical representation of the laboratory isoprene emission fluxes for the 19 plant species studied. The red error bars are +_ one standard deviation.

2.3. Measurement of Grasses Emissions

The combined emissions of biogenic VOCs from grass and cut grass have the potential to make a significant contribution to the production of photochemical ozone in large urban airsheds. Biogenic emission fluxes from six common turf grass cutting and grass species were determined. Measurement results showed that uncut grass could contribute about 3 x 10^9 grams of VOCs per year within the Sydney airshed (Nelson et al. 2004). The volatile compounds emitted by the uncut grass are primarily oxygenated hydrocarbons that are relatively stable in the atmosphere and would have lifetimes in the order of weeks. Only about 5 % of the emissions from uncut grass consist of reactive chemical species such as isoprene, monoterpenes and the hexenyl compounds, which have reaction rate constants with hydroxyl radicals comparable to those of xylene or ethylene. Cut grass, both through the transient emissions immediately after cutting and those resulting during the drying phase, produces about 4 x 10^9 grams of VOCs per year in the Sydney airshed (Nelson et al., 2004). Of these emissions, nearly 50 % are reactive hexenyl compounds. It is estimated that the VOC emissions from grass and cut grass contribute a total of 2 % of the annual VOC budget for the Sydney airshed.

3. DATA REQUIREMENTS

In order to generate spatially and temporally varying BVOC emission fluxes, the following data sets were used:

- Genus-specific emissions of the selected biogenic species (i.e. isoprene and monoterpenes) in units of µg per g-dm per h (where g-dm refers to grams of dry leaf mass) or µg per m^2 of leaf area (one-sided) per h;
- Spatial distribution of plant genera;
- Spatial distribution of leaf area index (LAI), which is a measure of the leaf area (m^2) per m^2 of ground area;
- Spatial distribution of leaf biomass (B_m), which is the leaf dry mass (g) per m^2 of ground area;
- Spatial distribution of canopy height (he) in metres;
- Spatial and temporal distribution of leaf temperature (T) in ºC;
- Geographical location (latitude, longitude) for the calculation of solar zenith angle and the determination of clear sky photosynthetically active radiation (PAR) in molecules or µE per cm^2 of surface area;
- Time and date as required for the determination of PAR.

As implemented, the GIS-Biogenic Emission Inventory (BEI-GIS) software has been designed to process a variety of data formats at arbitrary spatial resolution. This will allow users to readily import data sets with improved spatial resolution at a later date.

The spatial data (or spatial/temporal data in the case of temperature) data supplied with the BEI-GIS has been collected from three main sources.

- Geoscience Australian (formally AUSLIG – for the purpose of this document, this data set will be referred as the AUSLIG data). www.ga.gov.au/nmd/products/thematic/veg.htm
- CSIRO Division of Land and Water (DLW; Dean Greatz, personal communication), who provided gridded (0.05° horizontal grid spacing) estimates of LAI and B_m.
- Spatial/temporal distributions of leaf-level temperature as predicted by The Air Pollution Model (TAPM, http://www.dar.csiro.au/tapm/index.html).

4. CALCULATION OF BIOGENIC VOC EMISSION RATES

The BIE-GIS is operated using a simple, custom built graphical user interface (GUI), (Figure 3).

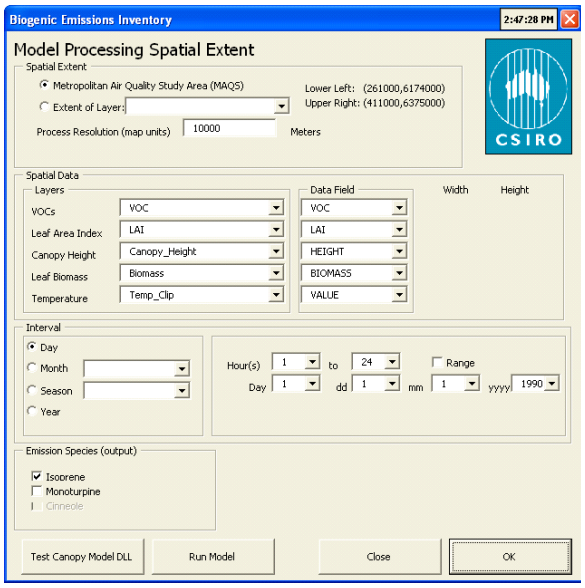

Figure 3: Figure 2: GUI interface used to drive the BIE-GIS

The GUI allows the user to prescribe variables such as extent of the study domain, spatial data sets, processing time intervals and BVOC species. Biogenic emission fluxes are then calculated for each grid point within the nominated domain.

Examples of the spatial distribution of canopy-total hourly emission fluxes of isoprene and monoterpenes are shown in Figure 4 for a typical summer day in the Sydney region. It can be seen that the emissions of both isoprene and monoterpenes peak in regions to the north of Sydney. This is a result of the greater biomass of trees in these regions.

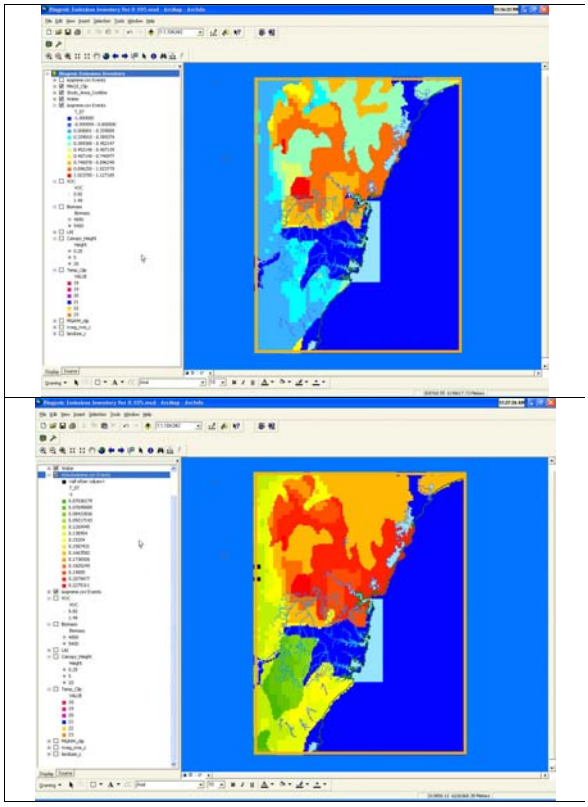

Figure 4. Example of the calculated spatial distribution of isoprene (top) and monoterpenes emission flux (mg m^{-2} h^{-1}) for the Sydney region for hour 7 of a typical summer day.

5 AIR QUALITY MODELLING APPLICATIONS

An important result of the project is a biogenic emissions inventory in a format suitable for photochemical air quality modelling applications.

A canopy model that divides a forest canopy into an arbitrary number of vertical layers (typically 10 layers are used) was developed (Nelson et al. 2004). Layer-specific biogenic fluxes are generated using a normalised emission rate (normalised to

30ºC and 1000 µmol m^{-2} s^{-1}) and descriptions of the in-canopy gradients of temperature, radiation and leaf mass. According to this approach, biogenic emissions from a forest canopy can be estimated from a prescription of the leaf area index, the canopy height, the leaf biomass, and a plant genus-specific leaf level VOC emission rate for the desired chemical species.
A pasture emission model developed by Kirstine et al., 1998, was used. The authors observed the total VOC emission rates to vary between zero and more than 1.5 mg-C m^{-2} h^{-1}. VOC emission rates were observed to have strong radiation and temperature dependencies. Emissions dropped to undetectable levels during night time conditions. In contrast to eucalypt VOC emissions, oxygenated species such as methanol, ethanol and acetone comprised the dominant VOC species emitted from pastures and grasses.

The methodology for the canopy and pasture source components of the inventory have been developed and coded in a modular form suitable for inclusion into numerical air quality modelling systems. The code set has been implemented and applied in the Caltech, Carnegie Mellon photochemical Airshed modelling system (CIT; Harley et al., 1993), which is used for strategic and environmental impact air quality modelling by New South Wales Department of Environment and Conservation (NSW-DEC). The CIT model was used to investigate the impact of replacing the MAQS biogenic emissions inventory (Carnovale et al., 1996) with the new inventory system. In order to provide a preliminary assessment of the impact of the revised biogenic emissions system on photochemical smog concentrations within the MAQS region, the model was run for the 6–8 February 1997, a period where concentrations of ozone were observed to approach the 1-hour NEPM standard of 100 ppb. Three test-cases were considered: 1/ MAQS 1992 biogenic inventory with leaf-level temperatures taken from 10 m modelled temperature fields; 2/ revised biogenic system with 10 m modelled temperature fields; 3/ revised biogenic system with leaf-level temperatures extrapolated from 10 m modelled temperature fields. Note that the MAQS 1992 anthropogenic emissions are used without change for all test cases.

A comparison of daily biogenic mass totals for the new system and for the MAQS 1992 system is presented in Table 1. For example, using the revised system and 10 m temperatures, daily biogenic emissions from forest canopies for 7 February 1997 total 1,213,768 kg. Biogenic emissions from grass total 833,896 kg. Thus the grass-specific emissions contribute about 30 % of total biogenic emissions. For the 1992 MAQS inventory, 1,019,970 kg of isoprene and monoterpenes are emitted. Thus the total emissions from canopy plus pasture exceed the 1992 MAQS inventory by a factor of two. Isoprene emissions from the revised system exceed the 1992 MAQS total by 20 %. A comparable difference is evident for all days for the 10 m temperature simulations.

Considering the leaf-level temperature simulations, it can be seen from Table 1 that total biogenic emissions generated by the revised system exceed the MAQS 1992 totals by up to a factor of three. Isoprene and monoterpene emissions from the revised system exceed the MAQS 1992 totals by about 60 %.

Table 1: Comparison of biogenic daily mass totals from the revised system and from the MAQS 1992 system for the period 6-8 February 1997. 10m–temp- 10 m model temperatures are used in the emission rate calculations. Leaf-level temp. temperatures are extrapolated from 10m to leaf-level are used in the emission rate calculations.

Date	Canopy total (kg)	Pasture total (kg)	MAQS 1992 (kg)	Combined /MAQS
19970206				
10 m temp.	1334259	874892	1101735	2.0
Leaf-level temp.	1759508	1413450		2.9
19970207				
10 m temp.	1213768	833896	1019970	2.0
Leaf-level temp.	1606145	1279339		2.8
19970208				
10 m temp.	1205995	650609	1009092	1.8
Leaf-level temp.	1503816	1102988		2.6

Results presented in Figure 5 for a selected day, shows the differences between ozone predictions for the revised biogenic inventory using 10m temperatures and the MAQS 1992 inventory. These are plotted against the ozone concentrations generated using the MAQS 1992 inventory (hereafter defined as the base-case). It can be seen that use of the revised biogenic inventory results in ozone concentrations increases of up to 15ppb to the base-case ozone concentrations in the range 40–60 ppb. The peak base-case

concentrations (80 ppb) are increased by up to 5 ppb.

Using leaf-level instead of 10 m temperatures results in a further 2-5 ppb increase to the base-case ozone concentrations (Figure 6).

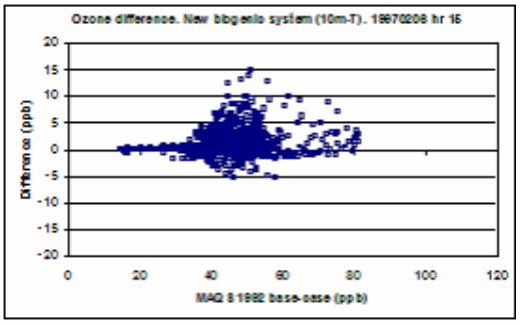

Figure 5: Concentration difference scatter plots, showing grid point differences between 1-hour ground-level ozone concentrations estimated by a PAQMS using biogenic VOC fluxes generated by the 1992 MAQS biogenic inventory and generated by the revised biogenic system (10 m temperature case)

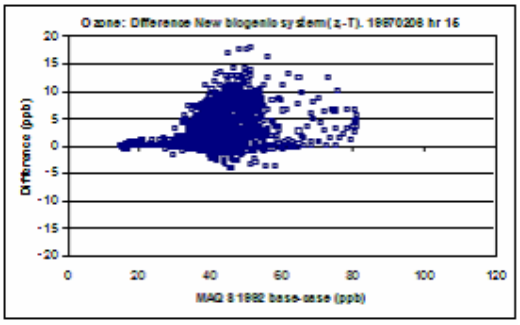

Figure 6: Concentration difference scatter plots, showing grid point differences between 1-hour ground-level ozone concentrations estimated by a PAQMS using biogenic VOC fluxes generated by the 1992 MAQS biogenic inventory and generated by the revised biogenic system (leaf-level temperature)

It can be seen that increases in biogenic VOC emissions by factors of 2–3 result in changes to peak base-case ozone concentration of about 10 %. Relative concentration changes become larger at lower base-case ozone concentrations (which presumably occur outside of the Sydney urban plume).

5 CONCLUSION

Emission fluxes of main biogenic compounds have been measured for selected trees and grasses found in NSW. A GIS based biogenic VOC emission inventory for the MAQS region of NSW has been developed which can be driven by observational and GIS data. The GIS system uses high resolution spatial vegetation characteristics, land use, temperature and radiation data together with models of BVOC fluxes from canopies and grass to generate spatial and time-varying fields of BVOC emissions. The system has been coupled to the photochemical air quality modelling system currently used by the Air Science Group at NSW-DEC for case study and emission scenario modelling.

Acknowledgments

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