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Ozone Monitoring

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Abstract

Stratospheric ozone performs the beneficial role of reducing the intensity of ultraviolet light reaching earth. In contrast, ozone causes several undesirable effects at ground level and is the key indicator of photochemical air pollution that results from vehicular exhaust fumes. Regional councils are instructed under the Ministry for the Environment's National Environmental Standards to monitor locations most at risk of significant ozone accumulation. Environment Waikato selected a monitoring site at the town of Coromandel, rationalising that reactive air masses generated from Auckland traffic are primarily transported in that direction by the prevailing westerly winds. During three consecutive monitoring periods in 07/08, 08/09 and 09/10, the highest level of ozone detected was 90.5 μ g/m³, calculated as a one hour mean, which is significantly less than the NES threshold of 150 μ g/m³.

1 Introduction

Although ozone (O_3) can be classified as an environmental trace gas, it exerts a variety of influences on dynamic atmosphere processes (Butukhanov 2008). Stratospheric ozone is known to protect the planet from damaging UV-B radiation, while an elevated ozone concentration in the troposphere is a key indicator of photochemical air pollution (Laurila 2009). Acute exposure to ozone is a serious respiratory and cardiovascular health risk, with symptoms including shortness of breath, nausea, lung damage and eye irritation (Raheem 2008). The strong oxidizing potential of ozone is also toxic to plants and may compromise the structural integrity of material substrates.

Ozone in the troposphere is produced when nitrogen oxides (NO_x) and volatile organic compounds (VOC), derived from internal combustion engine emissions, mix in the presence of UV radiation (Khan 2007). The mechanisms of photochemical air pollution formation are multifaceted, incorporating physical transportation of air masses and a series of complex chemical processes (Gimson 2005). It is generally established that photolysis of NO₂ produces oxygen atoms (1), which react with molecular oxygen to produce ozone (2). Where NO₂ is regenerated from the reaction of NO with ozone (3), levels of ozone may not be significantly increased. However, VOC react with OH radicals (4) and molecular oxygen to form peroxyl radicals (5) which also react with NO (6). The presence of VOC therefore provides an alternate pathway for the conversion of NO to NO₂, which reduces the rate of (3), allowing ozone to accumulate (Fleming 2006).

 $NO_{2} + UV \text{ radiation} \rightarrow NO + O(1)$ $O_{2} + O \rightarrow O_{3}(2)$ $O_{3} + NO \rightarrow NO_{2} + O_{2}(3)$ $RH + OH \rightarrow H_{2}O + R(4)$ $R + O_{2} \rightarrow R-OO(5)$ $R-OO + NO \rightarrow R-O + NO_{2}(6)$

In 2004, the *Resource Management (National Environmental Standards Relating To Certain Air Pollutants, Dioxins, And Other Toxics) Regulations* were enacted.¹ These are also known as the National Environmental Standards for Air Quality (NESAQ).

Under these regulations, the national standard for ozone is 150 μ g/m³, not to be exceeded at any time.

Section 15 of the NESAQ specifies that regional councils must monitor the air quality in airsheds where a standard is likely to be breached, and that monitoring should be carried out in that part of an airshed that is likely to represent a 'worst case' location.

In the case of ozone, it was initially unclear whether the national standard of $150 \ \mu g/m^3$ (one hour average) would be breached in any part of the Waikato region's 21 airsheds. Twenty of these airsheds are urban,² and the remaining airshed is defined as everything else, and called the "rest of region" airshed.

¹ For more information see: <u>http://www.mfe.govt.nz/laws/standards/amendments.html</u>

² For a listing and maps of the urban airsheds, see: <u>http://www.ew.govt.nz/Environmental-information/All-about-air/Airsheds/</u>

Some preliminary monitoring for ozone had taken place in Hamilton from 27 November 2003 to 25 March 2004, but concentrations detected in that instance were low.³

Given that (a) the two main prerequisites for photochemical air pollution are traffic emissions and sunlight, and (b) photochemical air pollution often materializes downwind from the source of precursor molecules (Adeeb 2004), it was thought likely that the highest concentrations of ozone over land in the Waikato region may be downwind of air pollutants generated by vehicles within the Auckland region. Prevailing westerly winds will drive these pollutants toward the western coast of the Coromandel Peninsula.

On this basis, Environment Waikato commissioned Watercare Services Ltd to conduct continuous ambient monitoring of ozone in their region at the township of Coromandel. Monitoring was carried out over three consecutive 3 month periods of the summers of 2007-08, 08-09 and 09-10: specifically 6 December 2007 to 27 March 2008, 21 Dec 2008 to 4 May 2009. 22 Dec 2009 to 1 May 2010.

The monitoring station was a shed located at the end of the Coromandel wharf. Further details of the instrumentation, site location and quality control are provided in two reports from Watercare Services Ltd., available as Environment Waikato documents 1713325 (08-09) and 1713311 (09-10).

Results

The statistics of the monitoring results (one hour and rolling eight hour means) are summarized in Table 1 and the one-hour mean results are graphically depicted in Figure 1. Note that periods of instrument maintenance are represented by gaps in the data. The official NES (2004) for ozone is 150 μ g/m³. This was not exceeded during the monitoring periods with the highest observed value being 90.5 μ g/m³ (Table 1). The complementary Ministry for the Environment Ambient Air Quality Guideline (AAQG – 2002) for ozone, as applied to eight hour rolling means, is 100 μ g/m³; this was also not exceeded.⁴ Collated results are available in Environment Waikato document 1699114.

	2007-08		200	8-09	2009-10	
Variable	1hr	8hr	1hr	8hr	1hr	8hr
Count	2666	2603	2806	2638	3062	2961
Mean	23.6	23.6	35.4	35.3	36.0	36.0
Median	23.8	23.6	36.0	35.8	36.3	36.2
Mid-Range	29.1	24.9	47.4	44.4	45.6	40.9
Standard Deviation	6.8	5.7	11.4	9.9	11.6	10.2
Minimum	5.6	8.0	4.2	9.3	3.6	9.8
Maximum	52.6	41.9	90.5	79.5	87.6	72.1
Standard Error	0.1	0.1	0.2	0.2	0.2	0.2
Lower 95th %tile	11.6	14.0	15.3	18.8	17.0	19.4
Upper 95th %tile	34.7	32.9	51.5	50.0	54.0	51.9
95% Confidence	0.3	0.2	0.4	0.4	0.4	0.4
95% CI - Lower	23.3	23.4	34.9	34.9	35.6	35.6
95% CI - Upper	23.9	23.8	35.8	35.6	36.4	36.3

Table 1:	Summary	v statistics	of one	-hour and	eiaht	hour	(rollina)	means
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Ozone concentrations in the troposphere are very sensitive to changes in meteorological conditions (Yamaji 2006). The measured ozone concentrations were significantly lower during the 07/08 monitoring period (average one hour mean of 23.6 μ g/m³) compared with the 08/09 and 09/10 periods (35.4 and 36.0 μ g/m³ respectively).

³ For a summary of results, see: <u>http://www.ew.govt.nz/Environmental-information/Environmental-indicators/Air/Air-guality/air5-keypoints/</u>

⁴ See: <u>http://www.mfe.govt.nz/publications/air/ambient-air-quality-may02/index.html</u>

This may be indicative of prevailing easterly winds during the 07/08 period, resulting in marine air masses, rather than urban, predominating over the testing region.



Ozone concentrations ($\mu q/m^3$) plotted from three consecutive December – Figure 1: May monitoring periods of 07/08, 08/09 and 09/10 in comparison with the NES of 150 μ g/m³.

Summary and recommendations

Ozone is the key indicator of photochemical air pollution and at elevated levels causes several undesirable health effects. Environment Waikato monitored the ozone concentration at Coromandel, a location considered at risk of significant ozone accumulation. The National Environmental Standards for Air Quality (NESAQ) for ozone were not breached at any point during the monitoring periods of 6 December 2007-27 March 2008, 21 Dec 2008-4 May 2009 and 22 Dec 2009-1 May 2010.

These monitoring periods represent the seasons of summer and autumn. It has been established in the literature that ozone levels are strongly influenced by meteorological conditions and the exact nature of seasonal effects are specific to each locality (Yamaji 2006). It is recommended in the future that a complete seasonal trend analysis is performed at Coromandel by monitoring the ozone concentration over an entire year.

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