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Use of a dense monitoring network of low-cost instruments to observe local changes in the diurnal ozone cycles as marine air passes over a geographically isolated urban centre

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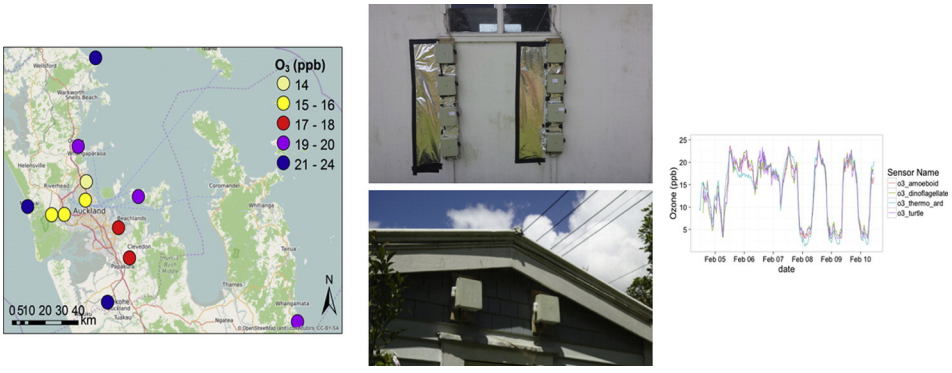
HIGHLIGHTS

- A network of low-cost ozone instruments was deployed in a geographically isolated city.
- Low-cost instruments are capable of identifying small within-city O_3 variability.
- Overall, Auckland is a net sink for ozone.
- Dry deposition rates at nighttime may be higher than assumed in urban environments.

GRAPHICAL ABSTRACT



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ABSTRACT

Ozone (O_3) concentrations in urban areas are spatially and temporally variable, influenced by chemical production, depletion through deposition and chemical titration processes and dispersion. To date, analysis of intra-urban variability of O_3 concentrations, and the influence of local controls on production and depletion rates, has been limited due to the low spatial and/or temporal resolution of measurements. We demonstrate that measurements made using a carefully managed multi-sensor network of low-cost gas-sensitive semiconductor instruments are sufficiently precise to resolve subtle but significant variations in ozone concentration across a region.

Ozone was measured at 12 sites in the isolated subtropical city of Auckland, New Zealand. Overall O_3 concentrations in the Auckland region were low (annual mean: 19 ppb) across all seasons, with a minimum in summer. Higher O_3 concentrations (max. 57 ppb) were observed when wind speeds were >5 m s^{-1} and from the W/SW, and were associated with maritime air masses.

Ozone formation in the Auckland region is low, which is attributed to a combination of the low O_3 background concentrations, the negligible contribution of long-range transport and the effect of NOx titration. Intra-urban variability showed that the lowest O_3 concentrations were measured at the residential sites, particularly at night and during rush hours. Ozone depletion from reaction with traffic-generated NO explains the rush-hour minima but did not fully account for the low night-time values. The results suggest that night-time depletion may result from other processes such as the reaction of ozone with nitrite on surfaces such as concrete, pointing towards the need for further studies concerning the rate and mechanism of dry deposition at night in urban areas.

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1. Introduction

O_3 concentrations in urban areas are highly variable, peaking in areas away from traffic but dropping to near zero close to immediate sources of primary pollutants. Typically, production terms dominate during the day and removal processes dominate at night generating strong diurnal cycles in concentrations which may vary considerably in space (Salmond and McKendry, 2002; Castell-Balaguer et al., 2012). The timing of the maxima and minima in the cycle is dependent on emissions patterns and may be strongly affected by long-range transport of O_3 (and O_3 precursors) (Sicard et al., 2016; Tarasick and Slater, 2008) and vertical mixing processes both from occasional stratospheric folding events (Davies and Schuepbach, 1994; Langford et al., 2009) and more common local transient mixing of elevated layers within the troposphere (Salmond and McKendry 2002). Previous studies in regions of complex coastal terrain have shown the presence and importance of elevated layers of O_3 in determining the local O_3 budget (Salmond and McKendry, 2005; Banta et al., 1998). Such layers are decoupled from the surface and cannot be detected until they are mixed to the surface. They are often formed as the result of convective venting processes associated with anabatic winds and sea breeze formation (McKendry and Lundgren, 2000).

However, although diurnal cycles of O_3 concentrations have been studied in urban areas in the Northern Hemisphere (Wolff et al., 2001; Klumpp et al., 2006), much less is known about ambient concentrations in the Southern Hemisphere, tropical or subtropical cities. In the Southern Hemisphere, background O_3 concentrations are lower compared to the Northern Hemisphere (McKenzie, 2003) and the contribution of long-range transport of ozone or its precursors is likely to be small or insignificant due to the small size of downwind urban areas and the large distances travelled.

Previous studies have established that surface O_3 concentrations in the Auckland Region are low, with mean annual hourly concentrations of 35–50 ppb (Adeeb and Shooter, 2004). This is thought to be due to the absence of upwind sources of both O_3 and its precursors (Adeeb and Shooter, 2004). In Auckland, 83% of the oxides of nitrogen are emitted from vehicle exhausts, 13% from industry, 3% from biogenic sources and 1% from domestic heating (Metcalfe et al., 2006). Generally, 92–97% of the NOx emitted from older vehicles (which make up a large proportion of the New Zealand fleet) is in the form of NO (Harrison and Shi, 1996). In Auckland, the formation of secondary NO_2 is thought to be limited by the availability of oxidants (Gimson, 2005) and any O_3 produced is representative of local scale formation processes.

Although there are some limited measurements of ozone concentrations at 300 m elevation above the city in Auckland little is known about the presence or importance of such reservoirs in the Auckland Region. Previous studies have shown the presence of a strong convergence zone over the Isthmus due to the convergence of sea breezes from the East and West Coasts over the Waitakere Ranges (McKendry, 1992), and have noted the importance of the sea breeze in determining local ozone concentrations (Khan et al., 2007).

In order to quantify O_3 production within the urban plume it is important to make representative measurements of both NO_2 and O_3 within and downwind of the urban region. Currently however, like in many Southern Hemisphere cities where financial and logistical constraints limit the number of regulatory monitoring sites, O_3 is only routinely measured at three surface sites in the Auckland Region and only at one site throughout the year. Adeeb & Shooter (2004) note the strong influence of local emissions of NO on data from three of these sites. Thus the existing network may not be representative of regional scale patterns and lacks the resolution required to understand the underlying processes that drive spatial and temporal variability of O_3 concentrations within urban areas in Southern Hemisphere cities (Bart et al., 2014; Wang and Brauer, 2014; Williams et al., 2013).

The recent development of low-cost, low-power and low-maintenance gas-sensitive semiconductor (GSS)-based instruments and electrochemical technology provides an opportunity to monitor O_3 concentrations at a high spatial and temporal resolution (Bart et al., 2014; Deville Cavellin et al., 2016, Mead et al., 2013, O'Connor et al., 2012; Snyder et al., 2013). Extensive instrument development, thorough testing and protocols to verify data reliability are needed to establish the reliability and accuracy of these low-cost instruments for measurements in the atmosphere (Bart et al., 2014; Miskell et al., 2015; 2016b; Williams et al., 2013). Consequently, studies using multi-instrument networks of low-cost instruments to monitor intra-urban variability of O_3 concentrations are still scarce and limited to short term deployments (Bart et al., 2014; Deville Cavellin et al., 2016).

In this study, we use novel low-cost sensor technology and exploit the geographical isolation of the sub- tropical city of Auckland to determine the impact of an urban plume dominated by vehicle emissions on diurnal cycles of ozone present in background marine air. We deployed low-cost instruments in a network to provide continuous measurements over a period of 12 months. We demonstrate the potential of such technology, when used with innovative quality control checks, to provide a robust data set to compliment the regulatory network. We examine the resulting spatial patterns in diurnal cycles of O_3 concentrations to determine the impact of traffic dominated emissions from an urban plume on marine background concentrations. This study provides further insights into the formation and depletion of O_3 in an isolated urban area in the Southern Hemisphere and the use of low-cost instruments for continuous measurements in a multi-site network.

2. Methodology

2.1. Study site

Auckland is New Zealand's largest and fastest growing city, contains approximately a third of New Zealand's population (~1.5 million inhabitants) and covers almost 5000 km^2 (Auckland Council, 2012; Statistics New Zealand, 2013). Auckland is located on a narrow isthmus, which is <2 km wide at its narrowest (Chappell, 2014), and is surrounded by the Tasman Sea to the west and the Pacific Ocean to the east. Auckland's climate is subtropical with summer- and wintertime maximum air temperatures ranging from 22 °C to 26 °C and 12 °C to 17 °C, respectively (Mackintosh, 2001). South-westerly winds dominate across the year, particularly in winter and spring. Competing sea breezes in summer and early autumn can increase the proportion of easterlies in the eastern Auckland areas, but sea breezes are complex due to the conflict of effects of the east and west coast of Auckland and the uneven terrain (Chappell, 2014; McKendry, 1989). Given Auckland's isolation from regional precursor and O_3 sources local road traffic is the largest contributor to air pollution, accounting for almost 80% of NOx (NO_2 and NO) emissions (Xie et al., 2014). However, local build-up of air pollutants is limited due to coastal wind patterns ensuring relatively high wind speed all year-round (Senaratne and Shooter, 2004).

2.2. O_3 and precursor measurements

O_3 concentrations in Auckland are monitored by the Auckland Council using UV photometric based ozone analysers at three sites located along a NS transect (Thermo Fisher Scientific, Maltham, MA, USA). The sites include one coastal site (Whangaparaoa (*wha*)), one urban site (Musick Point (*mp*)) and an agricultural site (Patumahoe (*pat*)) (see supplementary data for a map). Ozone at these sites is only measured during summer and autumn. Precursor emissions (NO, NO_2, NOx) are measured at a residential site (Henderson (*hen*)) and *pat* by the Auckland Council (model 200E, Teledyne API, San Diego, US).

In addition to the existing monitoring network, O_3 concentrations were measured for a period of 12 months using low-cost gas-sensitive semiconductor (GSS)-based instruments (Aeroqual Ltd., Auckland, New Zealand) (11 sites) and a UV photometric based ozone analyser (Thermo Fisher Scientific, Maltham, MA, USA) (*ard*) (Table 1). The