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

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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, pointing towards the need for further studies concerning the rate and mechanism of dry deposition at night in urban areas.

Keywords (6): O_3; southern hemisphere; low-cost sensors; network; air quality

1. Introduction

Ozone (O_3) is a significant atmospheric pollutant, which has both acute and chronic impacts on human health even at concentrations as low as 35 parts-per-billion (ppb) (Annan et al., 2008). It can damage

vegetation both in pristine and agricultural environments (Agathokleous et al., 2016; Wang et al., 2012), with the probability and extent of damage increasing with mean concentration (Smith, 2012). Tropospheric O_3 is formed *in-situ* as a secondary pollutant from photochemical reactions between natural and anthropogenic precursors in the presence of ultra-violet light (Atkinson, 2000; Martins et al., 2015) and can be removed from the atmosphere through chemical reactions with other pollutants such as NO (Crutzen, 1974) or dry deposition to the Earth's surface (Fowler et al., 2009; Hardacre et al., 2015). 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 concentration the characteristics of which may vary considerably in space (Salmond & 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 & McKendry 2001). 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 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.

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. 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 (Colville et al., 2001; Bart et al., 2014; Wang and Brauer, 2014; Williams et al., 2013).

93 The recent development of low-cost, low-power and low-maintenance gas-sensitive semiconductor (GSS)
94 and electrochemical technology provides an opportunity to monitor O_3 concentrations at a high spatial and
95 temporal resolution (Bart et al., 2014; Deville Cavellin et al., 2016, Mead et al., 2013, O'Connor et al.,
96 2012; Snyder et al., 2013). Extensive instrument development, thorough testing and protocols to verify data
97 reliability are needed to establish the reliability and accuracy of these low-cost sensors for measurements
98 in the atmosphere (Bart et al., 2014; Miskell et al., 2015 and in preparation; Williams et al., 2013).
99 Consequently, studies using multi-sensor networks of low-cost sensors to monitor intra-urban variability of
100 O_3 concentrations are still scarce and limited to short term deployments (Bart et al., 2014; Deville Cavellin
101 et al., 2016).
102 In this study we deploy low-cost sensors in a multi-sensor network to provide continuous measurements
103 over a period of 12 months. We demonstrate the potential of such technology, when used with innovative
104 quality control checks, to provide a robust data set to compliment the regulatory network. We examine the
105 resulting spatial patterns in diurnal cycles of O_3 concentrations to determine the impact of traffic dominated
106 emissions from an urban plume on marine background concentrations. This study provides further insights
107 into the formation and depletion of O_3 in an isolated urban area in the southern hemisphere and the use of
108 low-cost sensors for continuous measurements in a multi-site network.
109
110 2. Methodology
111 *2.1 Study site*
112 Auckland is New Zealand's largest and fastest growing city and contains approximately a third of New
113 Zealand's population (~ 1.5 million inhabitants) and covers almost 5000 km^2 (Auckland Council, 2012;
114 Statistics New Zealand, 2013). Auckland is located on a narrow isthmus, which is less than 2 km wide at
115 its narrowest (Chappell, 2014), and is surrounded by the Tasman Sea to the west and the Pacific Ocean to
116 the east. Auckland's climate is subtropical with summer- and wintertime maximum air temperatures
117 ranging from 22°C to 26°C and 12°C to 17°C, respectively (Mackintosh, 2001). South-westerly winds
118 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 conflicting of effects of the Auckland's east and west coast 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 material 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) sensors (Aeroqual Ltd, Auckland, New Zealand) (11 sites) and a UV photometric based ozone analyser (Thermo Fisher Scientific, Maltham, MA, USA) (*ard*) (Table 1). The sensors were mounted at 1.5 to 4 m height at three coastal (Leigh (*lei*), Muriwai (*mur*), Whiritoa (*whir*)), three agricultural (Ardmore (*ard*), Patumahoe (*pat*), Surfdale (*sur*)) and five residential sites (Botany Downs (*bd*), Henderson (*hen*), Mairangi Bay (*mib*), Northcote Point (*ncp*), Red Beach (*rb*)) and one residential site surrounded by native forest (bush: Swanson (*swan*)) (Table 1). O_3 concentrations were monitored from January – December 2015 with data coverage ranging from 41 to 99% (Table 1). Due to site access limitations (tenants moved) O_3 at *ncp* was only monitored until July (Fig. 2). *Ard* was used as a field calibration site, thus, measurements were not continuous. Other missing data were caused by isolated transmission or power issues or delays in the site being established.

144 The GSS sensors have been used successfully in previous studies (Deville Cavellin et al., 2016; Lin et al.
145 2015) and a study, which co-located the sensors with analyser stations in Vancouver, Canada reported a
146 standard error of 6 ppb for over 6000 measurements (Bart et al., 2014).
147 The low-cost sensors used in this study were calibrated against a UV photometric based ozone analyser
148 (Thermo Fisher Scientific, Maltham, MA, USA) in a laboratory chamber prior to measurements. The
149 instruments were run for at least two days to establish the offset and slope, which was used for the
150 linearization of the low-cost sensors. The same procedure was repeated in the field every three month on
151 average against an analyser located at *ard*, our field calibration site. An example for the lab and field
152 calibration is shown in the supplementary data (Fig. S2 – S5). Overall, the response of the low-cost sensors
153 was good with an average precision of 84% after calibration across all lab and field calibrations.
154 Data reliability from the low-cost instruments was verified using the methods described by Bart et al. (2014)
155 and Miskell et al. (2016) and sensors were replaced when a signal or baseline drift was detected (typically
156 every 2 - 5 months; median 3 months). This also reduced the systematic bias related to the calibration errors
157 between instruments. To further confirm data reliability, two devices were deployed at each site. Often only
158 one device of a pair was replaced at a given time so that there was an element of randomization of devices
159 at sites. The sensors co-located at each site showed a mean absolute difference varying between 3 - 6 ppb
160 of each other over the entire study period: that is, inclusive of all instrument changes. Analysis of variance
161 showed that the variance within site (between the co-located sensors and including any variance due to
162 changes of device) was significantly lower than the variance between sites across the different months (F
163 = 0.17 - 0.75, $p < 0.001$). This demonstrates that the sensors allow detecting spatial variability across a
164 region. The effects of instrument placement (on verandas, under roof eaves, on roofs) were also assessed
165 and results showed that these local siting differences were not important controls on ozone variability. We
166 thus showed that the precision (mean: 84%, standard deviation: 1%) of the GSS sensors, operated in a
167 carefully managed network and with site redundancy, was sufficient to detect small spatial variability in O_3
168 concentration. For the final analysis a mean of the two measurements at each site was used. Additional
169 statistical tests, detailed below, were used to confirm the significance of the variations observed.

Table 1. Description of study sites.

Site	Site name	Site type	Latitude	Longitude	Inlet height (m)	Data coverage (%)	Instrumentation
ard	Ardmore	Agricultural	-37.035	174.984	1.5	41	1 Ozone analyser
pat	Patumahoe	Agricultural	-37.204	174.864	3.5	80	2 GSS sensors[1)]
sur	Surfdale	Agricultural	-36.780	175.032	1.5	91	2 GSS sensors
swan	Swanson	Bush[2)]	-36.869	174.560	1.5	78	2 GSS sensors
lei	Leigh	Coastal	-36.265	174.798	2	97	2 GSS sensors
mur	Muriwai	Coastal	-36.839	174.429	4	80	2 GSS sensors
whir	Whiritoa	Coastal	-37.279	175.898	2	79	2 GSS sensors
bd	Botany Downs	Residential	-36.919	174.924	3.5	99	2 GSS sensors
hen	Henderson	Residential	-36.868	174.628	3.5	89	2 GSS sensors[1)]
mib	Mairangi Bay	Residential	-36.742	174.748	1.5	95	2 GSS sensors
ncp	Northcote Point	Residential	-36.814	174.743	2.5	50	2 GSS sensors
rb	Red Beach	Residential	-36.607	174.704	1.5	98	2 GSS sensors

[1)] These sites were also equipped with a NOx analyser run by the Auckland Council

[2)] This site is a residential site surrounded by native bush

2.3 Meteorological data

Relations between O_3 concentrations and wind direction were assessed based on data provided by Metservice, Wellington, from the Auckland airport, which is representative of the regional wind flow patterns across the Auckland region (see supplementary material for a map). Local wind data was available from the NIWA CliFlo Climate Database (www.cliflo.niwa.co.nz) for a subset of sites (*bd*, *hen*, *lei*, *mib*, *pat*) and was used to assess the representativeness of the regional wind data.

2.4 Statistical analysis

To determine flow pathways, sites were grouped into five transects sorted by wind direction (N-S, E-W, NW-SE, NE-SW). Statistical differences between sites along the transects were determined using one-way analysis of variance (ANOVA) for normally distributed data and the non-parametric alternative Kruskal-Wallis test for data that did not follow a normal distribution. The analysis was based on midday data (11:00 – 14:00, when concentrations are well mixed) and night-time data (01:00 – 04:00, when concentrations were most stable). Further, we used t-tests (normally distributed data) and Mann-Whitney-Wilcoxon (non normally distributed data) tests to investigate whether O_3 concentrations were significantly different when wind directions were in or out of the city. Kruskal-Wallis tests were used to test for significant differences in O_3 concentrations at different hours of the day. All results are reported in local standard time (NZST) on a 24-hour period.

3. Results and Discussions

3.1 Spatial and temporal variability of O_3

3.1.1 Seasonal variability

The annual variability of the daily mean O_3 concentration and the 90^{th} percentile (28 ppb) are illustrated in Fig. 2 and a summary of the O_3 measurements is provided in Table 2. In agreement with a previous study (Adeeb and Shooter, 2003; Adeeb and Shooter, 2004), O_3 concentrations in the Auckland region were low with a mean of 19 ppb. The highest daily mean (42 ppb) was observed at *ard*, an agricultural site south of

the city located north-east to a local airport. Thus, emissions of hydrocarbons and NOx at this site may explain the higher O_3 concentrations compared to other agricultural sites (Table 2).

As commonly observed in the southern hemisphere (Adeeb and Shooter, 2004; Ayers et al., 1997; Oltmans and Levy, 1994), maximum values were measured during winter (mean: 20 ppb) and spring (mean: 22 pbb) and a minimum was reached in summer (mean: 15 ppb) (Fig. 2). The seasonal patterns at the different sites in the Auckland region can clearly be classified by comparison with the results from Baring Head (*bhd*), NZ, which is considered as a 'clean air' site on the remote coast at the south-eastern tip of the North Island of New Zealand (Adeeb and Shooter, 2003; NIWA, 2014). At Baring Head, mean ozone concentrations measured in 2014 (16 – 28 ppb: the closest data in time available to us) were slightly above those monitored in the Auckland region reaching a maximum in winter (28 ppb) (NIWA, 2014) (Fig. 2). The seasonal pattern recorded at the three coastal sites (*lei*, *mur*, *whir*) and at *pat*, the agricultural site outside the city to the south, were very similar to that at *bhd*. In contrast, at the residential sites *mib* and *ncp* and at the bush site to the west, *swan*, the seasonal pattern was not detectable and ozone concentrations were constant and low throughout the year. Other sites showed behaviour in between these two cases except for *hen*, which was a residential site next to a busy traffic road. At *hen*, ozone was low in the summer but showed pronounced peaks in early winter and spring, reaching and in early summer exceeding the marine background.

The summer minimum seen at all sites has been observed in a previous study and was attributed to 1) clean ocean air masses, brought in by SW and NE winds, with high water vapour concentrations that increase the photochemical destruction of O_3, 2) conflicting sea breezes, which result in a sea-breeze convergence over the Auckland region increasing the mixing of the two air masses and, 3) O_3 destruction through sea salt, NO_2 and sunlight (Adeeb and Shooter, 2004).

Neither the daily maximum nor the 8-hour rolling maximum exceeded the national environmental standards for air quality (75 ppb) (Ministry for the Environment, 2011) (Table 2) and the 90^{th} percentile (28 ppb) was not exceeded at any sites during summer, with the exception of *mur* on the west coast (Fig. 2). In fact, 42% of the times daily O_3 exceeded 28 ppb was limited to one site (*mur*), followed by *pat* (14%), *lei* (10%) and

rb (9%). The remaining sites had < 20 days with mean O_3 values above 28 ppb, indicating generally low O_3 concentrations in the Auckland region.

O_3 concentrations in other cities, located in the northern hemisphere, were on average similar to those observed in Auckland (e.g. Montreal, Canada (19 ppb) (Deville Cavellin et al., 2016), Vancouver, Canada (26 – 33 ppb) (Vingarzan and Taylor, 2003), UK (9 ppb (London) – 33 ppb (rural sites)) (Jenkin, 2008)). However, maximum O_3 concentrations in these studies far exceeded those observed across the Auckland region reaching values > 100 ppb, particularly during summer and spring when photochemical formation and background concentrations reach a maximum (Jenkin, 2008; Vingarzan and Taylor, 2003).

Auckland's NO_2 concentrations are similar to those in northern hemisphere cities (Miskell et al., 2015) and the lower O_3 concentrations observed across the Auckland region are therefore unlikely due to low traffic emissions. Instead, we suggest three factors that likely contributed to the overall low O_3 concentrations in Auckland. First, it is possible that our downwind sites were not far enough downwind to measure higher O_3 concentrations. Some studies suggested that elevated O_3 concentrations may be observed as far as 40 – 70 km downwind from an urban area assuming that the mean wind speed is 4 m s^{-1} (McKendry, 1993). Elevated O_3 levels may therefore have been observed over the ocean in the Hauraki Gulf north-east of Auckland where O_3 was not measured. Second, studies in northern hemispheric cities suggested that O_3 concentrations were not only influenced by regional and local effects, but also global processes (e.g. changes in hemispheric O_3 background levels) and particularly by long-range transport (Kleanthous et al., 2014; Sicard et al., 2016). Background O_3 concentrations are generally lower in the southern hemisphere and reach a minimum in summer. Third, Auckland is isolated from large pollution sources and therefore less likely to be affected by long-range pollutant transport.

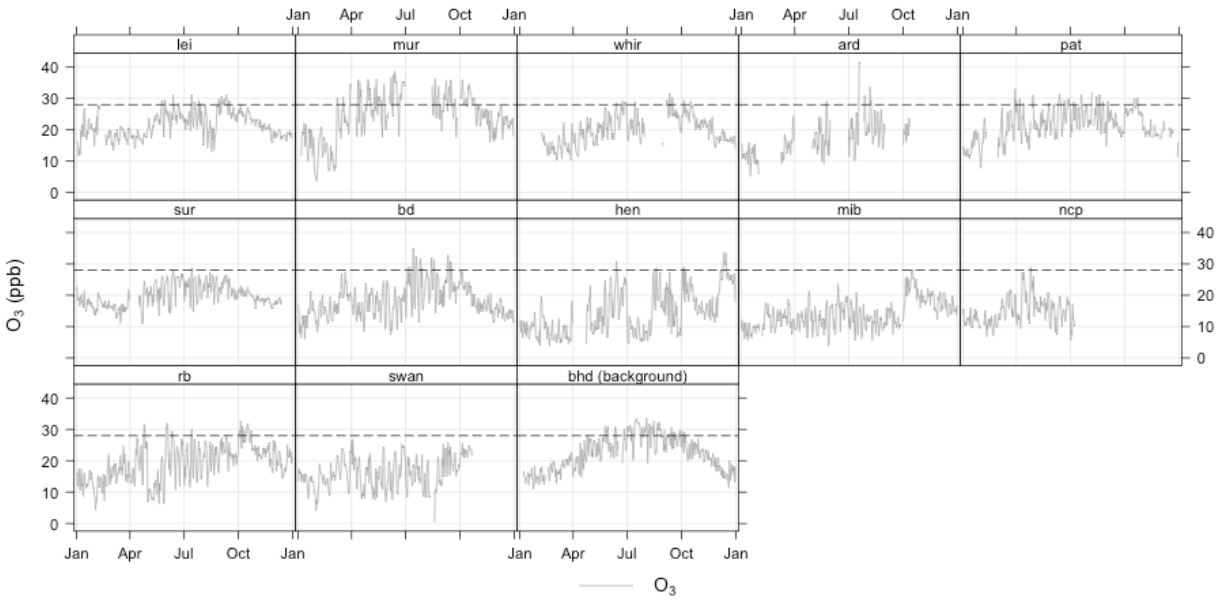

Fig. 2 Time-series of daily averaged O_3 concentrations measured at the 12 study sites in 2015. The annual cycle observed at Baring Head (*bhd*), which is considered as 'clean' background air is also shown (note: the *bhd* data for 2015 were not available and data from 2014 are shown) (the dashed line represents the 90th percentile (28 ppb)).

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Table 2. Descriptive statistics to summarise the O_3 concentrations measured at the 12 study sites.

Site	Mean (ppb)	Median (ppb)	Daily maximum (ppb)	8-hour rolling maximum (ppb)	Type
mur	24	25	39	43	Coastal
pat	22	22	33	42	Agricultural
lei	22	21	31	34	Coastal
whir	20	20	32	33	Coastal
sur	20	20	29	30	Agricultural/Coastal
rb	19	20	33	37	Residential
bd	18	18	35	38	Residential
ard	17	17	42	53	Agricultural
swan	16	16	27	29	Residential
ncp	15	15	29	34	Residential
hen	15	14	34	38	Residential
mib	14	15	28	31	Residential

3.1.2 Diurnal variability

The median diurnal pattern in O_3 concentration varied depending on sites, seasons and wind speed as shown in Fig. 3 and Fig. 4. Diurnal variability was significant (χ^2 = 109.48 (*swan*) – 531.15 (*sur*), $p < 0.001$ (across different times of the day)) at the majority of sites, particularly during summer, when diurnal amplitudes were highest due to higher photochemical O_3 formation (Brönnimann and Neu, 1997; Williams et al., 2013).

In spring, the median diurnal cycle was generally less pronounced (Fig. 3, 4). The diurnal pattern was particularly evident at residential and agricultural sites and when wind speed was below 4 m s^{-1} (Fig. 3, 4). *Mur* on the west coast showed no significant diurnal variability across all seasons ($\chi^2 = 28.65$, $p > 0.05$), which is likely due to the shallower marine boundary layer height and smaller O_3 deposition rates over the sea (Kleanthous et al., 2014). Similarly, diurnal variability was small at another coastal site (*lei*) and the bush site (*swan*) with insignificant changes in autumn (*lei*) ($\chi^2 = 24.57$, $p > 0.05$) and winter (*swan*) ($\chi^2 = 31.62$, $p > 0.05$) (Fig. 3, 4). The coastal site south east of Auckland (*whir*) followed the commonly reported diurnal pattern, of higher O_3 concentrations in the afternoon but with a small amplitude, at low wind speeds. However, relations between wind and O_3 concentrations at *whir* need to be interpreted with caution as the regional wind data from Auckland may not be representative for wind patterns 100 km south east of Auckland. No diurnal variability was seen at high wind speeds. This may be explained by a combination of weaker NOx titration effects and intrusion of background O_3 (Khan et al., 2007). The behavior when wind speeds were low thus corresponds to that observed due to formation of ozone by photolysis of NO_2 (e.g. Bart et al., 2014; Kumar et al., 2015; Lefer et al., 2010; Mazzeo et al., 2005) and depletion by deposition. A similar diurnal pattern, but with an overall larger range, was observed at the residential and agricultural sites, where median diurnal amplitudes across all wind speeds ranged from 8 – 14 ppb and 2 – 13 ppb during summer and spring, respectively (Fig. 3, 4). The diurnal amplitudes observed across the Auckland region are considerably below amplitudes observed in other cities. In Houston, US (Lefer et al., 2010) or Vancouver, Canada (Bart et al., 2014), diurnal amplitudes were approx. 30 – 40 ppb, while a diurnal amplitude of around 25 ppb was reported from Manitoba, Canada (Raddatz and Cummine, 2001). Also, these cities measured higher mean daytime maximums reaching values > 35 ppb and up to 70 ppb (Bart et al., 2014; Lefer et al., 2010; Raddatz and Cummine, 2001). Compared to northern hemispheric cities, O_3 formation observed across the Auckland region is low, resulting in much lower diurnal amplitudes. This is likely due to Auckland's isolation from large industrial pollution sources and long-range transport. In addition, wind speeds in Auckland are relatively high throughout the year due to its coastal location, which

enhances the dispersion of pollutants and limits depletion due to horizontal advection of O_3 rich air (Senaratne and Shooter, 2004). As shown in Fig. 4, the diurnal variability is particularly low at higher wind speeds.

A distinct feature of the residential sites and *ard* are the significantly ($p < 0.001$) lower night-time (01:00 – 04:00) O_3 concentrations compared to coastal background air (Fig. 3, 4). At *hen*, for example, night-time O_3 concentrations reached values close to zero (observed downwind and upwind from the main road), particularly during summer and autumn when background O_3 levels were also low (Fig. 3). However, this decline in the evening and at night-time was not observed at the coastal sites, *pat (*agricultural) and *sur* (agricultural). At higher wind speed, residential O_3 concentrations showed a slight increase after the evening rush hour, which was particularly visible during winter, suggesting that O_3 concentrations get replenished through advection of O_3 from the ocean (Fig. 4) (Adeeb and Shooter, 2004).

Night-time O_3 concentrations may be depleted through surface deposition and (in the presence of NO) NOx titration. Dry deposition is a key driver of the diurnal O_3 variability in rural areas and may have also contributed to the slightly lower night-time O_3 concentrations in mostly vegetated areas (*pat*, *sur*, *swan*) when wind speed was low (Fig. 3) (Tarasick and Slater, 2008; Hardacre, 2015). However, dry deposition to non-vegetated areas is generally reported to be slower and therefore would be assumed to play a minor role in night-time O_3 depletion in the residential areas (Nicholson et al., 2001; Simmons and Colbeck, 2008). The obvious conclusion would then be that low night-time O_3 concentrations at these sites are mostly a result of NOx titration (Adeeb and Shooter, 2004; Khan et al., 2007; Simmons and Colbeck, 2008). NOx titration in Auckland has previously been found to be strongest at low wind speeds, which prevent the dispersion of NO (Khan et al., 2007). Fig. 5 shows the median pattern of precursor concentrations (NOx, NO, NO_2) monitored at a residential (*hen*) and agricultural (*pat*) study site, indicating higher NO concentrations and therefore NOx titration at *hen*, particularly when wind speed was < 4 m s^{-1}. However, compared to the morning rush hour, NO concentrations at *hen* were relatively low, most clearly observed at night and NOx titration unlikely fully accounts for the low night-time O_3 concentrations observed at *hen* and other residential sites. A stable nocturnal boundary layer may have contributed to the low O_3

concentrations observed at the residential sites, which limited horizontal advection of O_3 rich air from the coast (Khan et al., 2007). Thus, O_3 concentrations at sites with heavy daytime traffic, such as *hen*, remained low after the evening rush hour at low wind speeds. Although, even at wind speeds < 4 m s^{-1} we would expect some horizontal advection of O_3 rich air from the west coast approx. 16 km west from the study site. Also, there is no evidence of build-up in NOx concentrations at night-time (Fig. 5), particularly in summer when night-time O_3 concentrations were lowest. Similarly, a study that investigated CO_2 concentrations across an urban to rural gradient in Auckland reported an accumulation of CO_2 at nighttime at *ard* at low wind speeds, but not at the residential (*bd*) and a central urban site, providing little evidence of a stable nocturnal boundary layer at residential sites in Auckland (Weissert et al., 2015). However, to date, very little is known about the spatial and temporal variability of the boundary layer structure in Auckland and no measurements have been published.

Thus, we speculate that the O_3 dry-deposition rate may not be as low as initially assumed. In a humid, damp environment like Auckland (mean monthly 09:00 relative humidity: 77 – 92 %, Chappell, 2014), NO_2 will be absorbed into concrete as nitrite (NO_2^-) and nitrate. Nitrite adsorbed onto a surface reacts efficiently with ozone and has indeed been used as an accumulation device for ozone analysis (Koutrakis et al., 1993). We therefore suggest that the reaction of O_3 with nitrite on concrete surfaces may have also contributed to the low night-time O_3 levels particularly observed at sites of high daytime traffic density. However, this finding requires further investigation. At higher wind speeds, night-time O_3 concentrations at *hen* were replenished with O_3 from the west coast, reaching values similar to or above the coastal mean when wind was from the west (Fig. 4, section 3.2). As wind data from the Auckland airport has been used for this analysis, we repeated the analysis at *hen* also using local wind data, which showed similar results (supplementary material, Fig. S7).

Ozone concentrations in the morning and afternoon followed the commonly observed pattern with decreasing values in the morning (e.g. Adeeb and Shooter, 2004; Lefer et al. 2010; McKendry, 1993) when NO concentrations reach a maximum (Fig. 5) and regeneration of O_3 in the afternoon through photochemical reaction with NO_2 (Williams et al., 2013) (Fig. 3, 4). However, O_3 formation during daytime

was not sufficient to exceed marine background concentrations. Thus, across the whole diurnal cycle O_3 depletion dominates at the residential sites, particularly when wind speed is low and NO concentrations high.

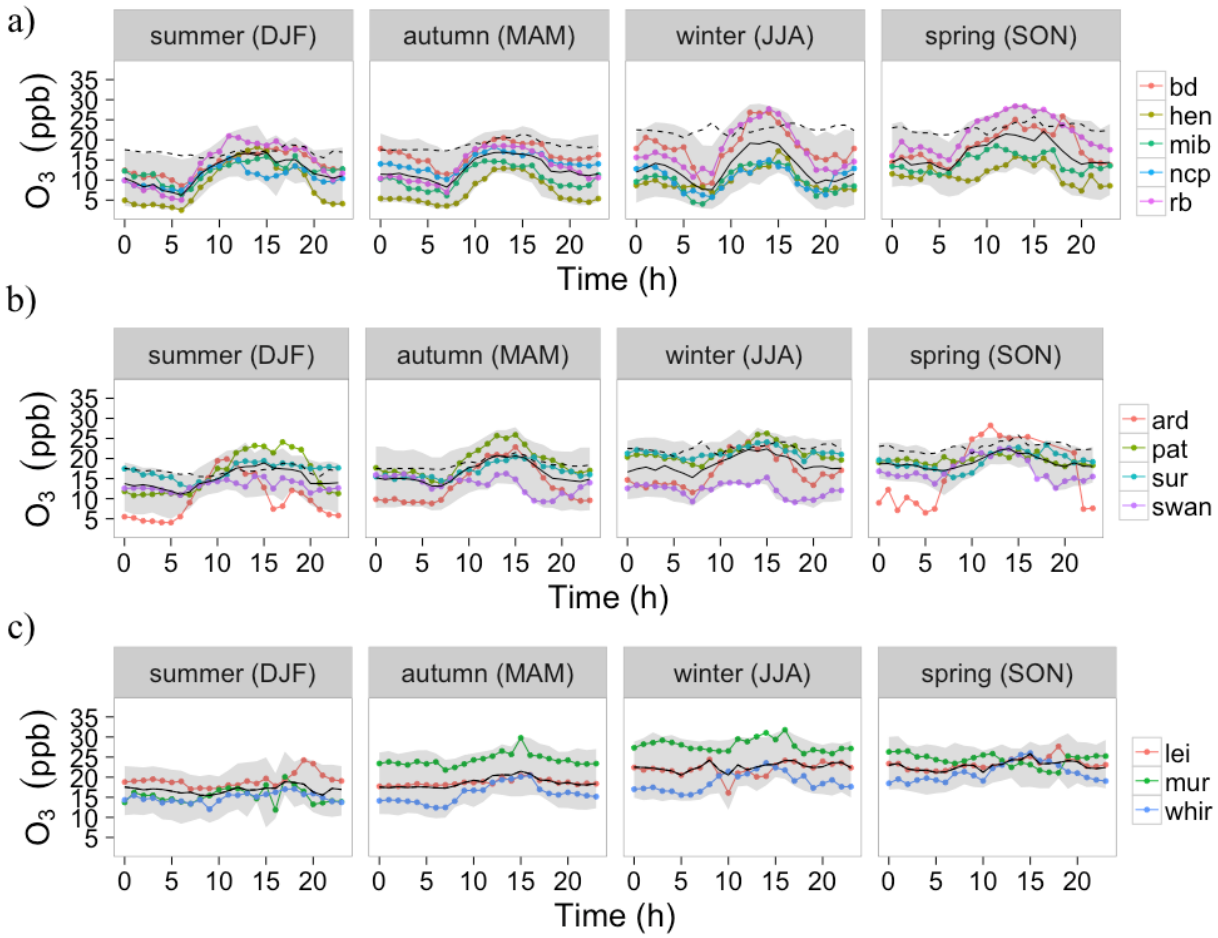


Fig. 3 Median diurnal variability of O_3 concentrations when wind speeds were < 4 m s^{-1} at a) residential sites, b) agricultural and bush sites c) coastal sites (the black line and shaded area represent the median and interquartile range across all plotted sites, the dashed line is the median diurnal cycle of the coastal sites).

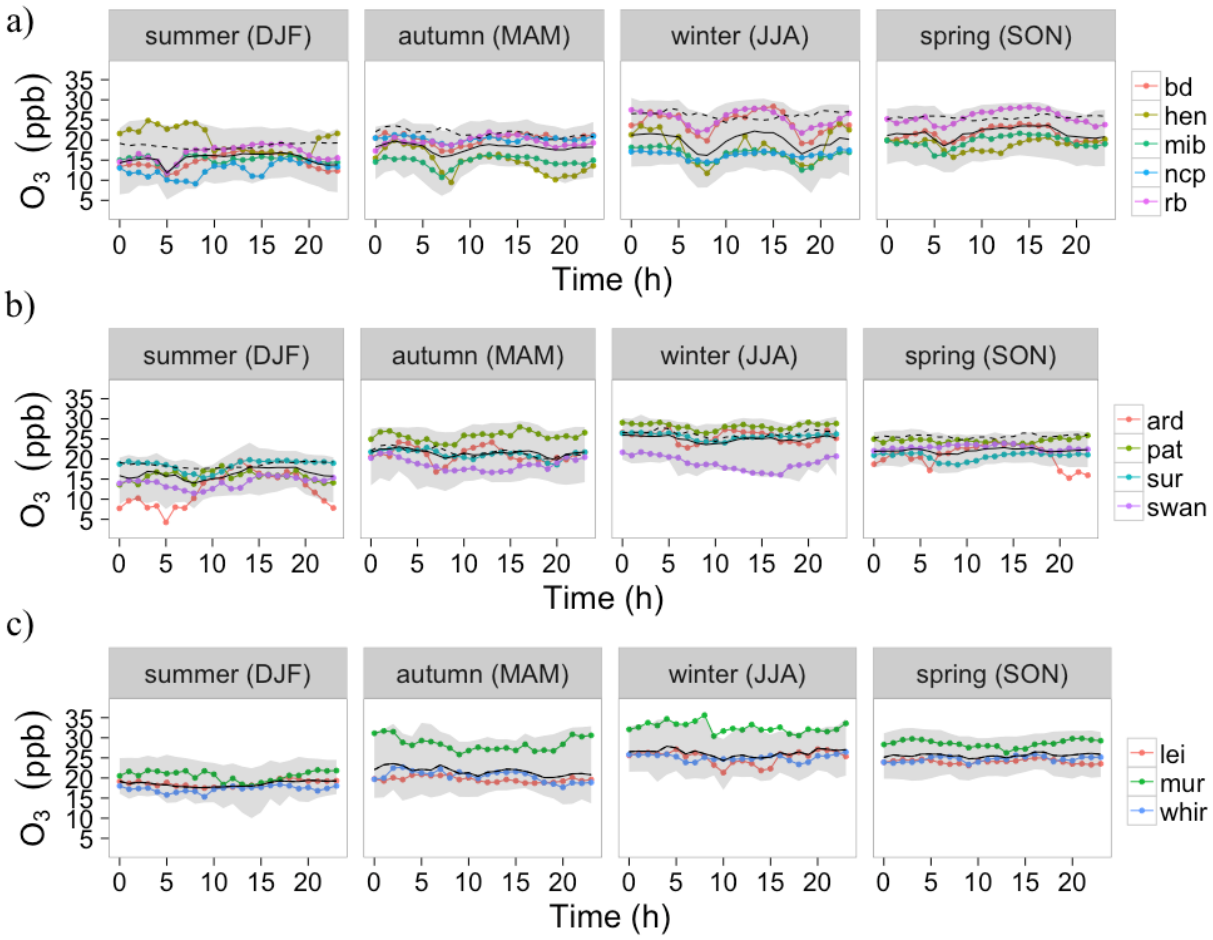


Fig. 4 Median diurnal variability of O_3 concentrations when wind speeds were > 4 m s^{-1} at a) residential sites, b) agricultural and bush sites c) coastal sites (the black line and shaded area represent the median and interquartile range across all plotted sites, the dashed line is the median diurnal cycle of the coastal sites).

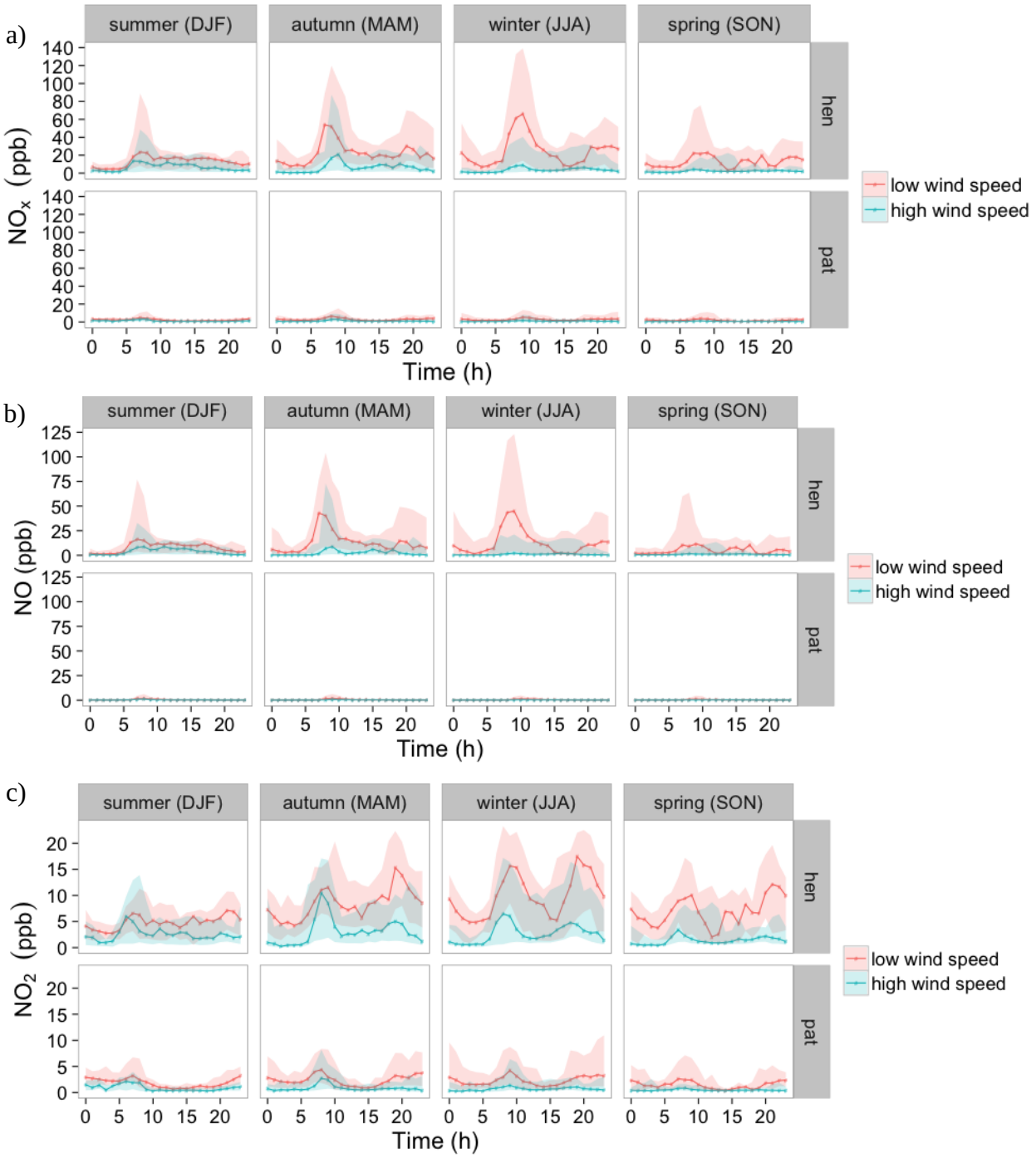


Fig. 5 Median diurnal variability of a) NOx, b) NO and c) NO_2 concentrations at low (< 4 m s^{-1}) and high wind speeds (> 4 m s^{-1}) observed at a) *hen* and b) *pat* during different seasons (the shaded area represents the inter-quartile range) (Note: the scales for NO and NO_2 differ).

350

351 *3.2 Wind flow pathways of O_3 through the Auckland region*

352 Relations between wind speed, direction and O_3 and NOx at the different sites are shown in Fig. 6 and Fig.
353 7. O_3 concentrations tended to be higher when related to wind from the west, particularly at wind speeds >
354 5 m s^{-1} (Fig. 6, Fig. 7). In fact, the highest O_3 concentrations (57 ppb) were observed at *ard* in July when
355 wind speed was > 10 m s^{-1} and wind flow from the SW (onshore). A positive trend between O_3
356 concentrations and wind speed was observed at all sites in winter using regional and local wind data,
357 however, the relationship was weaker at the coastal sites *mur* and *lei* and at two agricultural sites (*sur*, *pat*)
358 O_3 concentrations changed little at wind speed above 8 m s^{-1} (Fig. 7). During summer, the positive
359 relationship was still visible, but less pronounced at all sites (data not shown). In contrast, a previous study
360 in Auckland observed higher O_3 concentrations when wind speed was low and characteristic of local sea
361 breezes (Adeeb and Shooter, 2003). Similarly, findings in other urban areas suggested that high ozone
362 events were typically associated with low wind speeds, which reduce ozone dispersion (e.g. Jain et al.,
363 2005; Reddy, 2012; Zhao et al., 2015). Nevertheless, another study in Auckland, that investigated nocturnal
364 O_3 concentrations at *mp*, reported higher nocturnal O_3 concentrations during cyclonic conditions and wind
365 from the ocean (Khan et al., 2007). Our findings also compare to observations in Nanjing, China (Tu et al.,
366 2007) and at Baring Head in New Zealand (NIWA, 2014), where higher O_3 concentrations were related to
367 increased wind speed. The positive relationship between O_3 concentrations and wind speed could be
368 explained by two factors. On the one hand, higher wind speed may lead to stronger vertical mixing and
369 intrusion of O_3 from aloft (NIWA, 2014; Tu et al., 2007). On the other hand, higher wind speed enhances
370 the dispersion of pollutants, resulting in lower NO concentrations (Fig. 6) and, thus, reduced NOx titration
371 effects (Khan et al., 2007). This may explain the two apparent correlation lines of ozone against wind speed
372 observable for *hen* in most wind directions, where NOx concentrations are likely amongst the highest, and
373 also at *bd*, another residential site with high traffic density (Fig. 6).
374

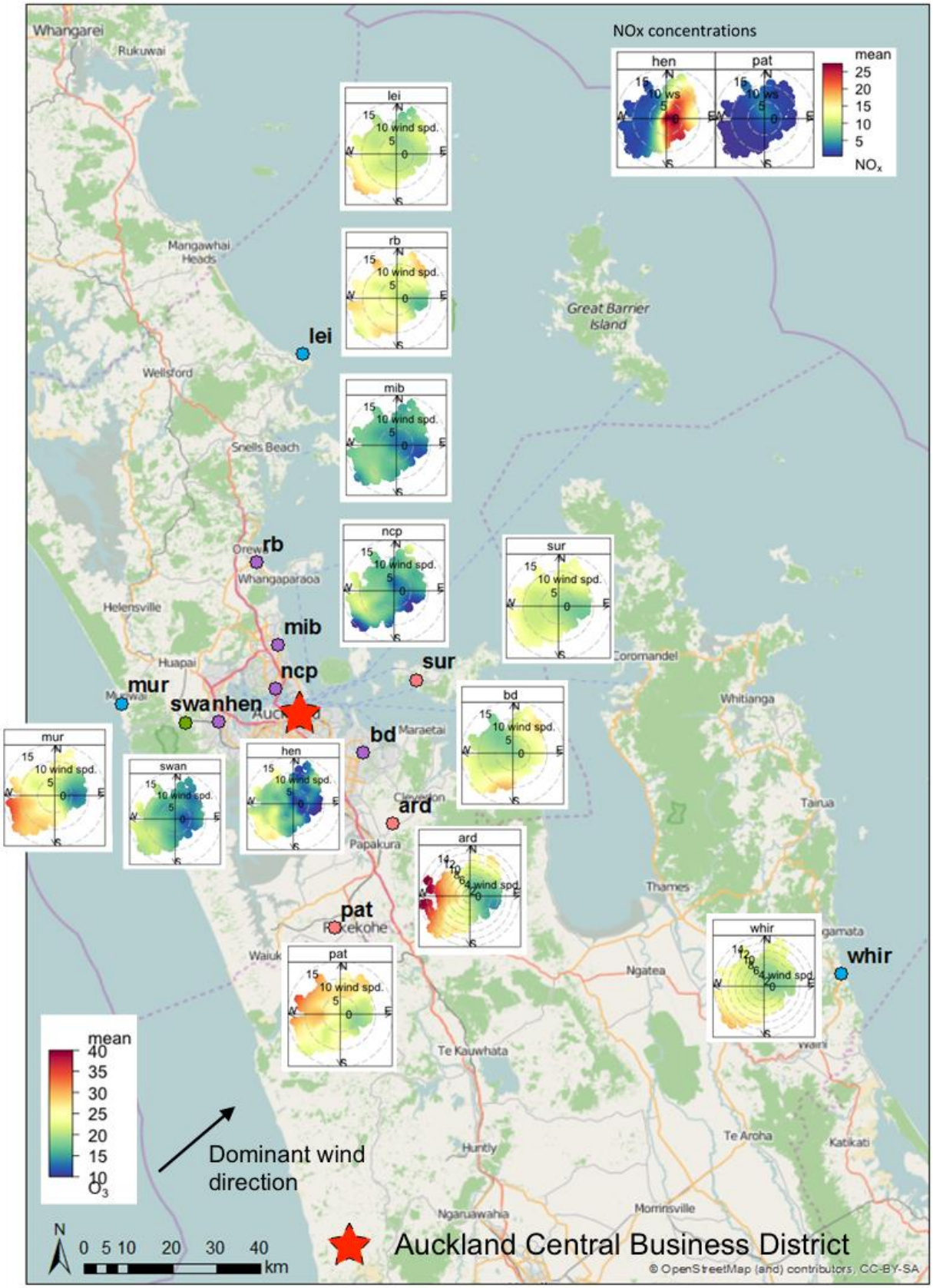

NOx concentrations
hen
pat
mean
25
20
15
10
5
NOx
lei
rb
mib
ncp
sur
bd
ard
pat
whir
mur
swan
hen
10 wind spd.
10 ws
4 wind spd.
Whangarei
Rukuwai
Mangawhai Heads
Great Barrier Island
Wellsford
Snells Beach
Orewa
Whangaparaoa
Helensville
Huapai
Coromandel
Whitianga
Maraetai
Clevedon
Papakura
Tairua
Thames
Pukekohe
Waiuku
Ngatea
Te Kauwhata
Te Aroha
Katikati
Huntly
Ngaruawahia
Morrinsville
mean
40
35
30
25
20
15
10
O3
Dominant wind direction
N
0 5 10 20 30 40
km
Auckland Central Business District
© OpenStreetMap (and) contributors, CC-BY-SA

Fig. 6 Mean O_3 concentrations (11:00 – 14:00) as a function of wind direction and wind speed for the 12 sites across the whole study period (OpenStreetMap, CC-BY-SA, na).

375

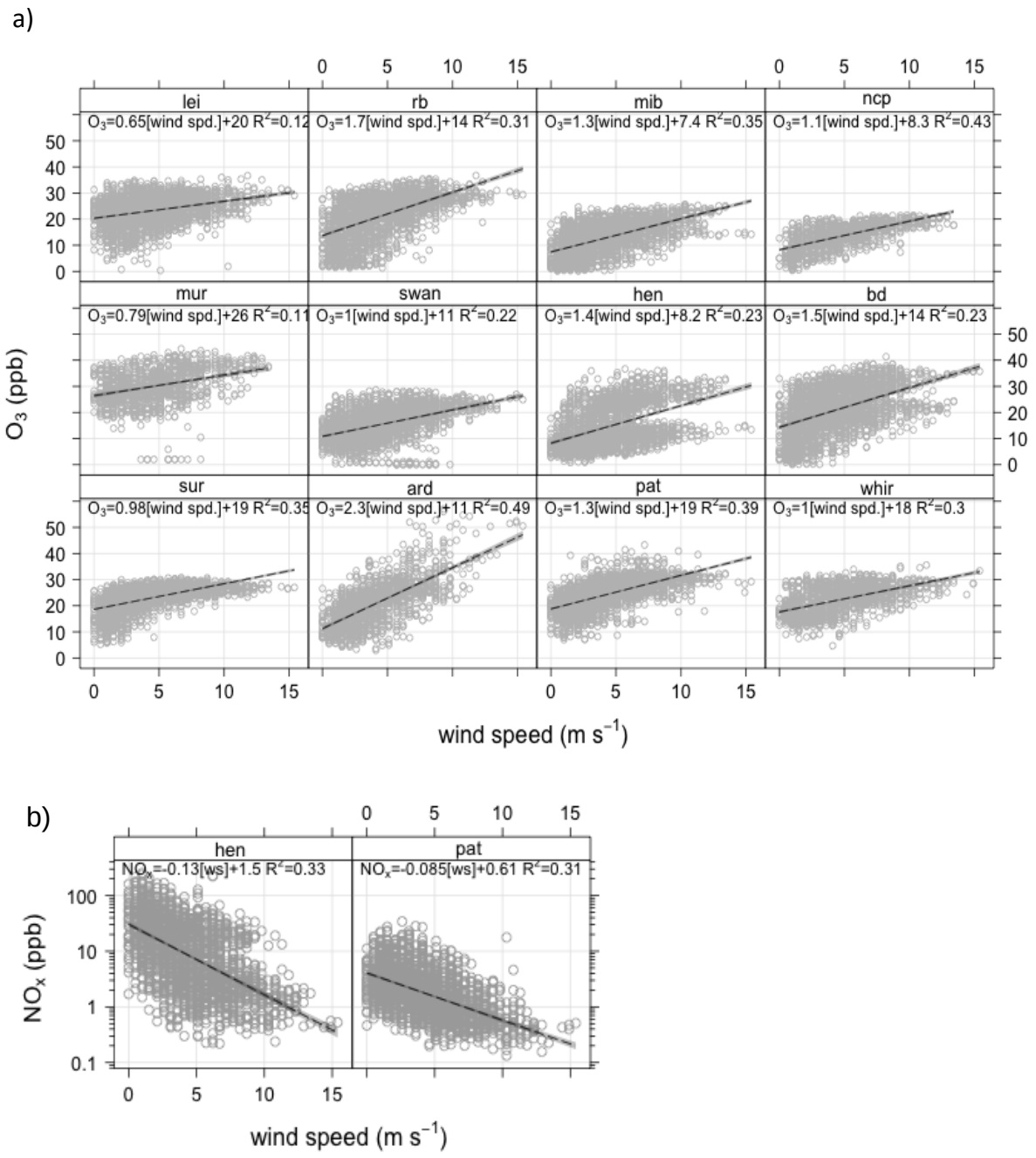
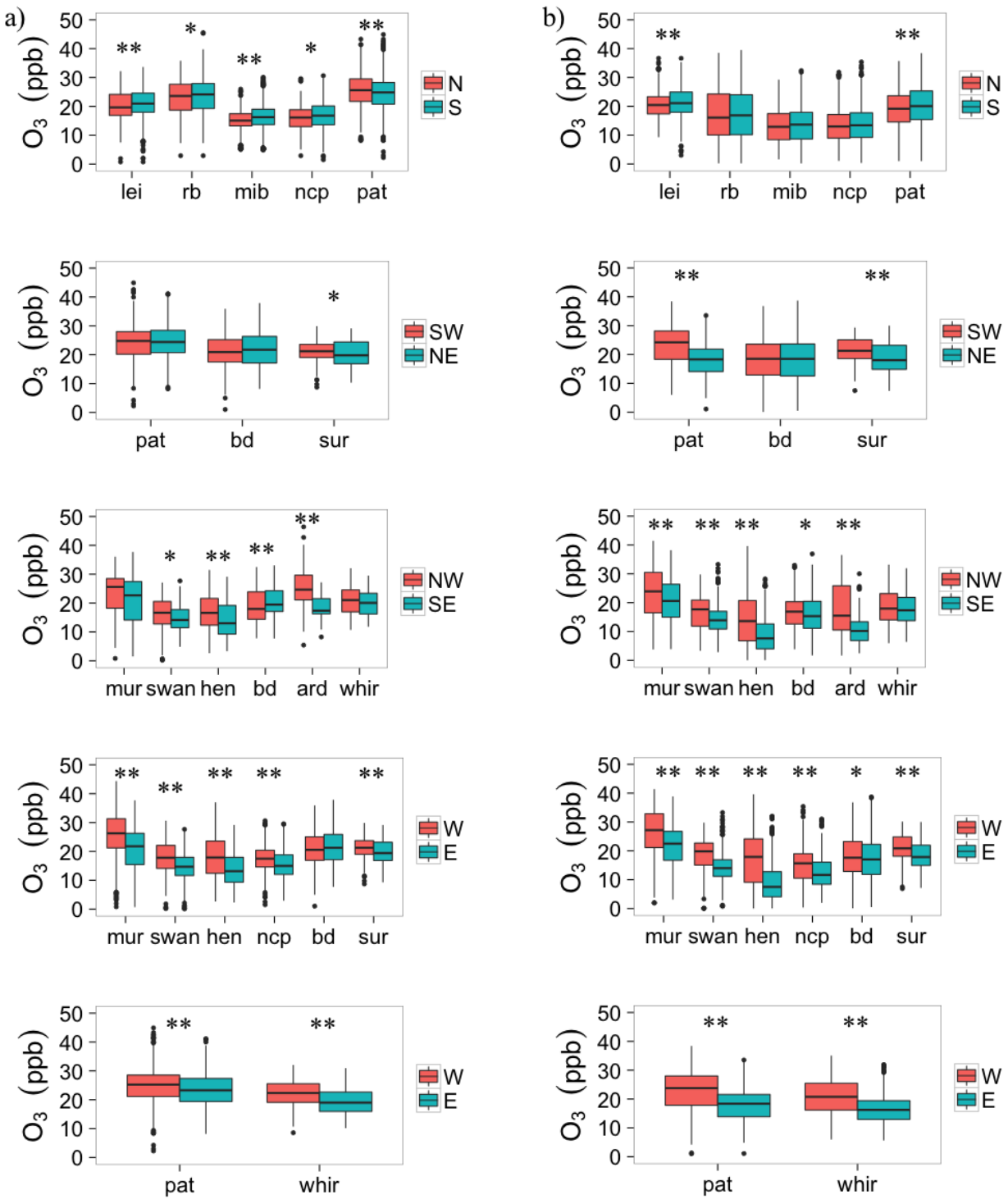


Fig. 7 Relationship between hourly O_3 concentrations and wind speed at the 12 sites (a) and between NOx and wind speed at *hen* and *pat* (note: NOx is log-transformed) (b) during winter when O_3 levels across the Auckland region were highest.

376 Fig. 8 shows the variability of midday and night-time O_3 concentrations related to wind directions in and
377 out of the city across the five transects. O_3 concentrations were significantly different between sites along
378 each transect during day and night-time ($p < 0.001$), showing a consistent spatial pattern (Fig. 8).
379 Coastal (*mur*, *whir*) and agricultural (*ard*, *pat*, *sur*) sites generally had higher O_3 concentrations, while O_3
380 concentrations observed at residential sites tended to be lower (*swan*, *hen*, *ncp*, *mib*) (Fig. 8). Higher O_3
381 levels at a rural site compared to the urban area were also reported from Montreal, Canada (McKendry,
382 1993) and Delhi, India (Kumar et al., 2015), results attributed to a lower number of O_3 sinks. Likewise, Yoo
383 et al. (2015) monitored lower O_3 concentrations at urban/suburban sites, where NOx levels were higher,
384 compared to coastal areas.
385 We also found significant differences in O_3 concentrations depending on whether wind was flowing in or
386 out of the city (Fig. 8). This was particularly visible at the WE (urban and rural) and NW/SE transect. O_3
387 concentrations associated with west and northwest winds exceeded O_3 concentrations related to easterlies
388 significantly at all sites (Fig. 8a, b) apart from *bd*, where O_3 concentrations related to SE exceeded those
389 from the NW at midday (Fig. 8a). Interestingly, O_3 concentrations associated with westerlies were highest
390 on the west coast, suggesting that O_3 is of maritime origin and that residential areas are a net sink of O_3
391 related to surface deposition and chemical reactions of O_3 with anthropogenic emissions (Kleanthous et al.,
392 2014).
393 Although not always significant, O_3 concentrations along the NS transect tended to be higher during
394 southerlies and as distance from the urban area increased (higher O_3 concentrations at *lei* and *rb* than *mib*
395 and *ncp*, Fig. 8), which could suggest O_3 formation downwind from the urban area. However, median O_3
396 concentrations at *lei* and *rb* were similar or below those at *pat*, the most southern site along the transect,
397 and it is unlikely that precursor pollutants from anthropogenic emissions transported north are the reason

for higher O_3 concentrations at *lei* and *rb*. Instead, it is more likely that O_3 was depleted due to titration effects related to higher NOx emissions at the two residential sites *ncp* and *mib*. Overall, we did not observe higher O_3 concentrations downwind from the urban area, suggesting that O_3 depletion from vehicle emissions dominates in the Auckland region and that higher O_3 concentrations are generally associated with onshore winds, particularly when from the SW and W. The patterns remained the same when calm conditions were removed, suggesting that the long-term spatial variability in O_3 concentrations across the Auckland region is not influenced by local winds. Also, this provides further evidence that a stable night-time boundary layer does not fully explain the lower night-time O_3 concentrations observed at residential sites compared to coastal and agricultural sites.

Using a smaller number of study sites (e.g. Auckland Council network consisting of two background (*wha, pat*) and an urban site (*mp*) provided similar results along the NS transect related to wind direction but did not show much variability between the three sites, which may be due to the selection of the sites (data not shown). *Mp* is less urban compared to some other sites, such as *mib* or *ncp*. Using only three study sites along a NS transect also lacks information about WE/SW and NW flow pathways through the Auckland region. Thus, previous studies of O_3 flow pathways through the Auckland region were limited (Adeeb and Shooter, 2003; Adeeb and Shooter, 2004). In fact, higher O_3 concentrations associated with winds from the SW were attributed to higher precursor emissions from the urban area (Adeeb and Shooter, 2004). However, our measurements on the west coast have shown that O_3 concentrations related to west winds are highest on the W coast and related to onshore winds. This highlights the importance of measuring O_3 concentrations upwind, within and downwind from cities.



421 Fig. 8 O_3 concentrations along the five transects during a) daytime (11:00 – 14:00) and b) night-time (01:00
422 – 04:00). The colours refer to O_3 concentrations related to different wind directions (the upper and lower
423 hinges represent the 25th and 75th percentiles, the upper and lower whisker extend 1.5 × inter-quartile range

from the hinge whereas dots correspond to outliers, ** and * illustrate significant differences in O_3 concentrations depending on wind direction at $p < 0.01$ and $p < 0.05$, respectively). The bottom right figure shows the NS transect based on data monitored by the Auckland Council.

4. Conclusions

Overall, the Auckland region is a net sink of ozone, particularly at night-time and during the morning rush hour. While highest O_3 concentrations were observed at higher wind speed and when wind was from the SW and W and onshore, higher precursor emissions related to traffic resulted in lower O_3 levels in suburban and urban areas. The maximum levels often observed in- and downwind of other urban areas were not found in this study. This must be partly due to the lower background O_3 concentrations typical of the southern hemisphere, which reach a minimum in summer when O_3 formation is generally at a maximum. In addition, Auckland is isolated from large pollutant sources and long-range transport is negligible.

This study has shown that, despite the lower accuracy, the low-cost instruments, if used in a carefully managed dense network, are capable of identifying small within-city variability of O_3 concentrations, and relations between O_3 concentrations and meteorological and land-use variables. In particular, they allowed the investigation of flow pathways of O_3 across the main wind directions, which was not possible with a lower number of study sites. Thus, low-cost sensors provide an opportunity to supplement routine ambient air quality networks.

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