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Article

Source contributions to ozone formation in the New South Wales Greater Metropolitan Region, Australia

Hiep Nguyen Duc[1*], Lisa T.-C. Chang[1], Toan Trieu[1], David Salter[1] and Yvonne Scorgie[1]

[1] New South Wales Office of Environment and Heritage, Sydney, Australia;
Hiep.Duc@environment.nsw.gov.au; LisaTzu-Chi.Chang@environment.nsw.gov.au;
Toan.Trieu@environment.nsw.gov.au; David.Salter@environment.nsw.gov.au;
Yvonne.Scorgie@environment.nsw.gov.au

***Correspondence author: Hiep Nguyen Duc**
Email: Hiep.Duc@environment.nsw.gov.au
Phone: +61 2 9995 5050
Fax: +61 2 9995 6250
Address: PO Box 29 Lidcombe, NSW 1825, Australia

Abstract: Ozone and fine particles ($PM_{2.5}$) are the two main air pollutants of concern in the New South Wales Greater Metropolitan Region (NSW GMR) region due to their contribution to poor air quality days in the region. This paper focuses on source contributions to ambient ozone concentrations for different parts of the NSW GMR, based on source emissions across the greater Sydney region. The observation-based Integrated Empirical Rate Model (IER) was applied to delineate the different regions within the GMR based on the photochemical smog profile of each region. Ozone source contribution is then modelled using the CCAM-CTM (Cubic Conformal Atmospheric Model-Chemical Transport Model) modelling system and the latest air emission inventory for the greater Sydney region. Source contributions to ozone varied between regions, and also varied depending on the air quality metric applied (e.g. average or maximum ozone). Biogenic volatile organic compound (VOC) emissions were found to contribute significantly to median and maximum ozone concentration in North West Sydney during summer. After commercial domestic, power station was found to be the next largest anthropogenic source of maximum ozone concentrations in North West Sydney. However, in South West Sydney, beside commercial and domestic sources, on-road vehicles were predicted to be the most significant contributor to maximum ozone levels, followed by biogenic sources and power stations. The results provide information which policy makers can devise various options to control ozone levels in different parts of the NSW Greater Metropolitan Region.

Keywords: Ozone; Greater Metropolitan Region of Sydney; source contribution; source attribution; air quality model; Cubic Conformal Atmospheric Model (CCAM); Chemical Transport Model (CTM)

1. Introduction

Ozone is one of the criterion pollutants monitored at many monitoring stations in the Sydney metropolitan area in the past few decades (from 1970 until now). It is a secondary pollutant produced from complex photochemical reaction of nitrogen oxides (NO_x) and mainly volatile organic compounds (VOC) under sunlight. In the metropolitan area of Sydney, NO_x emissions come

from many different sources including motor vehicles, industrial, commercial-domestic, non-road mobile (e.g. shipping, rail, aircraft) and biogenic (soil) sources. Similarly, VOC emission comes from biogenic (vegetation) and various anthropogenic sources.

In the early 1970s until the late 1990s, ozone exceedances at a number of sites in Sydney occurred frequently especially during the summer period. From early 2000 to 2010, ozone concentration as measured at many monitoring stations tended to decrease. This is mainly due to a cleaner fleet of motor vehicles compared to that in the past, despite an increase in the total number of vehicles. Recently, there has been a slight upward trend of ozone levels in the Sydney region.

Controlling ozone (either maximum ozone or exposure), with least cost and best outcome, is a complex problem to solve and depends on the meteorological and emission characteristics within the region. A study to understand and determine the source contribution to ozone formation in various parts of the Sydney metropolitan region is helpful to policy makers to manage ozone level. Ozone formation from NO_x and VOC under sunlight is a complex photochemical process. Sensitivity of ozone concentration to changes in emission rate of VOC and NO_x sources had been shown to be nonlinear in many experimental and modelling studies [1].

Source contribution to ambient ozone concentration is important to understand the process of dispersion of pollutants from various sources to a receptor point. Interests in this area, especially ambient particulates, has been expanded in recent years in numerous studies on particle characterisation or VOC via source fingerprints using Positive Matrix Factorisation (PMF) statistical method [2-4]. Rather than a backward receptor model, a forward source to receptor dispersion model can also be used to study the source contribution at the receptor point. To this end, an emission inventory and an air quality dispersion model can be used to predict the pollutant concentration at the receptor point, under various emission source profile scenarios, and hence can isolate the source contribution of various sources [5-9].

Using an urban air quality model called SIRANE with tagged species approach to determine the source contribution to NO_2 concentration in Lyon, a large industrial city in France, Nguyen et al. [9] have shown that traffic is the main cause of NO_2 air pollution in Lyon.

Dunker et al., [5] used a set of precursors and ozone tracers to determine the source contribution to ozone formation called the ozone source apportionment technology (OSAT) and implemented it in the CAMx air quality model. OST allows the air quality model such as CAMx to run only once and ozone formation at a receptor site can be attributed to different defined source regions and different source categories within each region. They applied OSAT to study the source contribution to ozone in Lake Michigan ozone study with good results as compared with using sensitivity analysis using decoupled direct method (DDM) which was implemented by them before in CAMx [6].

Li et al. [7] used CAMx with OSAT to study the source contribution to ozone in the Peral River Delta (PRD) region of China. They divided the whole modelling domain including the PRD and Hong Kong regions, south China region and the whole of China into 12 source areas and 7 source categories which include anthropogenic sources outside PRD, biogenic, shipping, point sources, areas sources such as domestic and commercial and mobile sources in PRD and in Hong Kong. Their results show that under mean ozone conditions, super-regional (outside regional and PRD areas) contribution is dominant but, for high ozone episodes, elevated regional and local sources are still the main causative factors. Among all the sources, mobile source is the source category contributing most to ozone in PRD region.

Wang et al. [10] used CAMx model with OSAT to study ozone source attribution during a smog episode in Beijing, China. The authors showed a significant spatial distribution of ozone in Beijing has strong regional contribution. Similar techniques have been used to study the source apportionment of $PM_{2.5}$ using source-oriented CMAQ, such as Zhang et al. [11] in their study of source apportionment of $PM_{2.5}$ secondary nitrate and sulfate in China from multiple emission sources across China.

The Sydney basin with a population of more than 5 million has a diverse source of air emission pattern. Beside biogenic emissions, anthropogenic source emissions such as motor vehicles and

industrial sources are two of the main contribution to ozone formation in Sydney. Duc, Spencer et al. [12] used modelling approach based on a model called TAPM-CTM (The Air Pollution Model – Chemical Transport Model) to show that the motor vehicle morning peak emission in Sydney strongly influences the daily maximum zone level in the afternoon at various sites in Sydney, especially downwind sites in the south west of Sydney.

Duc et al., [8] recently used CCAM-CTM (Cubic Conformal Atmospheric Model-Chemical Transport Model) modelling system to determine both the $PM_{2.5}$ and ozone source contribution based on the Sydney Particle Study (SPS) period of January 2011. Their results show that the biogenic emission contributes to about 15% to 25% to average $PM_{2.5}$ and about 40% to 60% to the maximum ozone at several sites in the Greater Sydney Region (GMR) during January 2011. In addition, the source contribution to maximum ozone at Richmond (North West Sydney) is different from other sites in Sydney in that the industrial sources contribute more than mobile sources to the maximum ozone at this site while the reverse is true at other sites.

This study extends the previous study [8] by using many additional sources including non-road mobile sources (shipping, locomotives, aircrafts), commercial domestic over the whole 12 months' period of 2008 and determining the source contribution of ozone for different sub-regions which have different ozone characteristics in its response to NO_x and VOC emission.

As the ozone response to NO_x and VOC sources is mostly nonlinear depending on the source region which is either NO_x or VOC limited, the nonlinear interaction among the impacts of emission sources lead to discrepancies between source contribution attributed from a group of emitting sources and the sum of contribution attributed to each component [1]. For this reason, source contribution is studied for the impact of each source to different regions in Sydney which is characterised by base state of emission and the meteorology pattern on the regions

Observation-based methods can be used to provide a mean to assess the potential extent of photochemical smog problem at various regions [13-14]. The Integrated Empirical Rate (IER) model, developed by Johnson [14] based on the smog chamber studies, is used in this study to determine and understand the photochemical smog at various regional sites in Sydney using ambient measurements at the monitoring stations. The IER model have been used by Blanchard [15] and Blanchard and Fairley [16] in photochemical smog studies in Michigan and California to determine whether a site or a region is in a NO_x-limited or VOC-limited regime.

Central to the IER model is the concept of smog produced (SP). Photochemical smog is quantified in terms of NO oxidation which defines Smog Produced (SP) as the quantity of NO consumed by photochemical processes plus the quantity of O_3 produced.

$$[SP]_0^t = [NO]_0^t - [NO]^t + [O_3]^t - [O_3]_0^t$$

where $[NO]_0^t$ and $[O_3]_0^t$ denote the NO and O3 concentrations that would exist in the absence of atmospheric chemical reactions occurring after time t=0 and $[NO]^t$ and $[O_3]^t$ are the NO and O_3 concentrations existing at time t. $[SP]_0^t$ denotes the concentration of smog produced by chemical reactions occurring during time t=0 to time t=t.

When there is no more NO_2 to be photolysed, and no more NO to be reacted with reactive organic compound to produce NO_2 and nitrogen products (such as peroxyacetyl nitrate (PAN) species), ozone production is stopped. This condition in photochemical process is called NO_x-limited regime. The ratio of the current concentration of SP to the concentration that would be present if the NO_x-limited regime existed is defined as the parameter "Extent" of smog production (E). The extent value is indicative of how far toward attaining the NO_x-limited regime the photochemical reactions have progressed. When E=1, smog production is in the NO_x-limited regime and the NO_2 concentration approaches zero. When E<1, smog production is in the light-limited (or VOC-limited) regime.

Previous study has shown that high ozone levels in the west, northwest and south west of Sydney are mostly in the regime of NO_x-limited while central east Sydney is mostly light-limited (VOC-limited) [17]. For sensitivity analysis, it is expected that in the NO_x-limited region, sensitivity of ozone on NO_x emission change (say per-ton) is positive while negative in the VOC-limited region.

Our study delineates the Greater Sydney Region into different sub-regions using IER method and Principal Component Analysis (PCA) statistical method. Source contribution to ozone formation is then determined in each of these sub-regions.

2. Methodology and data

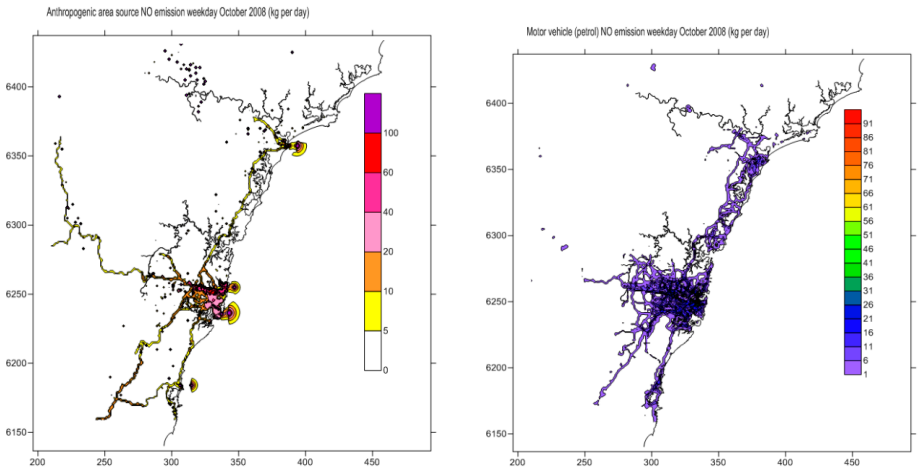
2.1 *CCAM-CTM Modelling system*

The CCAM-CTM modelling system is used in this study to simulate photochemical process which produce ozone over the NSW Greater Metropolitan Region (GMR). The schematic diagram of CCAM-CTM, details of domain setting, model configurations as well as model validation as compared to observations can be found in [18-19] of this issue of *Atmosphere.*

2.2 *Emission modelling*

The emission modelling embedded in CCAM-CTM modelling system consists of natural and anthropogenic components. All natural emissions from canopy, tree, grass pasture, soil, sea salt and dust are modelled and generated inline of CTM while the anthropogenic emissions is taken from the EPA NSW GMR Air Emissions Inventory for calendar year 2008 and prepared offline as input to the CTM.

The 2008 NSW GMR Air Emissions Inventory data was segregated into 17 major source groups : power generation from coal, power generation from gas, residential wood heaters, on-road vehicle petrol exhaust, diesel exhaust, other (e.g LPG) exhaust, petrol evaporation, non-exhaust (e.g brake) particulate matter, shipping and commercial boats, industrial vehicles and equipment, aircraft (flight and ground operations), locomotives, commercial non-road equipment, other commercial-domestic area and industrial area fugitive sources, biogenic sources, non-biogenic natural sources. Figure 1, as an example, shows the anthropogenic area source NO weekend emission, motor vehicle (petrol exhaust) NO weekday emission for October 2008 and locations of power stations in the GMR. The source-dependent fraction for major source groups used in emission modelling is reference in Appendix A of [20] in this issue of *Atmosphere*.



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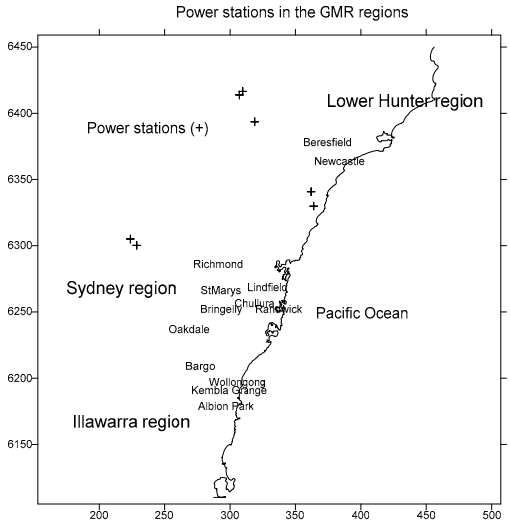

Figure 1. Anthropogenic area source NO weekend emission (left) and motor vehicle (petrol exhaust) NO weekday emission (right) for October 2008 (unit in kg/day) and locations of power stations (+) in the GMR (bottom).

The emission of NO_x and various species of VOC from area sources and power station point sources in the GMR for a typical summer month (January 2008 weekday) is shown in Table 1. These areas sources are commercial-domestic, locomotives, shipping, non-road commercial vehicles, industrial vehicles, passenger and light-duty petrol vehicles (VPX), passenger and light-duty diesel vehicles (VDX), all evaporative vehicle emission (VPV) and other vehicle exhaust (VLX).

Table 1. Emission of NO_x and VOC species from various area sources in the GMR for weekday in January 2008

Species (kg/h)	Commercial-Domestic	Locomotives	Shipping	Comm-Veh	Ind-Veh	VPX	VDX	VLX	VPV	Power (coal)	Power (gas)
NO	4794	11450	24230	310	52197	58248	43856	502	0	121957	1681
NO_2	387	924	1955	25	4213	3653	10501	31	0	6036	89
ALD2	4527	57	784	6	741	841	280	39	5768	30	9
ETH	1631	159	503	9	1208	3167	303	150	0	0	11
FORM	785	47	197	9	1027	561	454	26	435	1	73
ISOP	2	0	0	0	0	12	7	1	19	0	0
OLE	2094	43	421	3	336	1506	122	72	626	21	20
PAR	94905	291	14195	22	2283	10867	1915	518	46536	583	287
TOL	14480	24	3615	4	301	3523	172	167	1693	44	0
XYL	16495	22	4851	4	244	3997	494	190	1048	120	0
ETOH	22714	0	11	0	1	70	0	0	200	0	0
MEOH	4067	0	27	0	5	51	55	2	0	0	0

The biogenic emission is modelled and generated inline in CTM. For ozone, the main biogenic contribution (VOC, NO_x and NH_3) is from vegetation and soil. The biogenic VOC is the sum of these species, isoprene, monoterpene, ethanol, methanol, aldehyde and acetone.

The biogenic emission consists of emission from forest canopies, pasture and grass and soil. The canopy model divides the canopy into an arbitrary number of vertical layers (typically 10 layers are used). Biogenic emissions from a forest canopy can be estimated from a prescription of the leaf area index, LAI (m^2 m^{-2}), the canopy height hc (m), the leaf biomass Bm (g m^{-2}), and a plant genera-specific leaf level VOC emission rate Q (μg-C g^{-1} h^{-1}) for the desired chemical species. The LAI used in CTM is based on Lu et al [21] scheme which consists of LAI for tree and grass derived from Advanced Very High Resolution Radiometer (AVHRR) normalized difference vegetation index (NDVI) data between 1981 and 1994.

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Biogenic NO_x emission model from soil is based on the temperature-dependent equation (1).

$$Q = Q_{nox} \exp[0.71(T - 30)] \quad (1)$$

where Qnox is the NO_x emission rate at 30°C and T is the soil temperature (°C).

Ammonia (NH_3) emission is based on Battye and Barrows scheme [22]. This approach uses annual average emission factors prescribed for four natural landscapes (forest, scrubland, pastureland, urban).

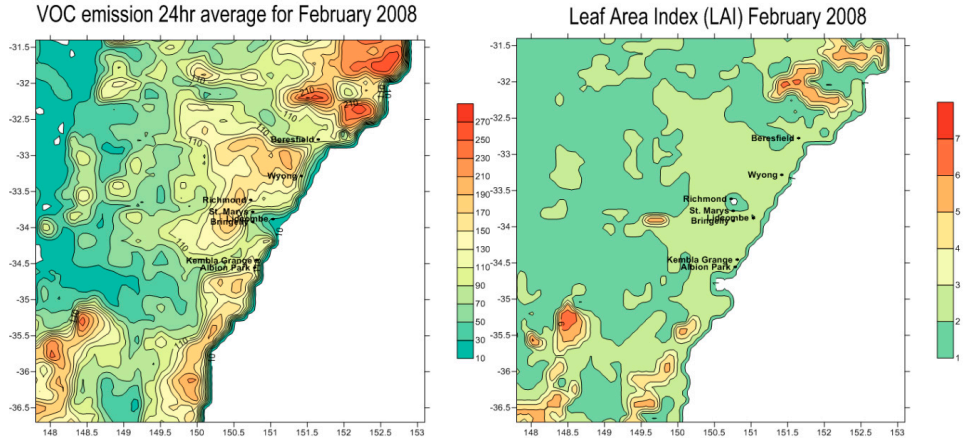

Figure 2. VOC monthly 24 hourly average emission (kg/hour) (left) and Leaf Area Index (LAI) (right) for February 2008.

Biogenic VOC is defined as the sum of isoprene, monoterpene, ethanol, methanol, aldehyde and acetone. As shown in Figure 2, biogenic VOC emission occurs mostly in west of Sydney and Blue Mountain area, the National Park areas in the north, the lower Hunter and the inland of the Illawarra escarpment. Isoprene and monoterpene in general have similar spatial patterns as VOC distribution and reflect the Leaf Area Index (LAI) distribution in the modelling domain [8]

2.3 *Emission scenarios*

The 2008 NSW GMR Air Emissions Inventory data is segregated into 16 major source groups then re-grouped in to 8 categories which are similar to those used by Karagulian, Belis et al. [23] to match with the six identified categories using the component profile of the European Guide on Air Pollution Source Apportionment with Receptor Models for particles [24]. The emissions scenarios used in this study are: 1. All sources; 2. All anthropogenic – with emissions from all anthropogenic sources; 3. All natural - with emissions from all natural sources; 4. Power stations: emissions from coal and gas power generations; 5. On-road motor vehicles: emissions from petrol exhaust, diesel exhaust, other exhaust, petrol evaporative and non-exhaust particulate matter; 6. Non-road diesel and marine: with emissions from shipping and commercial boats, industrial vehicles and equipment, aircraft, locomotives, commercial non-road equipment; 7. Industry: with emissions from all point source except power generations from coal and gas; 8. Commercial-domestic: with emissions from commercial and domestic-commercial area source excluded solid fuel burning (wood heaters).

2.4 *Source attribution to ozone formation in different sub-regions*

Using 2008 summer (November 2007 to March 2008) observed hourly monitoring data (NO, NO_2, Ozone and Temperature) in the IER method, the extent of photochemical smog production in various Sydney sites is determined and then classified using clustering statistical method. At low level of pollutant concentrations, near background levels, with little or no photochemical reaction, the extent can be equal to 1. For this reason, to better classify the degree of photochemical reaction, the ozone level or the SP (smog produced) concentration has to be taken into account in addition to the extent variable.

It is therefore more informative to categorise the smog potential using both the extent value and the ozone concentration such as

- category A : extent > 0.8 and ozone conc. > 7 pphm
- category B : 0.5 < extent < 0.8 and 5pphm < ozone conc. < 7 pphm
- category C : 0.5 < extent < 0.8 and 3 pphm < ozone conc. < 5 pphm
- category D : extent > 0.9 and ozone conc. < 3 pphm

Category A represents very high ozone episode, category B high ozone episode, category C medium smog potential and category D as background or no smog production.

Using similar techniques as those of Yu and Chang [25], the principal component analysis (PCA) via correlation matrix on the 2007/2008 (1/11/2007 to 31/3/2008) summer ozone data is then used to delineate the regions in the Sydney area.

3. Results

3.1 Regional delineation using Integrated Empirical Rate (IER) model and Principal component analysis (PCA)

The delineation of sub-regions in the GMR region based on their similar ozone formation patterns are performed using clustering method and PCA method. These methods produce similar results. We present here the PCA results with component scores which show that there are 3 principle components explaining most of the variances. The eigenvalues of the correlation matrix and the corresponding principal component scores for each site are derived. The contour plot of component scores for each component is used to delineate the regions.

The main sub-regions are western Sydney (North West, West, South West) and the coastal region consisting of eastern Sydney, Lower Hunter and the Illawarra as shown in Figure 3a. The patterns of sub-regional delineation are similar to those that was performed for summer 1997/1998 [26-27] as depicted in Figure 3b. This means that over the past 20 years the spatial pattern of ozone formation does not show much change.

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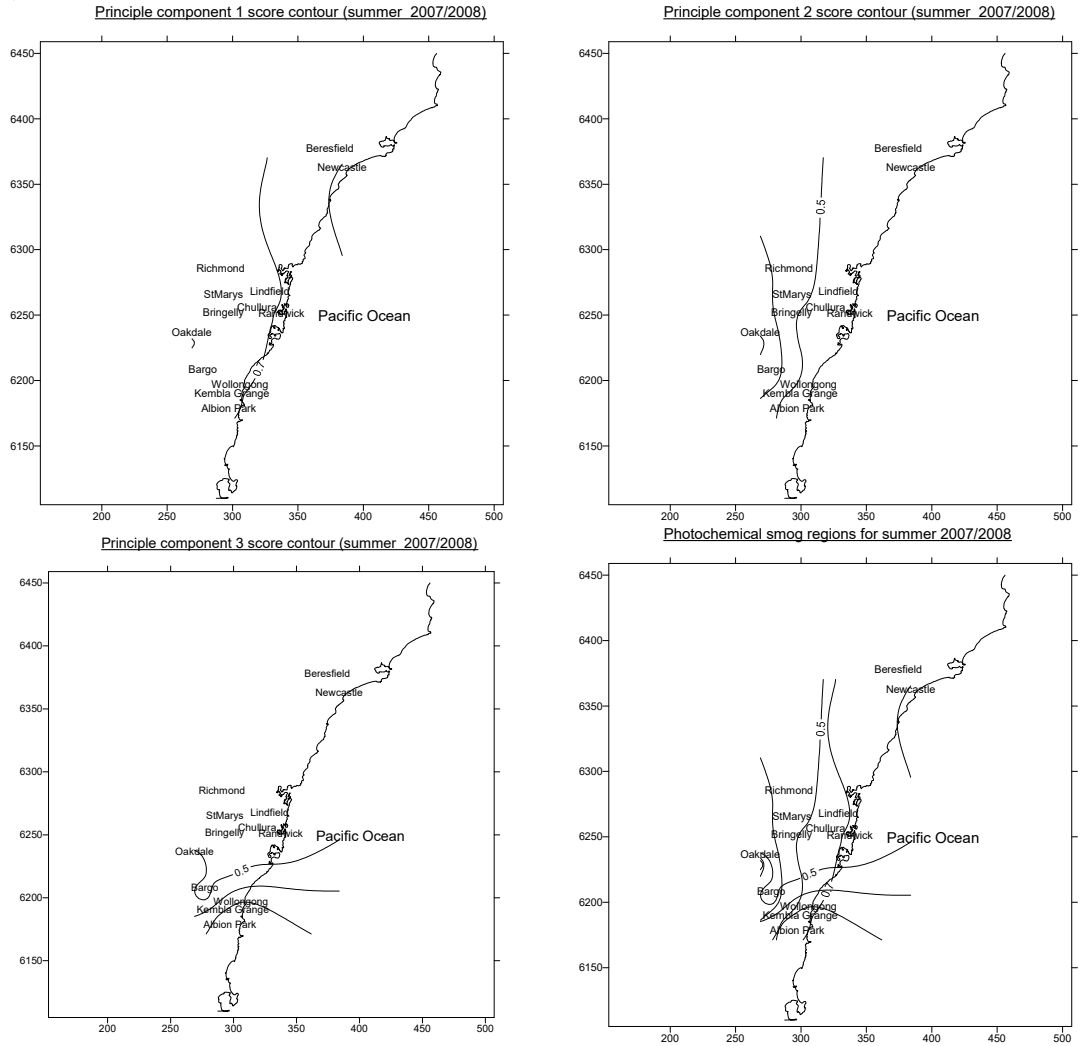
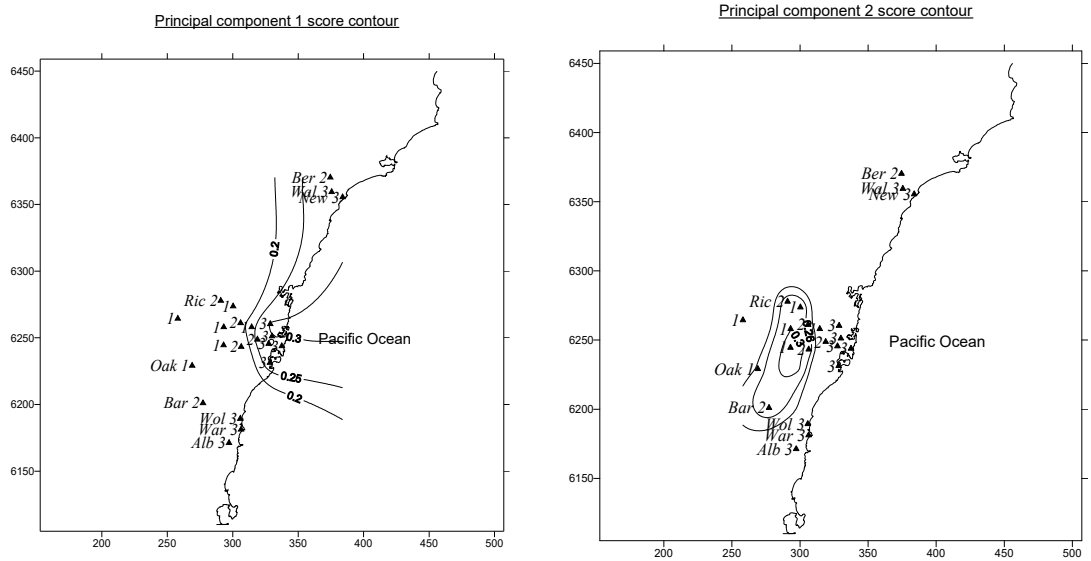
(a)



(b)



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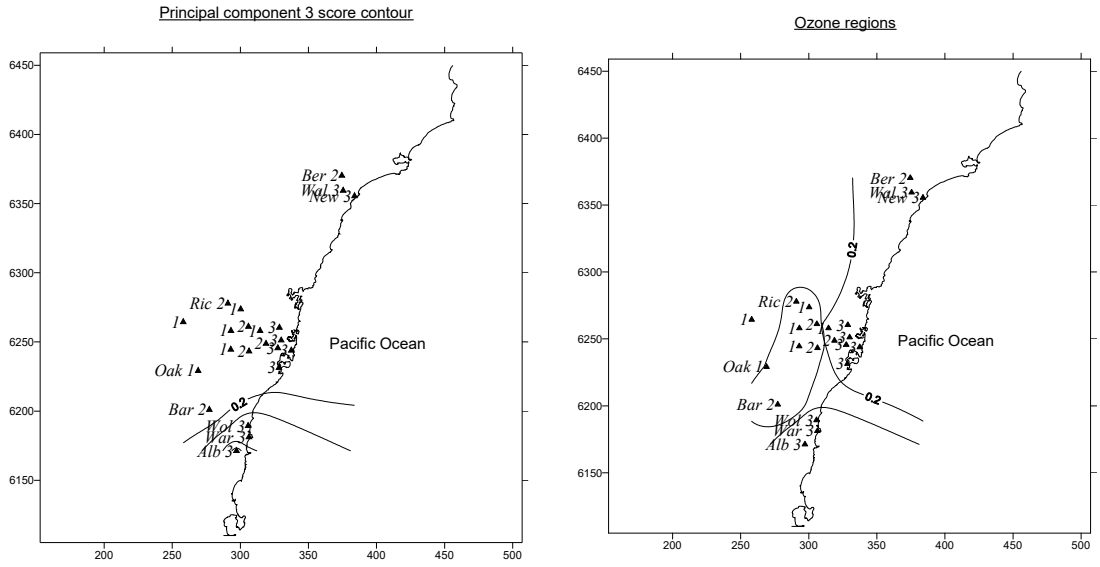

Figure 3. Contour plots of first 3 principal component scores depicting the regional delineation based on similarity of ozone formation pattern in (a) 2007/2008 and in (b) 1997/1998. The last plot in each graph is the combined plots of the 3 component score contours.

From the PCA analysis showing the spatial pattern of ozone formation, the Lower Hunter and Illawarra can be considered as separate from Sydney and the Sydney western region is separate from eastern and central Sydney. The western Sydney region is characterised by having high frequency of smog events (NO_x-limited or extent of smog production higher than 0.8) as shown in Table 2 of number of observed hourly data that are classified in each of the 4 smog potential categories for January 2008. Sites near the coast such as Randwick and Rozelle are in VOC-limited area with low smog events (zero number of observed hourly data in category A and category B).

Table 2. Number of observed hourly data that are classified into each **s**mog potential categories at different sites in the GMR for January 2008

Site	Category A	Category B	Category C	Category D
Randwick	0	0	12	1431
Rozelle	0	0	38	215
Lindfield	0	8	88	414
Liverpool	6	5	83	198
Bringelly	12	3	46	1138
Chullora	3	7	92	214
Earlwood	0	7	68	300
Wallsend	0	2	52	2060
Newcastle	0	0	1	597
Beresfield	0	0	26	598
Wollongong	0	1	24	797
Kemble Grange	0	0	53	1437
Richmond	4	1	9	863
Bargo	8	0	9	1061
St Marys	12	1	46	756
Vineyard	1	0	14	763
Prospect	13	2	62	225
McArthur	15	4	60	788
Oakdale	13	0	11	2007
Albion Park South	0	2	47	1441

The Sydney western region is also sub-divided into 3 sub-regions, northwest Sydney, west Sydney and southwest Sydney as the northwest is also influenced by sources in the Lower Hunter and the southwest is related to some extend the Illawarra region as shown by PCA analysis. The results confirm previous studies [17], [25-26] which have shown that the GMR region can be divided into sub-regions (north west, south west, west and central east) based on the ozone smog characteristics formed from the influence of meteorology and emission pattern in the GMR.

The GMR region are therefore can be divided into 6 sub-regions for ozone source contribution study: Sydney North West, Sydney South West, Sydney West, Central and East Sydney, the Illawarra in the south and the Lower Hunter region in the north.

3.2 Source contribution to ozone over the whole GMR region

The CCAM-CTM predicted daily maximum 1-hour and 4-hour ozone concentrations in the GMR domain (9 km x 9 km) for the entire calendar year of 2008 under various emission scenarios are extracted at grid point nearest to the location of the 18 NSW OEH air quality monitoring stations. Results from maximum 1-hour and 4-hour ozone analysis are very similar, therefore only results for 1-hour predicted maximum ozone are presented.

Table 3 and Figure 4 shows the average source contributions to daily maximum 1-hour ozone over the whole GMR. Apparently, natural sources are more significant in contributing to ozone concentration than all anthropogenic sources. During summer months (December, January and February), commercial domestic, power stations and on-road motor vehicles sources contribute most to ozone formation in that order. During winter months (Jun, July and August), most of anthropogenic sources contribute negatively to ozone formation (i.e. the presence of these sources decreases the level of ozone). Of anthropogenic sources beside commercial domestic sources, power stations contribute more to ozone formation within whole GMR than that contributed from on-road motor vehicle, industrial and non-diesel and marine sources in this order.

Table 3. Monthly average of daily maximum 1-hour predicted ozone concentration (ppb) in the GMR for different months in 2008 under various emission scenarios

Month	All sources	Power stations	Commercial-domestic	On-road motor vehicles	Non-road diesel and marine	Industry	All anthropogenic	All natural
Jan	33.41	3.30	8.38	2.53	0.63	0.36	15.21	18.20
Feb	26.29	1.70	5.54	1.06	0.18	0.38	8.86	17.43
Mar	28.42	1.43	7.62	0.79	0.16	0.37	10.37	18.05
Apr	18.39	0.16	2.32	-1.11	-0.11	0.011	1.29	17.10
May	23.03	0.22	3.94	-2.44	-0.30	-0.066	1.44	21.58
Jun	20.74	-0.012	0.88	-1.94	-0.30	-0.19	-1.55	22.29
Jul	18.81	-0.097	0.77	-1.75	-0.24	-0.13	-1.42	20.24
Aug	21.83	0.019	1.35	-1.44	-0.17	-0.082	-0.28	22.11
Sep	21.80	0.88	3.18	-0.95	-0.10	0.090	3.13	18.67
Oct	29.45	2.30	6.95	1.07	0.30	0.38	11.03	18.42
Nov	26.53	1.43	3.70	0.54	0.24	0.16	6.07	20.45
Dec	32.29	2.36	6.26	1.90	0.54	0.47	11.53	20.77
Annual average	25.11	1.14	4.25	-0.14	0.071	0.15	5.49	19.62

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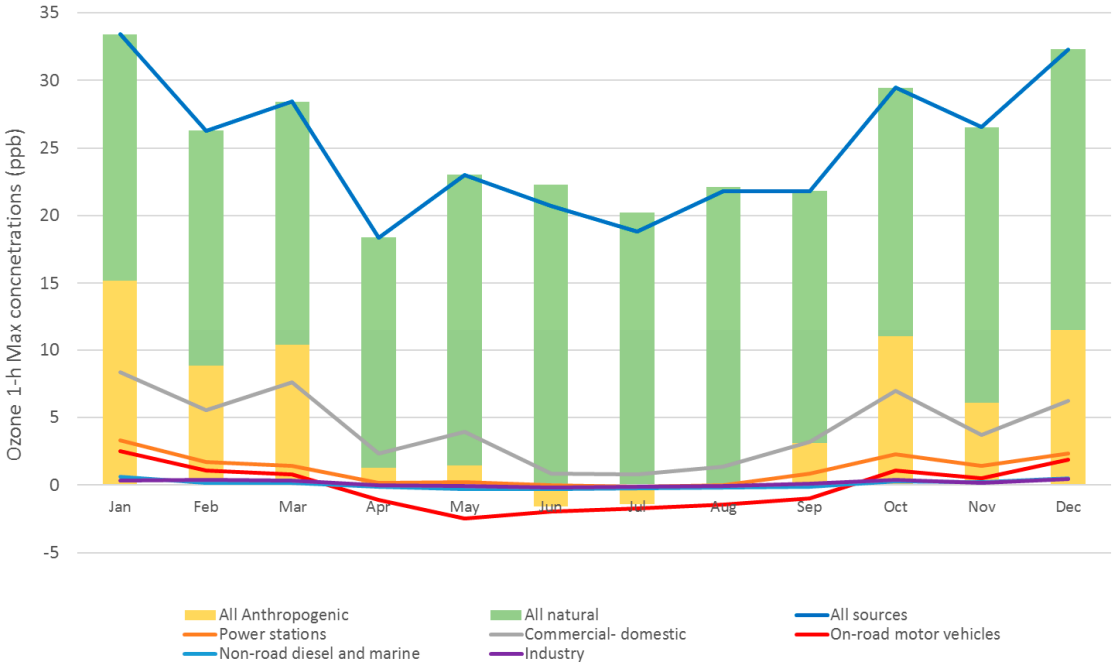
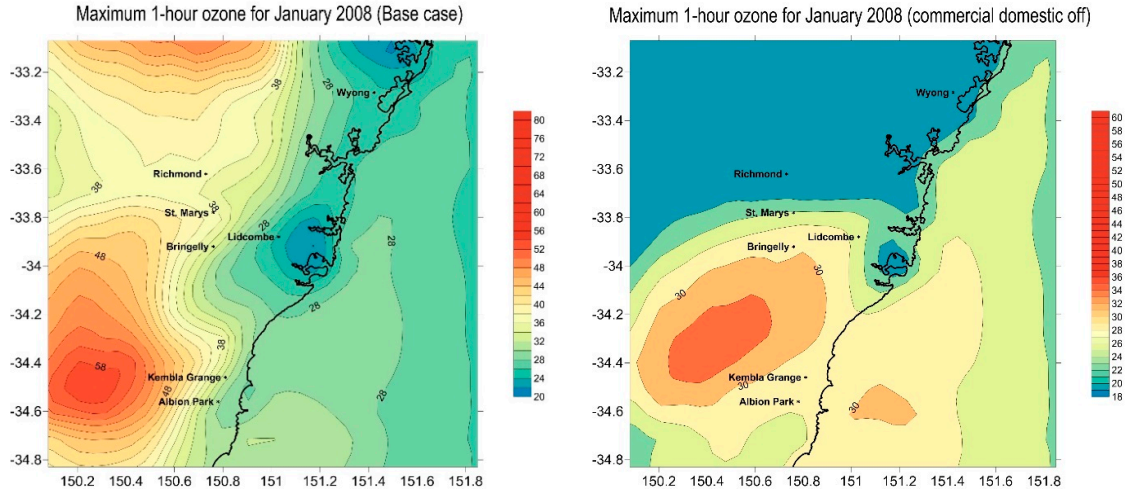


Figure 4. Contribution of all anthropogenic and natural emissions (bar graph) and different anthropogenic sources (line graph) to the monthly average of daily maximum 1-hour ozone concentration in 2008 in the GMR.

The monthly average of daily maximum 1-hour ozone concentration for January 2018 for the 4 emission scenarios: base case, commercial-domestic sources off, power stations sources off and on-road mobile sources off is shown in Figure 5. The spatial pattern in daily maximum 1-hour ozone from various source contribution is not uniform across the GMR as expected. The spatial pattern of maximum 1-hour ozone shows that the relative importance of source contribution is different for different sub-regions.

(a) (b)



(c) (d)

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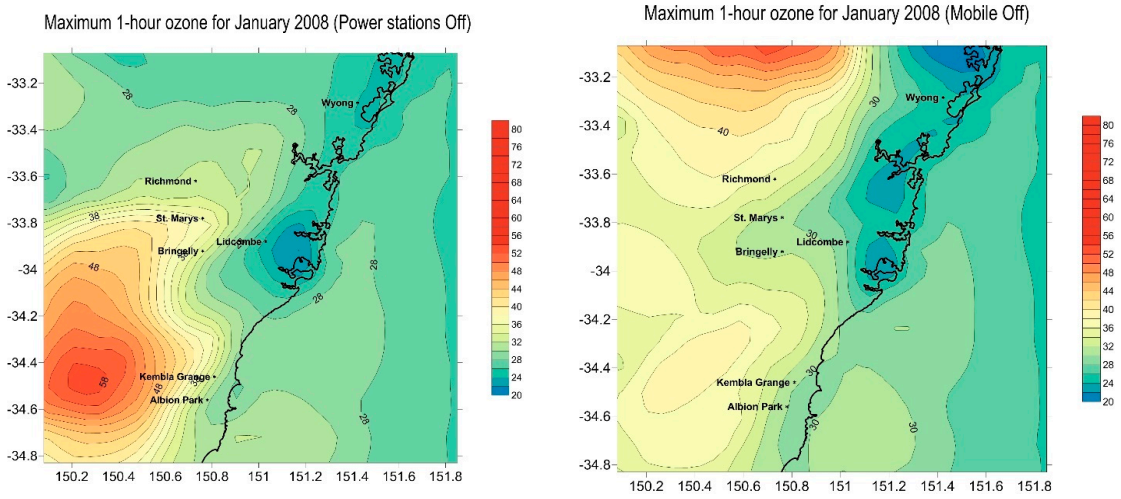

Figure 5. Monthly average of daily maximum 1-hour ozone concentration for January 2018 in (a) base case, (b) commercial-domestic sources off, (c) power stations sources off and (d) on-road mobile sources off emission scenarios

3.3 Source contribution to ozone concentrations over sub-regions within GMR

The daily maximum 1-hour and 4-hour predicted ozone concentrations under various emission scenarios are further analysed in this section to investigate the source contributions to ozone formation in each of the sub-regions across GMR for the year of 2008. As shown above from PCA analysis, the different sub-regions have different smog characteristics as represented by the extent of smog production or NO_x/VOC relationship with ozone level production. The 6 regions of the GMR are Sydney north-west (Richmond and Vineyard), Sydney west (Bringelly, Prospect and St Marys), Sydney south-west (Bargo, Liverpool and Oakdale), Sydney east (Chullora, Earlwood, Randwick and Rozelle), Illawarra (Albion Park, Kembla Grange and Wollongong) and Lower Hunter or Newcastle (Newcastle) regions. As for the whole GMR region analysis, only results for 1-hour predicted ozone are presented here since the 4-hour ones are very similar.

3.3.1 Sydney north-west region

This region is characterised as mostly NO_x-limited during ozone season (summer). Table 4 and Figure 6 show that, of the anthropogenic sources, commercial domestic sources (except wood heaters) contribute most to the 1-hour ozone max, especially in the summer months. Then power stations and motor vehicles are next in importance in contribution to ozone in the north west. Interestingly, during cold winter months, on-road motor vehicles have a negative contribution to maximum 1-hour ozone in the northwest of Sydney (i.e., increase in motor vehicle emission actually decreases the maximum ozone level in that region). This is due to the fact that photochemical ozone production never or rarely reach NOx-limited during daytime, that is it is mostly in light-limited (or VOC-limited) regime everywhere in the basin.

Table 4. Monthly average of daily maximum 1-hour ozone concentration (ppb) in the Sydney north-west region for different months in 2008 under various emission scenarios

Month	All sources	Power stations	Commercial -domestic	On-road motor vehicles	Non-road diesel and marine	Industry	All anthropo genic	All natural
Jan	26.26	2.72	4.39	1.29	0.49	0.22	9.11	17.15
Feb	21.81	1.39	3.29	0.28	0.15	0.15	5.26	16.54
Mar	23.27	1.15	4.95	-0.28	0.11	0.14	6.08	17.19
Apr	16.01	0.09	1.59	-1.51	-0.20	-0.11	-0.12	16.13
May	18.99	0.08	2.89	-3.23	-0.38	-0.21	-0.79	19.78

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Jun	17.57	-0.08	0.58	-2.77	-0.37	-0.26	-2.89	20.46
Jul	15.81	-0.16	0.48	-2.46	-0.29	-0.18	-2.61	18.42
Aug	19.02	-0.07	0.97	-1.94	-0.24	-0.16	-1.40	20.42
Sep	18.67	0.44	2.33	-1.36	-0.19	-0.04	1.20	17.47
Oct	24.49	2.00	4.48	0.23	0.21	0.23	7.17	17.32
Nov	22.25	1.15	2.40	-0.10	0.15	0.09	3.69	18.56
Dec	26.54	1.99	3.29	1.02	0.41	0.30	7.00	19.54
Annual average	20.91	0.90	2.64	-0.90	-0.01	0.01	2.65	18.26

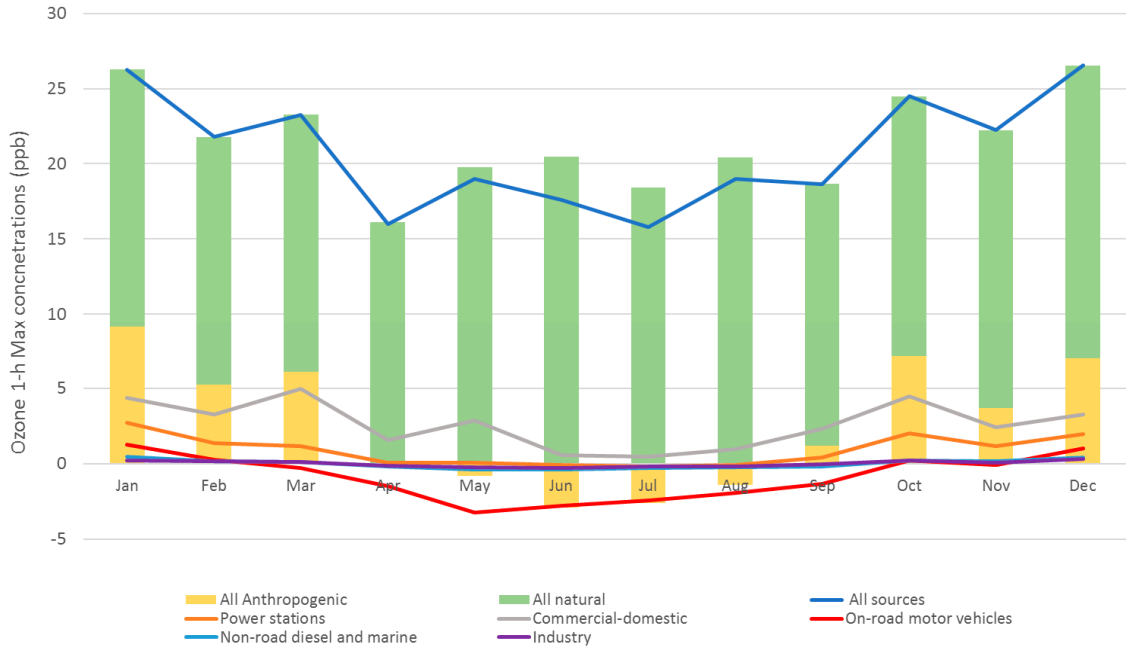

Figure 6. Contribution of all anthropogenic and natural emissions (bar graph) and different anthropogenic sources (line graph) to the monthly average of daily maximum 1-hour ozone concentration in 2008 in the Sydney north-west region

To examine in details the change in ozone level, Figure 7 shows difference in predicted 1-hour ozone (ppb) at Richmond for January 2008 between base case and for scenarios when no biogenic emissions is present and when there is no emission from power station. Biogenic emission significantly increases the ozone level and is the most important source contribute to ozone maximum. Power station emission from neighbouring region in the Lower Hunter also strongly influences the 1-hour maximum ozone level in Sydney north-west as also shown in Figure 7. Note that, at night, ozone level is higher than the base case when coal-gas power station emissions are off as there is less NO_x emission to scavenge the ozone

To be able to summarise the whole distribution of predicted ozone with minimum, maximum, median values, Figure 8 shows the box plots of ozone prediction for January 2008 under different emission scenarios.

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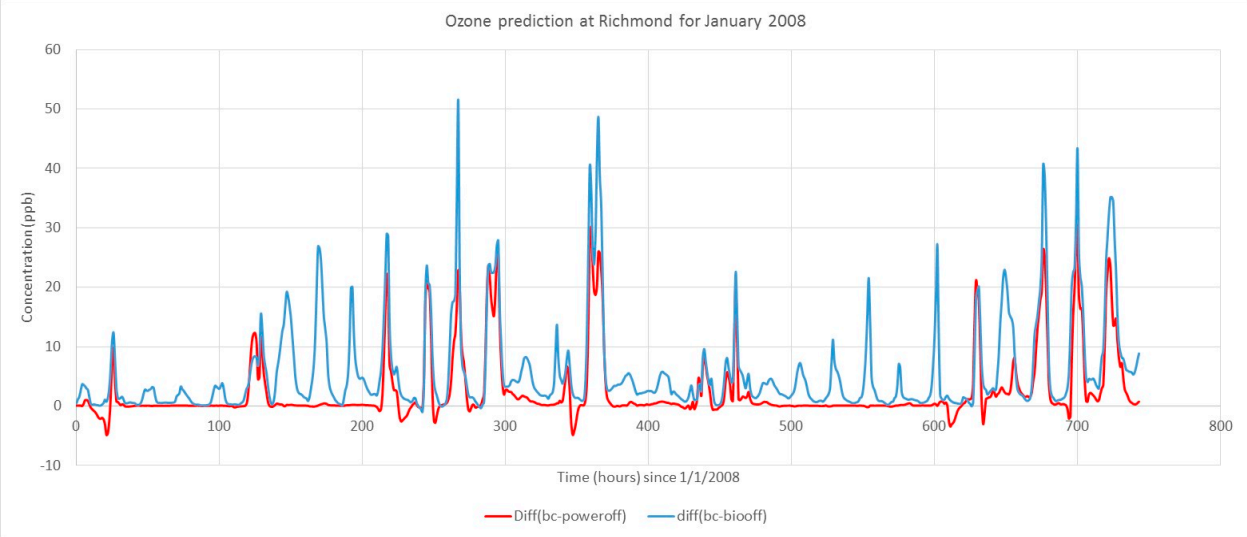

Figure 7. Time series of difference in predicted 1-hour ozone (ppb) at Richmond for January 2008 between base case and biogenic emissions off (blue) and between base case and power stations emissions off (red)

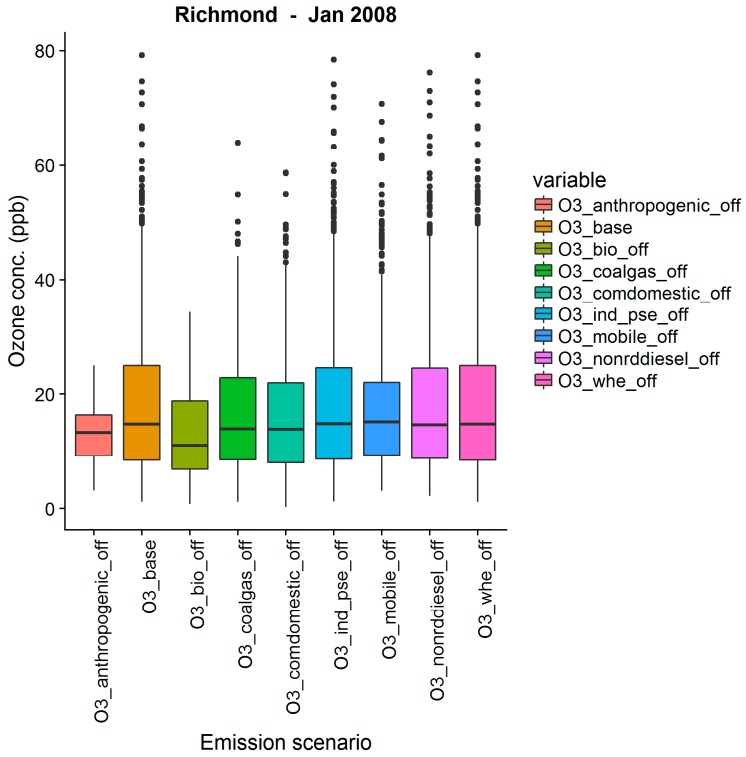

Figure 8. Box plot for 1-hour ozone concentration (ppb) in January 2008 under different emission scenarios at Richmond.

3.3.2 Sydney west, Sydney south-west, Sydney east regions

In the Sydney west region, the on-road motor vehicle emission has slightly more contribution to ozone 1-hour max than that from power stations in the summer months. But during cooler months

in autumn and winter, motor vehicle has a negative contribution to daily maximum 1-hour ozone level

Appendix A shows the tables and graphs summarising the effect of each source to the ozone formation in each of the regions.

In the Sydney south-west region, which is mostly in NO_x-limited during ozone season and is downwind from Sydney central east region, the on-road motor vehicle emission has more contribution to daily maximum 1-hour ozone than that from power stations in the summer months. Next is industry and then non-diesel and shipping sources in that order as ranked contribution to ozone concentration.

In Sydney east region, the motor vehicle emission, on average for each month, contributes negatively to the 1-hour maximum ozone concentration in all months of the year 2008 in this region (as represented by the 3 sites listed above). As this region is in light-limited regime (or VOC-limited), an increase in NO_x emission from motor vehicle sources will reduce the ozone level.

As shown in Figure A.6 (Appendix) of the box plots of ozone concentration at Chullora for January 2008, even though the monthly maximum is reduced when mobile source is turned off but the median ozone increased slightly. This is because the night time ozone increases when there is less NO_x emission to scavenge the ozone. Ozone level also increases during day time, when ozone level is low and in the VOC-limited photochemical process, if NOx emission is decreased. This can be seen in the time series of difference in predicted ozone levels at Chullora for January 2008 under base case and no motor vehicle emission scenario as shown in Figure 9. Maximum ozone is reduced for days where the ozone is high but, for days when ozone is low and at night, ozone level is higher when motor vehicle emission is turned off. The time series shows that Chullora, most of the time during January 2008, is in in VOC-limited regime. Also shown in Figure 9 is the time series of difference in predicted ozone under base case and when no power station emission present. Higher level of local NOx due to emission from motor vehicle compared to that received downwind from power station has a more dramatic effect on ozone level at Chullora.

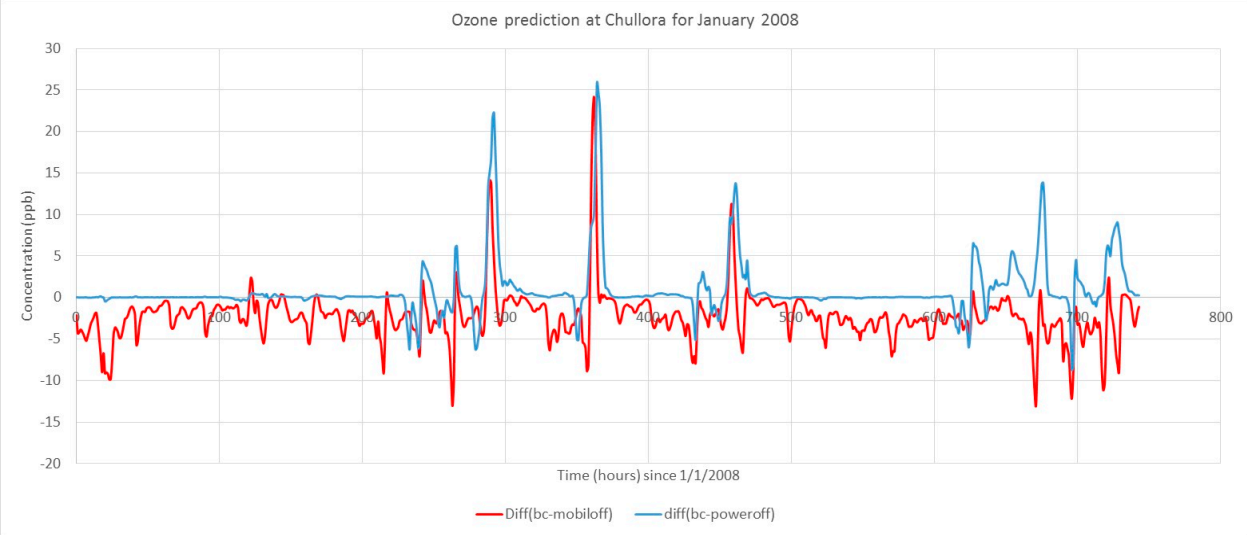

Figure 9. Time series of difference in predicted 1-h ozone (ppb) at Chullora for January 2008 between base case and motor vehicle emissions off (red) and between base case and power station emission off (blue)

3.3.3 Illawarra and Lower Hunter regions

In the Illawarra region, after commercial domestic sources, power stations and motor vehicles are next in importance in contribution to ozone formation. However, in Lower Hunter (Newcastle) region, of anthropogenic contribution, power stations, non-road diesel and shipping sources are more important than motor vehicle and industrial sources (see Appendix A).

Table 7 summarises the order of importance in source contribution to 1-hour ozone maximum in each of the 6 sub-regions of the GMR Sydney region.

Table 7. Ranked order of contribution from anthropogenic sources to maximum 1-h ozone (warm months). For Central and East Sydney, motor vehicle or industry emission decreases the maximum 1-hour ozone (negative contribution) and is denoted by x in the table.

Region	Ranked order of contribution from anthropogenic sources to maximum 1-h ozone (warm months of Dec, Jan and Feb of 2008)			
	First	Second	Third	Fourth
Sydney North West	Commercial domestic	Power stations	Motor vehicles	Non-road diesel and shipping
Sydney West	Commercial domestic	Power stations	Motor vehicles	Industry
Sydney South West	Commercial domestic	Motor vehicles	Power stations	Industry
Sydney Central and East	Commercial domestic	Power stations	x	x
Lower Hunter	Commercial domestic	Power stations	Non-road diesel and shipping	Motor vehicles
Illawarra	Commercial domestic	Power stations	Motor vehicles	Non-road diesel and shipping

4. Discussion

Air quality models have been used recently to study the source contribution to air pollution concentration at a receptor by various authors. The main models that are currently used are the source-oriented CMAQ model and the CAMx model with OSAT. The main advantage of these models are that they treated emitted species from different sources separately and hence can identify source contributions to ozone in a single model run rather than multiple runs by the chemical transport models (CTM) using brute force method as used in this study [7].

Caiazzo et al [28], in their study of quantifying the impact of major sector on air pollution and early deaths in the whole US in 2005 using WRF/CMAQ model, estimated that ~10,000 (90% CI: -1,000 to 21,000) premature deaths per year due to changes in maximum ozone concentrations. The largest contributor for early deaths due to increase in maximum ozone is road transportation with ~5,000 (90% CI: -900 to 11,000) followed by power generation with ~2000 (90% CCCCI: -300 to 4000) early deaths per year.

Our study on source contribution to ozone formation in the Greater Metropolitan Region (GMR) of Sydney in 2008 has identified biogenic sources (mainly vegetation via isoprene and monoterpene emission) is the major contributor to ozone formation in all regions of the GMR. This result confirms the previous study of Duc et al. [8] on ozone source contribution in the Sydney Particle Study (SPS) period of January 2011. Similarly, Ying and Krishnan [29] in their study of source contribution of VOC in southeast Texas based on simulation using CMAQ model have found for maximum 8-hour ozone occurrences from 16 August to 7 September 2000., the median of relative contributions from biogenic sources was approximately 60% compared to 40% of anthropogenic ones. As biogenic emission is a major contribution to ozone formation, it is important for model to account it as accurate as possible. Emmerson et al. [30] has found that the Australian Biogenic Canopy and Grass Emission Model (ABCGEM), as implemented in the current CCAM-CTM model

used in this study, accounts for biogenic VOC emission (especially monoterpenes) from Australian eucalyptus vegetation better than The Model of Emissions of Gases and Aerosols from Nature (MEGAN) when compared these modelled emissions with observations.

Among the anthropogenic sources, commercial and domestic sources are the main contributors to ozone concentration in all regions. While power station or motor vehicles sources, depending on the regions, are the next main contributors of ozone formation. In the cooler months, these sources (power stations and motor vehicles) instead decrease the level of ozone. From Table 1, commercial domestic sources (except wood heaters) have much higher emission of most VOC species than other sources even though they emitted less NO_x than other mobile sources. For this reason, it is not surprising that commercial and domestic sources contribute most to the ozone formation in all the metropolitan regions.

As it is not possible or practical to control biogenic emission sources, the implication of this study is that to control the level of ozone in the GMR, the commercial and domestic sources should be the focus for policy makers to manage the ozone level in the GMR. As shown in Figure 5, when commercial domestic sources are turned off, a reduction in ozone is attained in all regions in the GMR.

A reduction in power station emission will significantly improve the ozone concentration in the north west of Sydney but less so in other regions of the GMR. Gégo et al. [31] in their study of the effects of change in nitrogen oxides emissions from the electric power sector on ozone levels in eastern U.S using CMAQ model for the 2002 model year, have shown that ozone concentrations would have been much higher in much of the eastern United States if NO_x emission controls had not implemented by the power sector and exceptions occurred in the immediate vicinity of major point sources where increased NO titration tends to lower ozone levels.

Motor vehicle is less a problem compared to commercial domestic and power station sources except for the south west of Sydney. However, south west of Sydney has more smog episodes than other regions in the GMR, therefore, to reduce high frequency of ozone events, control of motor vehicle emission should be given more priority than control of emission from power station sources. As shown in Figure 5, a significant reduction of ozone in the southwest compared to other regions is achieved when on-road mobile sources were turned off. This region is downwind from the urban area of Sydney where the largest emission source of NO_x and VOC precursors is motor vehicle and hence will cause elevated ozone downwind in the south west of Sydney. Various studies have shown that areas downwind from the upwind emission of precursors experience high ozone [32-33].

Li, Lau et al. [7] showed that ozone in upwind area of the Pearl River Delta in China is mostly affected by super-regional sources and local sources while downwind area has higher ozone and is affected by regional sources in its upwind area beside the super-regional and local source contribution.

It should be noted that our results on the source contribution to ozone is only applied to the base 2008 emission inventory data. If this "base state" of emission is changed to a different composition of VOC and NO_x emissions (such as the 2013 or 2018 emission inventories), then the source contribution results could be different as the relation of ozone formation with VOC and NO_x precursors emissions at various regions in the GMR is nonlinear and complex.

As ozone response to emitting sources of VOC and NO_x is nonlinear, the contribution of each source to maximum ozone is depending on the "base state" consisting of all other emitting sources in the region. Uncertainty in the emission inventory of these sources therefore also affects the contribution of ozone attributed to this source. Cohan et al. [1] has shown that underestimates of NO_x emission rates lead to underprediction of total source contribution but overprediction of per-ton sensitivity.

Fujita et al. [34] in their study of source contributions of ozone precursors in California's South Coast Air Basin to ozone weekday and weekend variation had shown that reduced NO_x emission of weekend emission from motor vehicle caused higher level of ozone than during the weekday due to the higher ratio of NMHC (Non-methane Hydrocarbon) to NO_x in this VOC-limited basin.

It is therefore important to determine and understand which region in the GMR is NO_x-limited or VOC-limited. The observation-based IER method which uses monitoring station data is proved to be useful in delineation different regions of photochemical smog profiles within the GMR where monitoring stations are located. Based on the results from IER method, the results of source contribution to maximum ozone in the GMR using air quality model for different emission scenarios can be understood and explained adequately from emission point of view and therefore facilitate policy implementation.

As for policy implementation in reducing ozone, it should be pointed out that even though Sydney ozone trend in the past decade has decreased but background ozone trend is actually increasing [35] which is part of a world-wide trend of increasing background level in many areas of the world. This will make the reduction of ozone further in the future much more difficult such as shown and discussed by Parrish et al. [36] in their study of background ozone contribution to the California air basins.

5. Conclusions

This study provides a detailed source contribution to ozone formation in different regions of the Greater Metropolitan Regions of Sydney. The importance of each source in these regions is depending on the ozone formation potential of each of these regions and whether they are in NO_x-limited or VOC-limited photochemical regime in ozone season. Extensive monitoring data available from the OEH monitoring network and many previous studies using observation-based method have provided an understanding of the ozone formation potential in various sub-regions of the GMR.

Biogenic emission is the major contributor to ozone formation in all regions of the GMR due to their large emission of VOC. Of anthropogenic emission, commercial and domestic sources are the main contributors to ozone concentration in all regions. These commercial domestic sources (except wood heaters) have much higher emission of most VOC species but less NO_x than other sources such as mobile sources and hence contribute more to the ozone formation in all the metropolitan regions compared to others. The commercial and domestic sources should be the focus for policy makers to manage the ozone level in the GMR

While power station or motor vehicles sources, depending on the regions, are the next main contributors of ozone formation, in the cooler months, these sources (power stations and motor vehicles) instead decrease the level of ozone.

In the north west of Sydney, a reduction in power station emission will significantly improve the ozone concentration there.

Motor vehicle is less a problem compared to commercial domestic and power station sources except for the south west of Sydney. As the south west of Sydney has more smog episodes than other regions in the GMR, control of motor vehicle emission should be given more priority than control of emission from power station sources to reduce high frequency of ozone events in the Sydney basin.

Our next study in relation to source contribution to ozone formation will focus on the health impact of each emission source on various health endpoints from their contribution to poor air quality (e.g. ozone and PM2.5) in the GMR.

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Author Contributions:

Conceptualization, Hiep Duc.; methodology, Hiep Duc, Lisa T.-C. Chang.; software, Hiep Duc, Toan Trieu, David Salter; validation, Lisa T.-C. Chang, Toan Trieu and David Salter; formal analysis, Hiep Duc.; investigation, Hiep Duc, Lisa T.-C. Chang; resources, Hiep Duc, David Salter, Yvonne Scorgie; data curation, Hiep Duc, Lisa T.-C. Chang, Toan Trieu, David Salter; writing—original draft preparation, Hiep Duc.;

552 writing—review and editing, Hiep Duc, Lisa T.-C. Chang; visualization, Hiep Duc, Lisa T.-C. Chang;
553 supervision, Hiep Duc; project administration, Yvonne Scorgie.; funding acquisition, Clare Murphy.

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557

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Appendix A

1. Sydney west region

Table A1. Monthly average of daily maximum 1-hour predicted ozone concentration (ppb) in the Sydney west region for different months in 2008 under various emission scenarios

Month	All sources	Power stations	Commercial -domestic	On-road motor vehicles	Non-road diesel and marine	Industry	All Anthrop ogenic	All natural
Jan	38.53	4.02	10.23	5.24	0.52	0.28	20.29	18.23
Feb	29.33	2.52	6.83	1.72	0.11	0.64	11.82	17.51
Mar	31.89	1.24	10.57	1.66	-0.07	0.32	13.72	18.17
Apr	18.61	0.09	2.95	-1.44	-0.08	0.09	1.63	16.97
May	23.6	0.36	4.8	-2.94	-0.16	0.02	2.19	21.41
Jun	20.68	0.13	0.88	-1.97	-0.18	-0.14	-1.26	21.94
Jul	18.99	-0.04	0.86	-1.42	-0.09	-0.04	-0.72	19.71
Aug	22.27	0.01	1.58	-1.25	-0.09	-0.01	0.29	21.98
Sep	23.02	1.53	3.47	-0.84	-0.01	0.19	4.38	18.63
Oct	32.28	2.39	8.24	2.5	0.24	0.48	13.87	18.41
Nov	28.36	1.69	4.8	0.96	0.15	0.19	7.79	20.57
Dec	34.12	2.33	6.62	3.24	0.36	0.47	13.03	21.09
Average	**26.84**	**1.35**	**5.17**	**0.46**	**0.06**	**0.21**	**7.27**	**19.56**

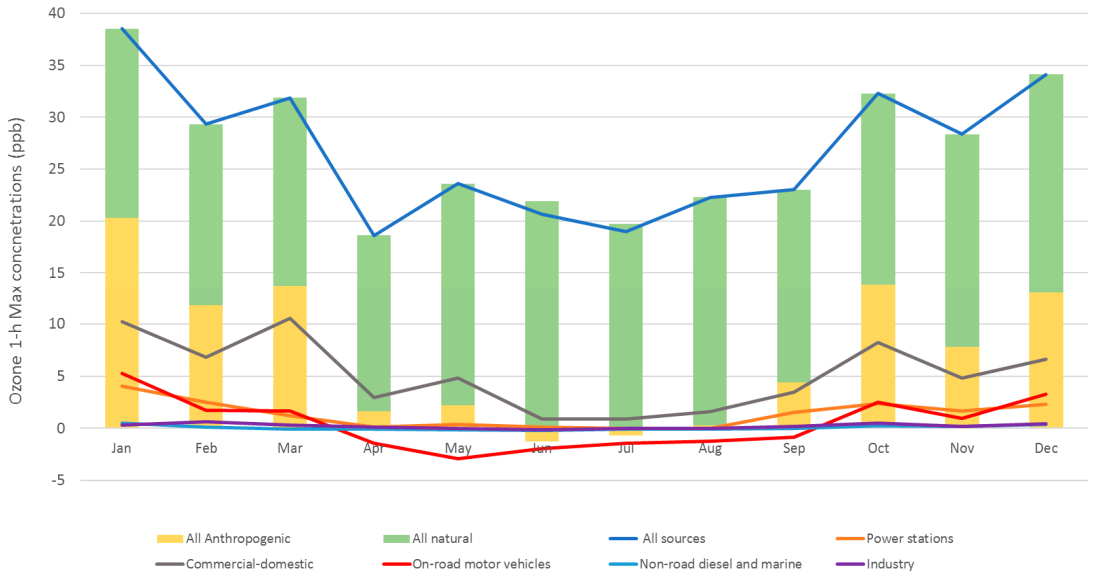

Figure A1. Contribution of all anthropogenic and natural emissions (bar graph) and different anthropogenic sources (line graph) to the monthly average of daily maximum 1-hour ozone concentration in 2008 in the Sydney west region

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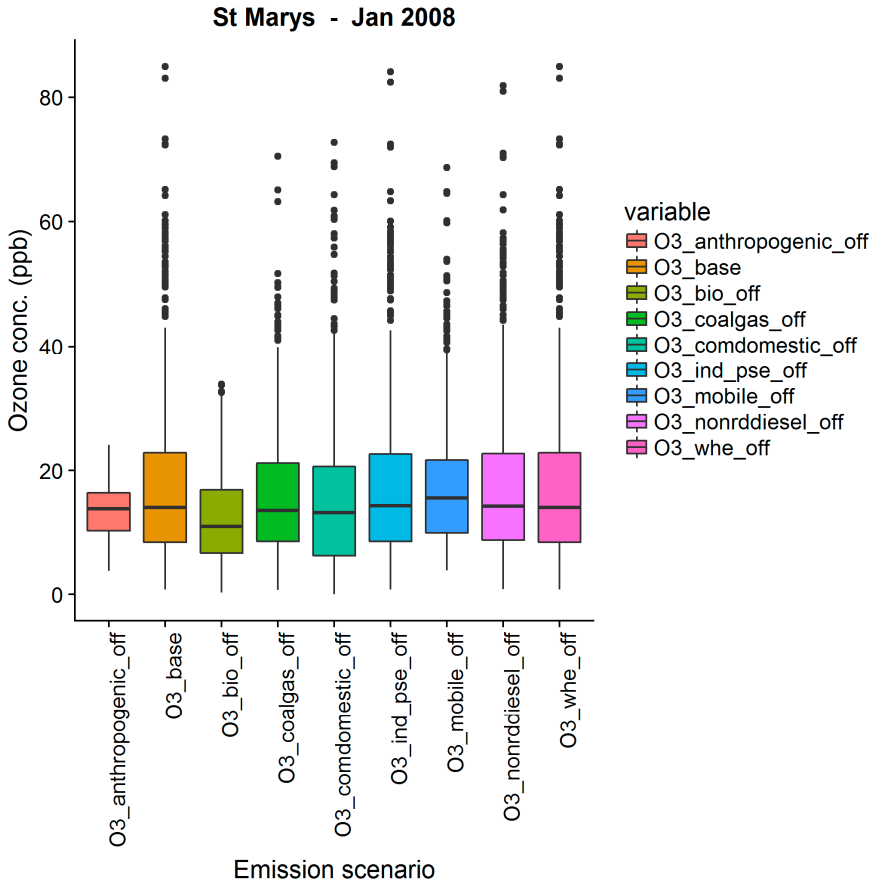
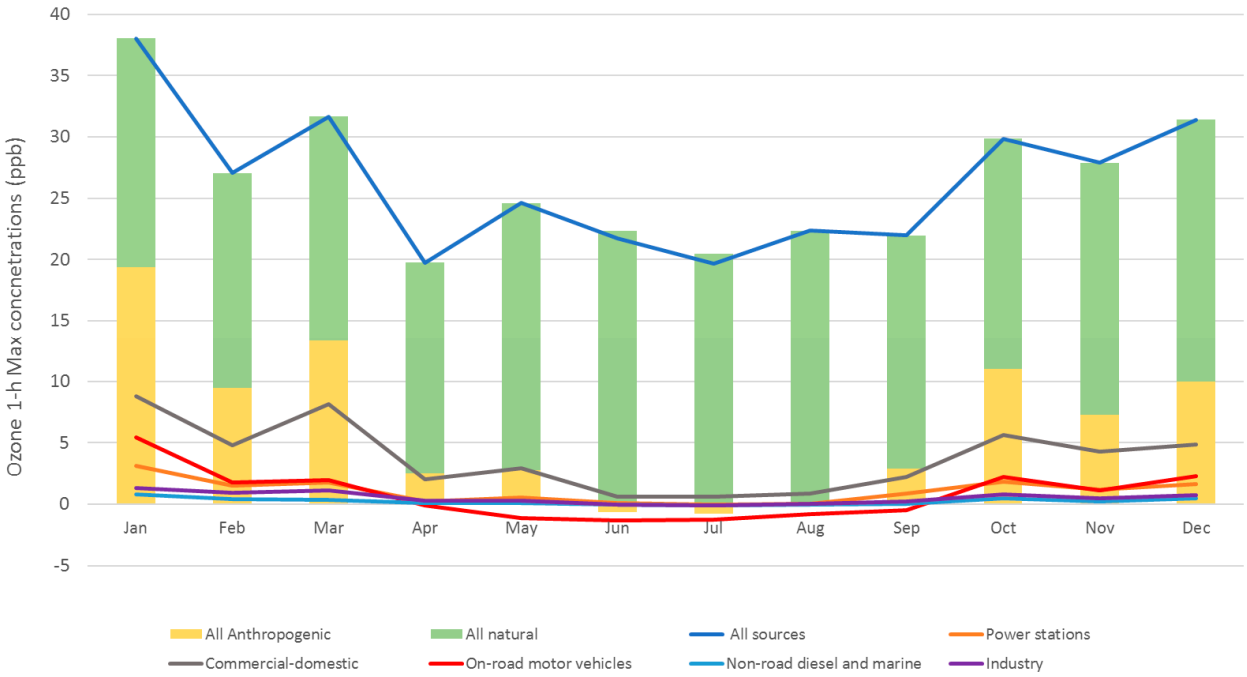


Figure A.2 Box plot for 1-hour ozone concentration (ppb) in January 2008 under different emission scenarios at St Marys

2. Sydney south-west region

Table A.2 Monthly average of daily maximum 1-hour predicted ozone concentration (ppb) in the Sydney south-west region for different months in 2008 under various emission scenarios

Month	All sources	Power stations	Commercial-domestic	On-road motor vehicles	Non-road diesel and marine	Industry	All Anthropogenic	All natural
Jan	38.05	3.12	8.76	5.41	0.79	1.31	19.4	18.65
Feb	27.07	1.54	4.79	1.78	0.4	0.95	9.46	17.61
Mar	31.66	1.75	8.17	1.96	0.35	1.11	13.35	18.32
Apr	19.76	0.23	2.01	-0.11	0.11	0.26	2.52	17.24
May	24.62	0.54	2.91	-1.1	0.07	0.27	2.76	21.86
Jun	21.71	0.11	0.63	-1.29	-0.06	-0.05	-0.64	22.35
Jul	19.7	-0.01	0.62	-1.26	-0.07	-0.09	-0.8	20.5
Aug	22.37	0.05	0.85	-0.81	-0.02	0.05	0.16	22.21
Sep	21.97	0.89	2.25	-0.51	0.05	0.21	2.92	19.06
Oct	29.87	1.81	5.66	2.22	0.46	0.83	11	18.86
Nov	27.91	1.18	4.29	1.1	0.21	0.5	7.28	20.63
Dec	31. 4	1.62	4.83	2.26	0.49	0.74	9.95	21.45
Average	26.37	1.07	3.83	0.81	0.23	0.51	6.47	19.91



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674 **Figure A.3** Contribution of all anthropogenic and natural emissions (bar graph) and different
675 anthropogenic sources (line graph) to the monthly average of daily maximum 1-hour ozone
676 concentration in 2008 in the Sydney south west region

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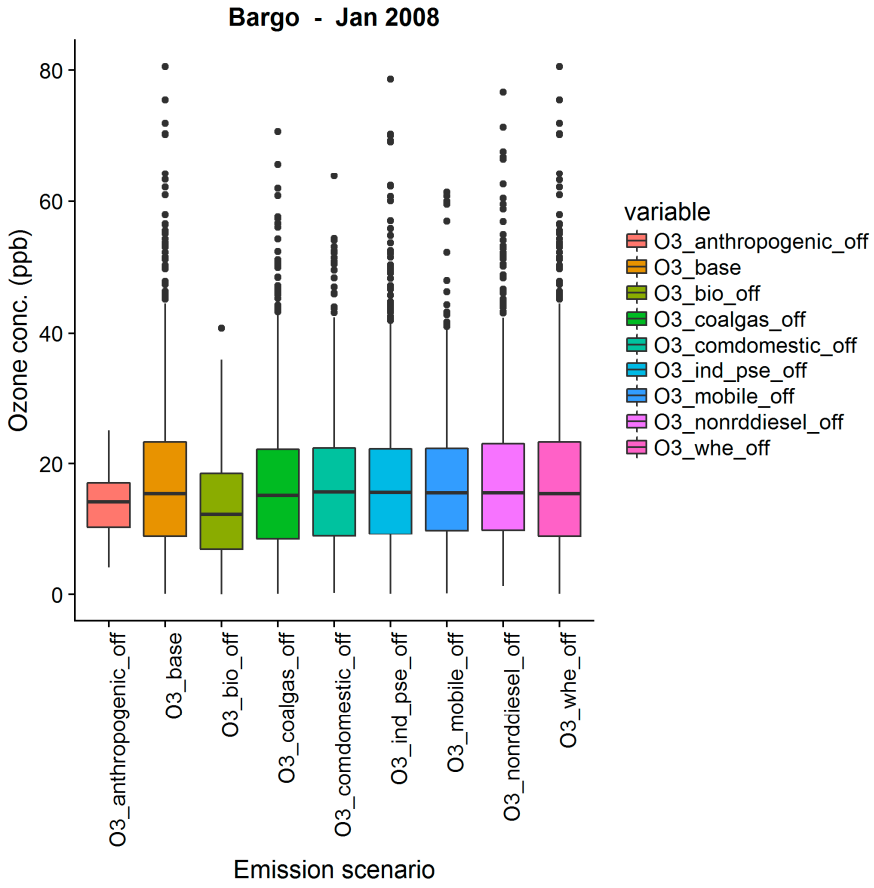

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Figure A.4 Box plot for 1-hour ozone concentration (ppb) in January 2008 under different emission scenarios at Bargo

3. Sydney east region

Table A.3 Monthly average of daily maximum 1-hour predicted ozone concentration (ppb) in the Sydney east region for different months in 2008 under various emission scenarios

Month	All sources	Power stations	Commercial-domestic	On-road motor vehicles	Non-road diesel and marine	Industry	All Anthropogenic	All natural
Jan	27.91	2.29	8.63	-0.88	0.09	0.16	10.29	17.61
Feb	23.5	1.41	6.07	-0.82	-0.3	0.17	6.53	16.97
Mar	22.79	0.93	6.59	-1.96	-0.37	0.12	5.32	17.47
Apr	15.82	0.09	1.98	-2.37	-0.46	-0.1	-0.84	16.66
May	18.94	0.05	4.05	-5.08	-0.88	-0.17	-1.9	20.85
Jun	17.77	-0.01	0.82	-3.67	-0.77	-0.26	-3.88	21.65
Jul	15.79	-0.11	0.81	-3.46	-0.68	-0.18	-3.6	19.39
Aug	19.39	0.03	1.43	-3.02	-0.51	-0.13	-2.16	21.55
Sep	19.32	0.29	3.91	-2.39	-0.62	-0.02	1.2	18.12
Oct	26.23	2.04	8.14	-1.61	-0.32	0.12	8.39	17.85
Nov	23.79	1.11	3.38	-0.85	-0.09	0.13	3.68	20.11
Dec	30.73	2.26	8.31	-0.37	0.17	0.34	10.71	20.01
Average	21.85	0.87	4.52	-2.21	-0.39	0.02	2.82	19.03

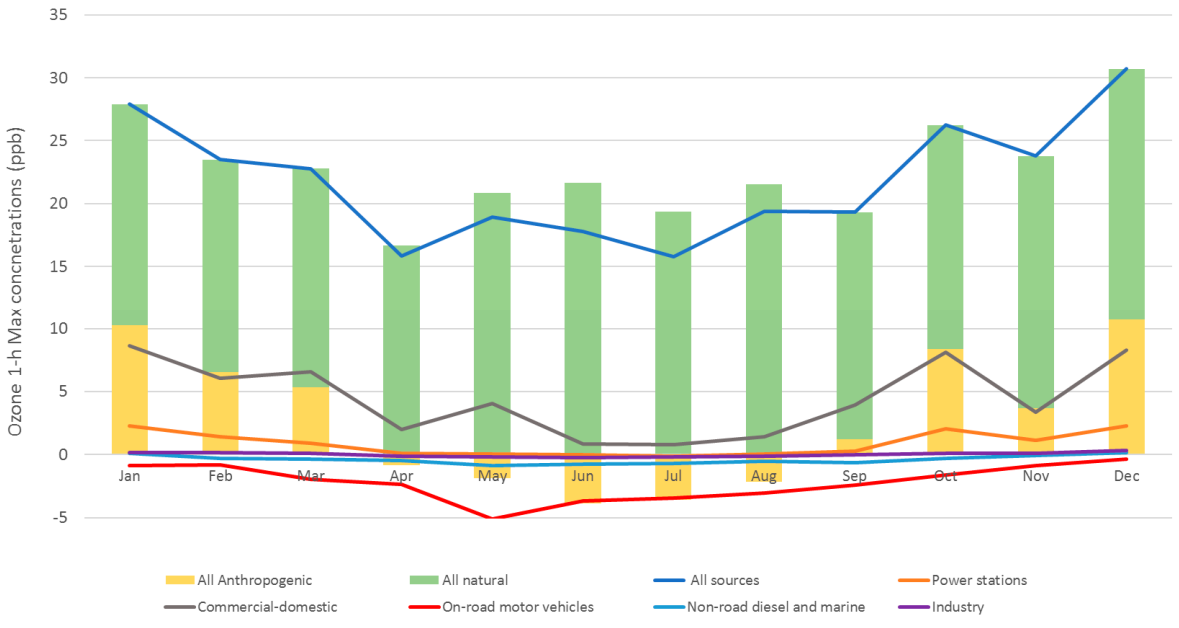

Figure A.5 Contribution of all anthropogenic and natural emissions (bar graph) and different anthropogenic sources (line graph) to the monthly average of daily maximum 1-hour ozone concentration in 2008 in Sydney east region

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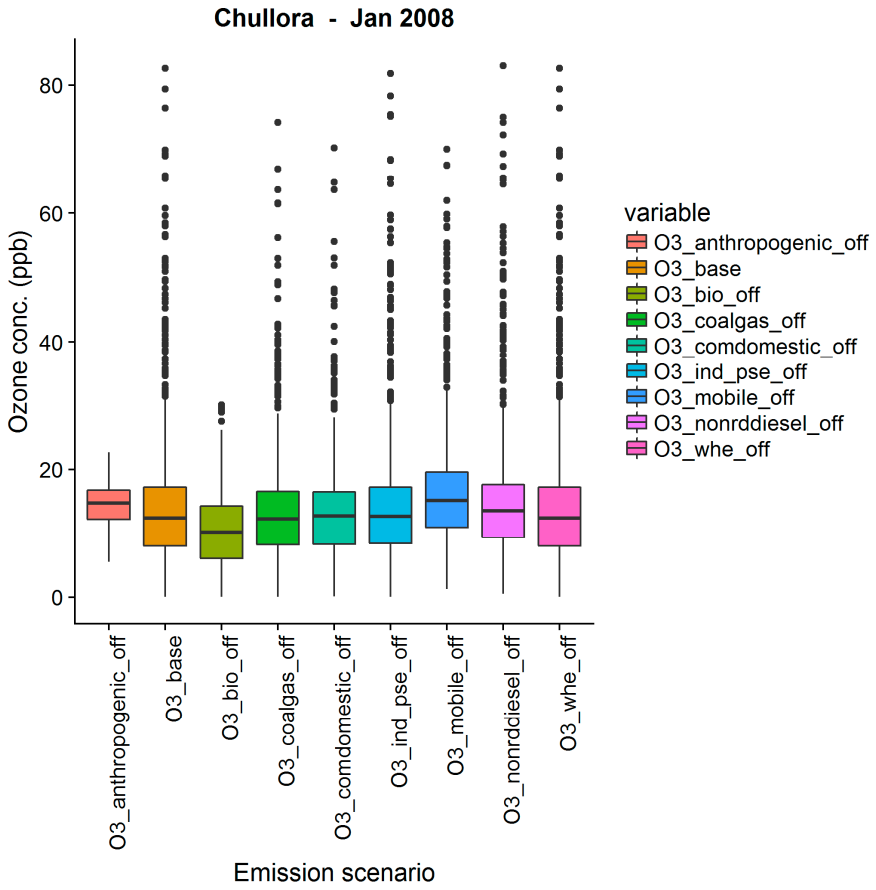

Figure A.6 Box plot for 1-hour ozone concentration (ppb) in January 2008 under different emission scenarios at Chullora

4. Illawarra region

Table A.4 Monthly average of daily maximum 1-hour predicted ozone concentration (ppb) in the Illawarra region for different months in 2008 under various emission scenarios

Month	All sources	Power stations	Commercial-domestic	On-road motor vehicles	Non-road diesel and marine	Industry	All Anthropogenic	All natural
Jan	33.99	4.02	8.99	2.48	0.48	-0.1	15.86	18.13
Feb	27.45	2	5.87	1.82	0.14	0.21	10.05	17.41
Mar	29.34	1.75	8.02	1.4	0.08	0	11.25	18.1
Apr	18.36	0.19	2.44	-1.05	-0.1	-0.12	1.37	16.99
May	23.35	0.43	3.84	-2.09	-0.2	-0.25	1.82	21.53
Jun	20.78	0.05	0.82	-1.9	-0.22	-0.21	-1.45	22.23
Jul	19.04	-0.02	0.72	-1.59	-0.14	-0.11	-1.12	20.16
Aug	22.22	0.12	1.21	-1.2	-0.07	-0.04	0.06	22.16
Sep	21.85	1.22	2.96	-0.92	-0.08	-0.01	3.2	18.65
Oct	29.7	2.69	6.94	1.28	0.23	0.18	11.35	18.35
Nov	26.68	1.76	3.65	0.62	0.22	-0.11	6.14	20.54
Dec	32.17	2.39	5.95	2.23	0.52	0.25	11.33	20.84
Average	25.44	1.39	4.3	0.09	0.07	-0.03	5.84	19.6

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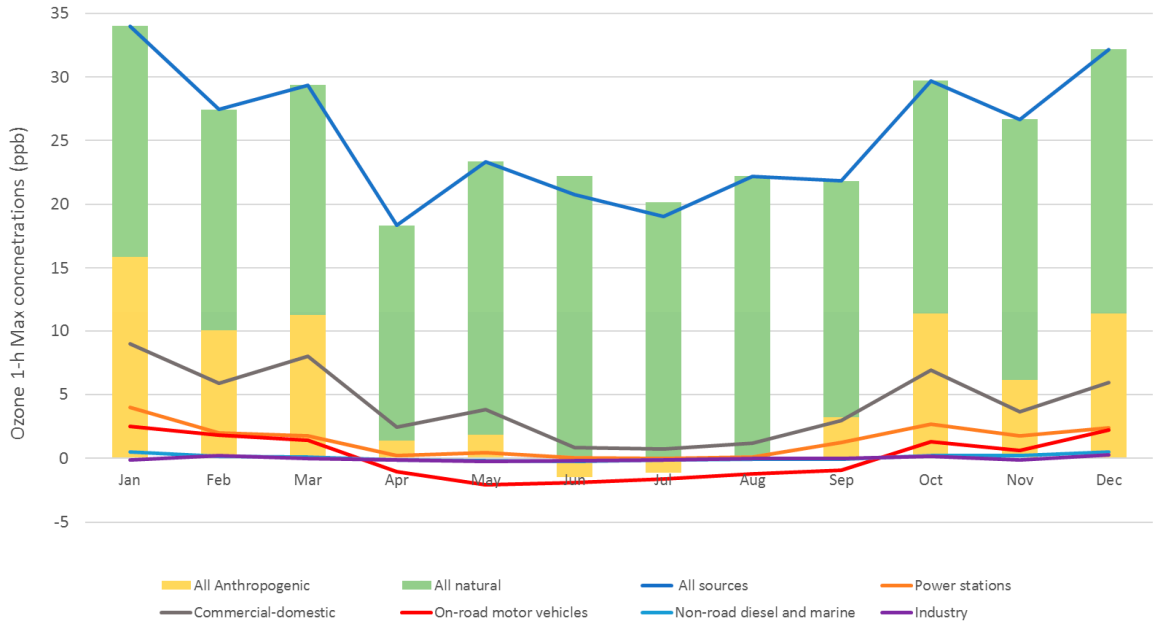

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702 **Figure A.7** Contribution of all anthropogenic and natural emissions (bar graph) and different
703 anthropogenic sources (line graph) to the monthly average of daily maximum 1-hour ozone
704 concentration in 2008 in the Illawarra region

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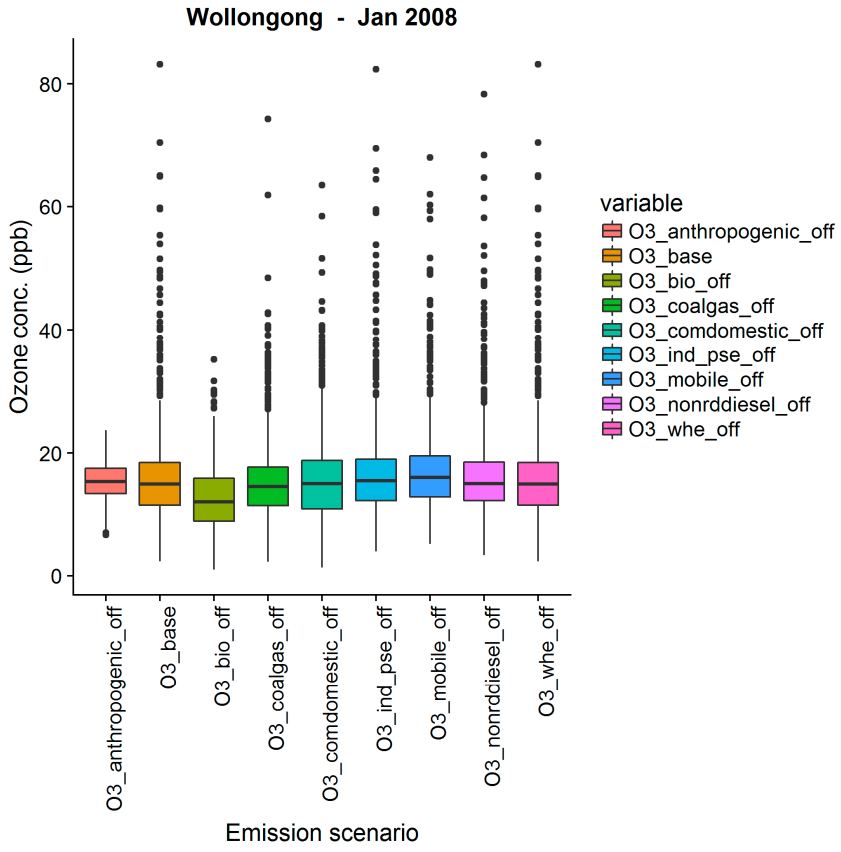

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707 **Figure A.8** Box plot for 1-hour ozone concentration (ppb) in January 2008 under different emission
708 scenarios at Wollongong

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5. Lower Hunter (Newcastle) region

Table A.5 Monthly average of daily maximum 1-hour predicted ozone concentration (ppb) in the Newcastle region for different months in 2008 under various emission scenarios

Month	All sources	Power stations	Commercial-domestic	On-road motor vehicles	Non-road diesel and marine	Industry	All Anthropogenic	All natural
Jan	24.91	0.78	3.65	0.33	1.64	0.25	6.67	18.25
Feb	25.55	1.10	5.00	0.92	0.73	0.25	8.00	17.55
Mar	25.52	0.95	4.12	0.67	1.19	0.40	7.35	18.17
Apr	20.82	-0.10	3.31	-0.19	-0.05	-0.01	3.01	17.80
May	25.49	-0.98	5.44	-0.62	-0.38	-0.02	3.51	21.98
Jun	23.24	-1.18	2.47	-0.62	-0.38	-0.09	0.23	23.00
Jul	20.91	-1.00	1.46	-0.52	-0.31	-0.04	-0.38	21.30
Aug	23.77	-1.15	3.05	-0.44	-0.18	0.00	1.37	22.40
Sep	24.69	0.98	3.95	0.26	0.30	0.13	5.65	19.04
Oct	29.86	3.28	6.16	0.43	1.00	0.26	11.16	18.70
Nov	26.06	1.63	3.27	0.52	0.60	0.22	6.24	19.82
Dec	34.31	3.91	7.81	1.12	1.37	0.45	14.66	19.65
Average	25.45	0.69	4.15	0.15	0.46	0.15	5.63	19.82

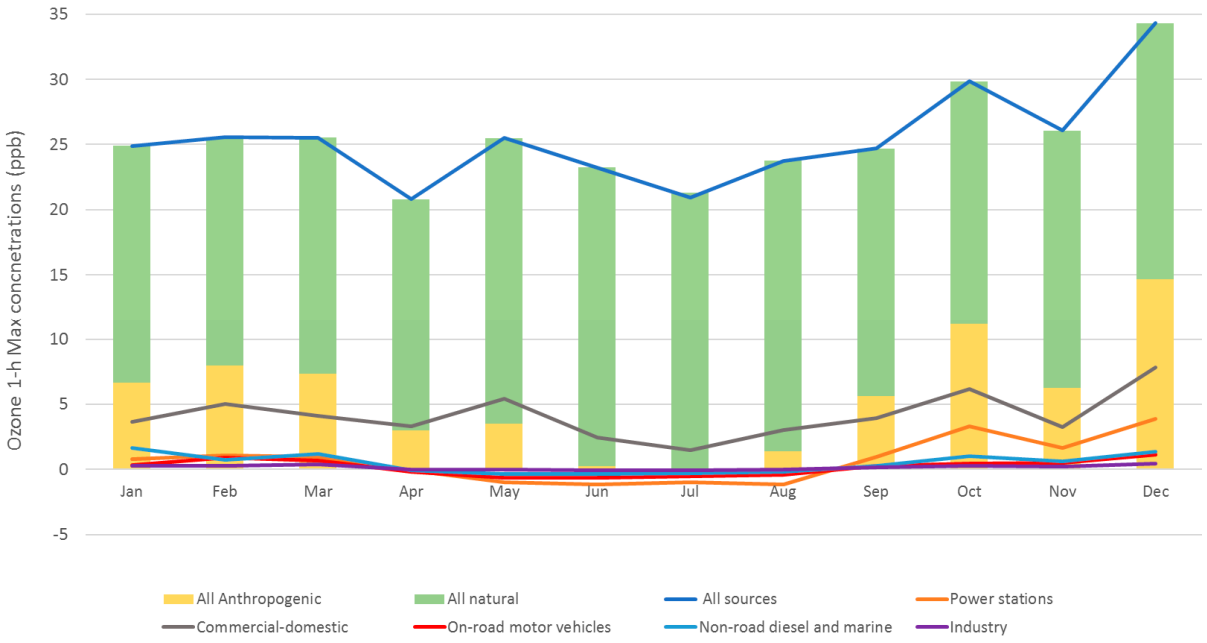
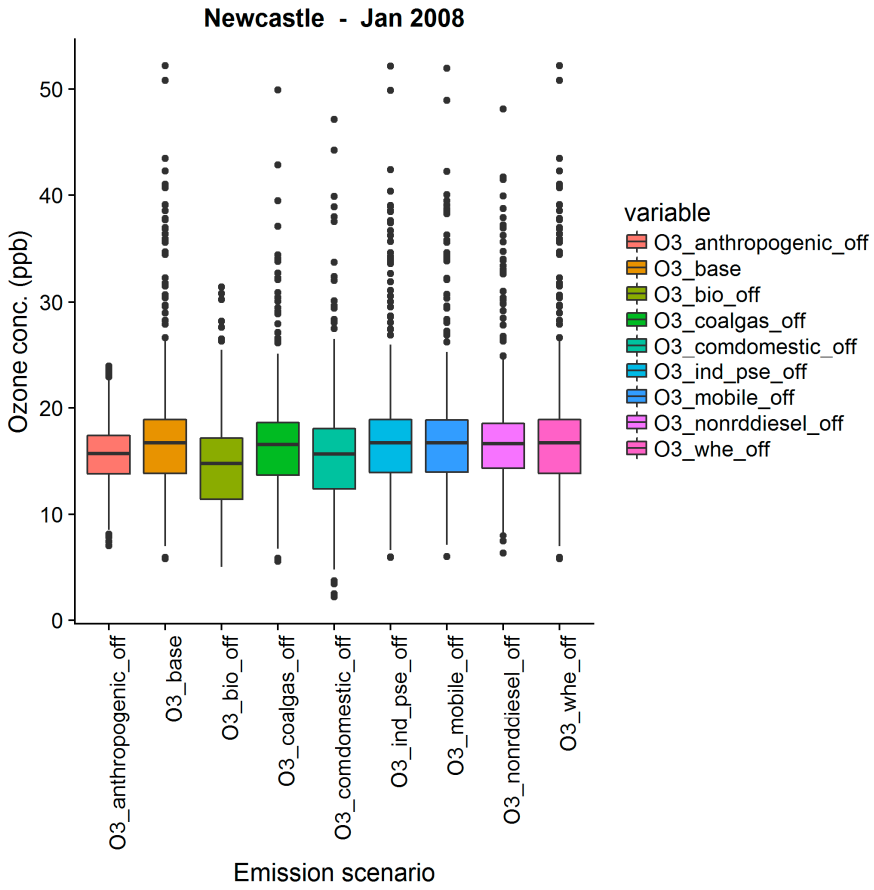


Figure A.9 Contribution of all anthropogenic and natural emissions (bar graph) and different anthropogenic sources (line graph) to the monthly average of daily maximum 1-hour ozone concentration in 2008 in the Newcastle region



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719 **Figure A.10** Box plot for 1-hour ozone concentration (ppb) in January 2008 under different
720 emission scenarios at Newcastle