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# Measurement Report: Observations of Ground-Level Ozone Concentration Gradients Perpendicular to the Lake Ontario Shoreline

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**Abstract.** Ground-level ozone (O3) is a secondary air pollutant that has harmful effects on human and ecosystem health. Close to larger bodies of water, the well-known sea- (or lake)-breeze phenomenon plays a role in regulating ground level ozone levels. An observed lake-edge removal effect, where ozone concentration decreases within the first 500 m to 1 km perpendicular to the lake, is thought to be related to the lake-breeze circulation as well as several dilution and removal pathways. A field campaign was conducted in summer 2022 and winter 2023 in two locations on the north shore of Lake Ontario: the urban centre of Toronto, and suburban Oshawa, some 50 km east, to assess how the local environment and season effects the lake-edge removal effect. Ozone, wind speed, and wind direction were measured on 6-7 different days in each season and city along transects perpendicular to Lake Ontario's shoreline. A consistent negative linear relationship between ozone concentration and distance from shore over the first 500 m (i.e. a lake-edge removal effect) was observed in both cities and both seasons. The ozone gradient changed in Oshawa from -23.5 ± 8.5 (1 standard deviation) ppb/km in summer to -8.1 ± 5.1 ppb/km in winter. The slope remained consistent in Toronto at -15.4 ± 6.7 ppb/km in summer and -16.7 ± 7.3 ppb/km in winter. The year-round observation of an ozone gradient and lake-edge removal effect suggests that factors other than lake-breeze circulation, such as vegetation and titration by NO, have an influence on ozone levels at the lake-land boundary.

## 1 Introduction

Ground-level ozone ($O_3$) is a secondary air pollutant which, at higher concentrations, has harmful effects on human health (Nuvolone et al., 2018) and ecosystems (Grulke & Heath, 2020). This has motivated considerable efforts at understanding its production, chemistry, and removal from the lower atmosphere. Lake-breeze circulation is a well-established meteorological phenomenon that plays a role in regulating ozone levels in nearshore environments. Lake breezes are driven by heat flux differences between land and water, due to the difference in their respective heat capacities. A pressure difference is generated between the warmer air over land and cooler air over water in the daytime, with airflow moving landward to replace the lofting, warmer air over land. The opposite effect occurs at nighttime, as the water holds heat better after the sun is no longer directly heating the surface (Sills et al., 2011). An offshore "land-breeze" moves ozone precursors emitted during the night and early morning from the land to the lake where they are trapped in a shallow layer of cool and stable air over the water, as illustrated in Fig. 1. The increase in fresh emissions and the lower deposition rates over water than land builds up the over-water ozone concentration during the night and early morning (Levy et al., 2010). During the day, the wind direction switches, and an onshore "lake-breeze" transports the newly produced $O_3$ inland in the afternoon and early evenings (Dye et al., 1995). Clear calm skies are favourable for lake-breeze circulation formation and most develop in the summer from May to September in the northern hemisphere when the temperature differences are most pronounced (Wentworth et al., 2015).

Studies have connected elevated ozone concentrations over the lake compared to land due to lake breeze circulation since the late 1960s (Cleary et al., 2015; Doak et al., 2021; Dye et al., 1995; Lennartson & Schwartz, 2002; Levy et al., 2010; Lyons & Cole, 1976; Makar et al., 2010; Wentworth et al., 2015). Measurements have been made by ferry (Cleary et al., 2015), aircraft campaigns (Levy et al., 2010), and with ground data (Lyons & Cole, 1976) to model and understand the local scale flow pattern. The relationship has been studied in the Norther American Great Lakes region such as Lake Michigan (Cleary, De Boer, et al., 2022; Cleary, Dickens, et al., 2022; Cleary et al., 2015; Lennartson & Schwartz, 2002), Lake Erie (Levy et al., 2010), Lake Ontario (Wentworth et al., 2015), and globally, such as in Lake Taihu in China (Zhang et al., 2017). The concentration differences between lake and land are most pronounced below the overlake layer up to 200 m altitude (Levy et al., 2010; Tirado et al., 2023). In the afternoon, the highest ozone concentrations over land are seen at the top of the internal boundary layer (Tirado et al., 2023).

The advection of ozone-rich air inland by lake-breeze can lead to high $O_3$ at nearshore land regions. Lake-breezes have been reported to penetrate over 100 km inland in the Great Lakes region (Sills et al., 2011) with ozone enhancement effects observed typically up to 30-50 km inland (Lennartson & Schwartz, 2002; Lyons & Cole, 1976). Correlations with lake-breeze have been observed with daily $O_3$ maxima (Wentworth et al., 2015), the occurrence of secondary daily ozone peaks (Lyons & Cole, 1976), and ozone exceedances in nearshore sites in time and space following the movement of the lake breeze front (Lennartson & Schwartz, 2002). Average daytime $O_3$ concentration in the Greater Toronto Area was 42-49% higher when lake breeze was present, with mixing ratios at least 30 ppb higher in sites within the circulation than outside, despite similar meteorological conditions and regional synoptical regimes (Wentworth et al., 2015).

Surface gradients of ozone perpendicular to the lake shoreline over the adjacent land have also been correlated with lake breeze circulation. Ozone is typically highest near the lake and decreases inland (Blanchard & Aherne, 2019; Cleary, Dickens, et al., 2022; Lennartson & Schwartz, 2002). The Lake Michigan Ozone Study 2017 investigated coastal ozone gradients and measured ozone amounts of 81.4 ppb and 87.4 ppb at the beginning and end of the transect near the shore, and 57.4 ± 1.6 ppb (error bars represent 1 standard deviation) at distances more than 4.1 km (Stanier et al., 2021). The steepness of the ozone gradient is also correlated with the strength of the lake-breeze as nearshore lake breeze events are reported to give rise to a steeper ozone gradient than inland lake-breezes that penetrate further (Cleary, Dickens, et al., 2022).

A recent field campaign in Sandbanks Provincial Park, located on the north shore of Lake Ontario about 220 km east-northeast of Toronto, during summer 2018 found a distinct lake-edge removal effect, where surface ozone concentration decreases sharply within the first 500 m to 1 km perpendicular to the lake, in addition to a shallower gradient extending beyond 1 km from the lakeshore (Blanchard & Aherne, 2019). Sites < 500 m from shore had an ozone gradient of -37.6 ppb/km, ($R^2$ = 0.72) while sites > 500 m from shore had a gradient -4 ppb/km with a weaker correlation with distance from shore ($R^2$ = 0.17). The authors hypothesized that polluted air masses transported onshore experienced increased removal effects as they interacted with fragmented vegetation, similar to the forest-edge effect (Karlsson et al., 2006). In addition, they hypothesized that sand dunes running parallel to the coast may generate turbulent air flow, leading to additional mixing with vegetation and subsequent removal (Blanchard & Aherne, 2019).

A recent study shows that even high-resolution ozone air quality models still show bias that can be attributed to transport and lake breeze errors (Abdi-Oskouei et al., 2020). A better understanding of this edge effect can improve models and better inform policy related to land use and human health. The present study aims to provide a better understanding of this lake-edge removal effect, that has to date only been described once, by Blanchard & Aherne (2019), to the best of the authors' knowledge. A field campaign was conducted from June-August 2022 (summer) and December 2022-February 2023 (winter) to investigate the short-term reproducibility, seasonal dependence, and effect of land local forms on the lake-edge removal effect.

## 2 Method

### 2.1 Study Sites

The field campaign consisted of measurements from June-August 2022 (summer) and December 2022-February 2023 (winter) in Toronto, a built-up urban environment, and in Oshawa, a more suburban setting located about 50 km east of Toronto. Sampling sites within Toronto and Oshawa were chosen to evaluate the spatial variation of ground-level ozone along a linear transect perpendicular to the lake in urban and suburban areas respectively. Both cities have stations in Ontario's Ambient Air Monitoring Network that measure $O_3$, $NO_2$, $NO_x$, $SO_2$ and $PM_{2.5}$, providing a basis for comparison and calibration points. These more urban locations were selected as a direct contrast to the previous study by Blanchard & Aherne (2019) that sampled in Sandbanks Provincial Park, a public beach and forested park outside Belleville Ontario. The cities are also close enough that differences in regional background ozone levels should not interfere with nearshore measurements. Both cities were sampled again twice in June-July 2023 (summer) to confirm observations were a persistent

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yearly phenomenon. Six sampling sites lying between the two cities were also selected to evaluate ozone levels parallel to the lake and sub-regional ozone differences.

### 2.2 Toronto Sites

The Toronto lakeshore site lies in the harbourfront area of downtown Toronto. Figure 2 displays the sampling locations chosen. The major features near the shore consist of a concrete and wood boardwalk, docks, sidewalks, roads, and mid to high-rise buildings. High vehicular and foot traffic occur along major roads. The Gardiner Expressway runs parallel to the shoreline within the region. Some boat and ferry traffic operates from spring-fall.

Thirteen locations ranging from 3580 m to 15 m from shore were sampled during 6 days in the summer and 7 days during the winter measurement period (see Table S1, available at https://doi.org/10.5683/SP3/KETM5Z). The weather in summer was mostly consistent, ranging from sunny to cloudy with mean daily temperatures from 19.0°C to 26.3°C. In winter, only locations within 1 km of the shore were sampled, location IDs 29 to 37 (see Fig. 2), spanning a distance of 820 m to 15 m from shore. One additional location (ID 34) was added during the winter period that were not sampled in summer to increase the number of locations within 1 km of shore. The weather in winter was highly varied from sunny to heavy rain and light snow. Temperatures ranged -1°C to -7°C.

### 2.3 Oshawa Sites

The Oshawa study area is within Lakeview Park (see Fig. 3), with a few shoreline features such as a beach, a headland to the south-west, a stream with surrounding marshes running into the harbour, and low-rise residential housing. There is some vehicular traffic and foot traffic, especially during spring-fall. Fifteen locations ranging from 11000 m to -143 m from shore were sampled in summer. Lakeview Park Lighthouse sits on a structure that extends into the lake, and so was regarded as negative distance. The weather was consistent during the summer sampling days, sunny to cloudy with mean daily temperatures 16.6°C to 23.2°C. A subset of 10 locations were sampled in the winter period, ranging from 873 m to -34 m from shore. Two new locations (ID 8 and 12) were added in winter to increase the number of locations within 1 km and one location, the Lakeview Park Lighthouse (ID 14), was inaccessible in winter. Lakeview Park Rocks (ID 18) was only sampled on 2 occasions as weather conditions made it unsafe to access. Weather conditions ranged from sunny to light snow with temperatures -1°C to 6°C. Sampling was done on 7 days in both summer and winter.

### 2.4 Sites Parallel to Shore

Six locations from Scarborough, in eastern Toronto, to Oshawa were chosen to measure ozone concentration gradients parallel to the coast. The locations are identified in Fig. 4. Five of the six locations were at commuter train stations: Oshawa, Whitby, Ajax, Pickering, and Rouge Hill. The stations were isolated from nearby residential housing that were mostly low to medium density. There was regular train and vehicular traffic. The sixth site was at the University of Toronto Scarborough

Campus (ID 24). The campus is located north of Highland Creek, and contains river and parkland features, along with low to medium rise buildings and some small pockets of woodlots and shrubbery. There was regular foot and vehicular traffic mainly at the intersection and parking lots. Distance from shore ranged from 3640 m (ID 24) to 70 m at Rouge Hill station (ID 23). Six days were sampled in summer with weather mostly sunny to cloudy and temperatures between 24°C and 30°C. Full information about location sites is provided in Supplemental Information Table S1.

### 2.5 Instruments and Measurements

Ground-level ozone was measured using an Aeroqual 500 handheld monitor. The Aeroqual 500 is a commercial ozone monitor with a gas sensitive semiconductor sensor, with a stated detection limit of 0.001 ppm, and a measurement error ± 0.001 ppm, according to manufacturer's calibration. The monitor was held perpendicular to the wind direction 1.5 m high above ground elevation. Five consecutive values at 1 min intervals were recorded and averaged to generate a single reading. All measurements were made in the afternoon between 12:00 and 20:00 EDT except for those made on July 14th, 2022, when measurements were made up to 21:00 EDT. All measurements were made within an approximate 4-hour timeframe on a single day. Nearshore sites under 1 km on a single day were measured within an approximate 1.5-hour timeframe. Wind speeds and wind chill temperature were measured using an AOPUTTRIVER 816B handheld anemometer at the same time as the ozone measurements. Wind direction was measured using a digital compass. GPS information of each sampling site, including longitude, latitude, and elevation, were obtained using the GPS essentials phone application. Daily mean temperatures were obtained from Environment Canada from https://climate.weather.gc.ca/historical_data/search_historic_data_e.html and weather conditions recorded from personal observations.

The Aeroqual 500 monitor was manually compared with the real-time unverified data from Ontario air quality stations in Oshawa and Downtown Toronto. An average of 10 measurements were taken immediately outside the provincial air quality stations and compared with unverified data from the nearest hour. Monitor measurements agreed with station measurements within 1 standard deviation (see Tables S2 and S3, available at https://doi.org/10.5683/SP3/KETM5Z).

Hourly $O_3$ and $NO_2$ data was extracted from Ontario's Ambient Air Monitoring Network in the Oshawa and Toronto Downtown stations from http://www.airqualityontario.com/. Hourly data from January 2021 and July 2021 was extracted on June 22, 2022, and used as a baseline representation of both cities for winter and summer respectively (see Tables S4 and S5, available at https://doi.org/10.5683/SP3/KETM5Z).

### 2.6 Data Treatment

The average ozone concentration, expressed as ppbv, and its standard deviation were calculated for each location for each measurement day. Summer and winter values for each city on each measurement day were separately plotted against distance from shore, with a linear least-squares regression applied to all data points within 1 km of shore. Data measured in

Toronto on December 10th, 2022, was removed as an outlier from subsequent statistical treatment due to low $R^2$. Slopes were averaged for each city and each season and a two-way ANOVA was applied to average ozone concentration as a function of season and city. Ozone values from the transects parallel to shore in summer were plotted against distance from shore and against distance from Oshawa with Oshawa station (ID 19) set as zero point. Linear regression was applied to these data to determine any gradient present. Wind direction and speed were plotted on a wind rose diagram and a Pearson r correlation and linear regression was applied to determine whether any relationship existed between transient wind speed and ozone concentration. Hourly $O_3$ and $NO_2$ data from the provincial stations in January and July 2021 were averaged to a daily value. A two-way t-test was applied comparing both cities within each month.

## 3 Results

### 3.1 Summer Ozone Gradients

Figures 5 and 6 show a negative linear relationship between ozone concentration and distance from shore in summer on all measurement days for both Toronto and Oshawa. The average slope over the nearest 1 km from shore was -15.4 ± 6.7 ppb/km in Toronto and -23.5 ± 8.5 ppb/km in Oshawa, where the uncertainties given represent one standard deviation from the mean. Ozone gradients were greater on average in Oshawa, which also typically showed more elevated levels of ozone nearshore. There was no statistical difference in slope on weekends compared to weekday (two sample t-test, $p > 0.05$).

Similar to results by Blanchard & Aherne (2019) ozone concentrations reached a minimum just under 1 km from shore and then generally plateaued or increased somewhat at distances further from shore. In Toronto, as illustrated in Fig. 5, ozone levels tended to increase moving further inland. This is particularly noticeable on August 13th, 2022, when the 2 points farthest from the lakeshore had concentrations higher than the highest nearshore levels. The observations illustrated in Fig. 6 show that in Oshawa, ozone levels remained constant or continued to decline gently at distances further than ~ 1 km away from shore, up to 11.5 km, and they did not regain the higher levels measured nearshore. This observation may reflect the lack of measurements within the 750 m – 2000 m region or be due to a lack of source emissions to generate more ozone in the daytime in areas not influenced by lake breeze.

Despite the differences in nearshore trends, there were no differences in regional ozone levels between the two cities. Pre-campaign, daily ozone averages from Ontario’s Ambient Air Monitoring Network in July and January 2021 were compared and no significant difference was found in summer (see Table S4, available at https://doi.org/10.5683/SP3/KETM5Z). To test this, ozone was measured at sites parallel to the shore, shown in Fig. 4, and an average increase 0.26 ± 0.28 ppb/km (1 standard deviation) was measured, negligible compared to changes perpendicular to the shore. See supplemental information Fig. S1 and S2, available at https://doi.org/10.5683/SP3/KETM5Z, for further information.

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The Toronto and Oshawa locations were sampled twice each in summer 2023 to confirm if the trends reported in Fig. 5 and Fig. 6 are consistent (see Fig. S3 and S4, available at https://doi.org/10.5683/SP3/KETM5Z). All days displayed a negative linear relationship between ozone concentration with distance from shore and a lake edge-removal effect was observed. Slopes calculated from linear regression were within two standard deviations of the means from summer 2022, showing a consistency year to year.

### 3.2 Winter Ozone Gradients

Figures 7 and 8 show that in winter, ozone gradients within 1 km of the shoreline were again consistently observed in both Toronto and Oshawa. In Toronto, the steepest slope was observed on Dec 04, 2022, -19.5 ppb/km, approximately twice the value of all other days (see Table S6, available at https://doi.org/10.5683/SP3/KETM5Z). The steepest slope in Oshawa was also observed at a similar time on December 02, 2022 (see Table S7, available at https://doi.org/10.5683/SP3/KETM5Z). The lowest slope was in Toronto was measured on December 10th, 2022, with poor fit ($R^2$ = 0.00013) and removed from further data analysis. Weather and temperature on these days were not noticeably different from the other days that can be attributed.

Ozone gradients were higher in Toronto than in Oshawa, the opposite of what was observed in summer. The average slope was -16.7 ± 7.3 ppb/km in Toronto and -8.1 ± 5.1 ppb/km in Oshawa, where the uncertainties given again represent one standard deviation from the mean. The range of ozone values was similar for both cities, around 25-45 ppb at the lakeshore (distance to shore = 0 m), unlike in summer where Oshawa values were typically higher.

## 4 Discussion

### 4.1 Seasonal Changes in Ozone Gradient

A year-round negative linear relationship between ozone and distance from lakeshore was observed in Toronto and Oshawa. Figure 9 shows that median and mean slopes of the nearshore ozone gradient in Oshawa were smaller in winter compared to summer. The spread of data is smaller in winter, with outliers on the earliest sampling date Dec 04, 2022, below the minimum, and the latest sampling date February 20th, 2023, above the maximum. The median and mean slopes in Toronto did not vary seasonally. A two-way ANOVA was performed to compare the effects of season and city on mean slope. There was no statistically significant difference between the mean gradients observed in the two cities for each season ($p = 0.926$) There was a statistically significant change in slope within Oshawa between summer and winter ($p < 0.001$) and no seasonal difference in Toronto ($p = 0.767$). This seasonal difference is further supported by the sampling completed in summer 2023. Oshawa slopes were once again at similar levels to summer 2022 while Toronto remained consistent (see Fig. S3 and S4, available at https://doi.org/10.5683/SP3/KETM5Z).

The significant seasonal variation in ozone gradients observed in Oshawa but not in Toronto suggests vegetation as a key controlling mechanism for the lake-edge removal effect. Vegetation plays an important role in regulating tropospheric $O_3$, providing both a removal mechanism via uptake to leaves, and a source, via VOC emission, in addition to indirect effects on air chemistry by cooling and shading (Fitzky et al., 2019). Previous studies have reported a forest edge effect, where ozone concentration was reduced within forests compared with open regions, through increased rates of stomatal uptake and dry deposition above ozone replacement from horizontal wind or higher air layers (Karlsson et al., 2006). Blanchard & Aherne (2019) hypothesized that fragmented vegetation at the Sandbanks site increased removal effects as polluted air masses were transported onshore from Lake Ontario. Comparing summer values among Toronto, Oshawa and Sandbanks, the average ozone gradient away from shore increases going from less to more vegetated areas: -15.4 ± 6.7 (1 standard deviation) ppb/km in Toronto, -23.5 ± 8.5 (1 standard deviation) ppb/km in Oshawa, and -37.6 ppb/km in Sandbanks Provincial Park.

The seasonal stability of the ozone gradient in Toronto suggests a different regime not affected by seasonal changes. Net chemical loss by $O_3$ + NO could play a more important role in urban environments. Using data from Ontario's Air Quality Monitoring system, average daily $NO_x$ levels in 2021 were higher in Toronto than Oshawa and this difference was statistically significant ($p < 0.05$) for both seasons (see Table S3, available at https://doi.org/10.5683/SP3/KETM5Z). Net chemical loss by titration of $O_3$ + NO is known to decrease ozone levels in urban areas compared to nearby rural regions (Cleary, Dickens, et al., 2022). This chemical loss has also been reported by Levy et al. (2010) when tracking the Lake Erie lake-breeze front during a case study on July 6-7, 2007, at Harrow, a rural town located approximately 6 km from Lake Erie. As the front passed through, a sharp decrease in ozone was observed at Harrow with a coinciding dramatic increase in $NO_y$, NO, and $NO_2$, followed by rapid recovery in ozone mixing ratio after the drop. In the present case, the Toronto transect passes by both the Gardiner Expressway and Union Train Station at 500-800 m inland mark, both potentially significant sources of $NO_x$ emissions. It could be that at the lake-land boundary in Toronto, fresh pools of local NO may be destroying ozone before increasing ozone production further from shore brings the photochemical production back to its regional level.

### 4.2 Lake Breeze and Ozone Gradients

Lake-breezes are known to influence shoreline ozone pollution levels (Cleary, Dickens, et al., 2022) and are common during the summer in the Great Lakes region. Lake breezes were observed 74% of summer days 2010-2012 in Lake Ontario(Wentworth et al., 2015) and over 90% of study days in the southern Great Lakes region during the BAQS-Met study in summer 2007.(Sills et al., 2011) . A slight positive relationship in Toronto in summer between wind speed and ozone concentration was observed using Pearson's correlation ($r = 0.45$, $p < 0.001$) and linear regression ($R^2 = 0.20$) (Fig. S5, available at https://doi.org/10.5683/SP3/KETM5Z). A stronger positive relationship was observed in Sandbanks Provincial Park in summer ($R^2 = 0.84$) (Blanchard & Aherne, 2019). Both wind direction and wind speed suggest ozone mixing ratios are correlated to lake breeze circulation in the summer. The wind rose of Toronto summer 2022 displayed in Fig. 10a shows an onshore wind typical of lake breezes from a predominantly SW-SE direction (69.1%) from all wind measurements collected during sampling. However, the wind direction had no obvious correlation on the strength of the ozone gradient; the steepest negative gradient was measured on 13-Aug-22 with winds present over a wide range of directions: SW-SE, W, and E at various sample sites. Wind measurements were not made during ozone sampling in Oshawa summer 2022.

In winter, this circulation pattern is reversed as daytime land-breezes leads to a convergence, a net inflow of air, over the lake (Passarelli & Braham, 1981). This was observed in Toronto where winds were strongly SW (30.6%) and E-NE (27.8%) as well as in Oshawa where winds were evenly split SW-N (77.4%) and SE (16.7%) (Fig. 10b and c). Elevated levels of ozone over the lake and near the shore would not be expected as precursor pollution is transported from the land to lake and moved aloft. However, we observe an ozone gradient in both cities in winter. It's possible that the frequent SW winds in both Oshawa and Toronto are moving ozone pollution from upstream sources and urban centres further west to the shore. Toronto's Billy Bishop airport is located directly SW of the shoreline sampling location and represents a possible source of ozone pollutant precursors. A study in Japan reported that in winter and early spring, daytime $O_3$ is described more by the development of a mixing layer and the emission strength of NO near the observation site rather than sea-breeze circulation (Mizuno & Yoshikado, 1983). There is also a possibility of ozone being produced over land and transported to the lake where lower deposition rates cause an accumulation of ozone. However, the lack of relationship between wind speed and ozone concentration in either Oshawa (Pearson's correlation coefficient $r = -0.047$, $p > 0.05$) or Toronto (Pearson's correlation coefficient $r = 0.079$, $p > 0.05$) suggest otherwise. There are currently only a limited number of studies focused the connection between lake-or sea-breeze circulation and ozone in winter and this should be further investigated.

The observation of a year-round ozone gradient and stability of the nearshore ozone gradient in winter in Toronto despite the lack of onshore winds suggests a decoupling of the lake-edge removal effect from lake-breeze circulation. A potential "baseline" removal process occurs along the coastline in both cities driven by reactions with NO, the general dilution of air masses, and lower rates of deposition over water as outlined by Cleary et al. (2022). In Oshawa, lake-breeze circulation, and increased removal through uptake by vegetation may drive seasonal changes in slope and increases from the baseline. The seasonal factors may enhance one another, as a study has reported the removal of $O_3$ by vegetation can be enhanced by the presence of sea-breeze through increased relative humidity and turbulent mixing at the surface (Li et al., 2019). In Toronto, the baseline may be established by processes of dry deposition to urban surfaces, transport to indoor environments, and gas phase reactions with NO, which are not strongly seasonal. Urban areas have increased NOx and other precursor pollutants that may be responsible for establishing a steeper baseline gradient.

## 5 Conclusion

Ground-level ozone gradients perpendicular to Lake Ontario were investigated in Toronto and Oshawa. A linear ozone gradient with respect to distance from shore was consistently observed in both cities throughout the year that included a lake-edge removal effect, consisting of an ozone minimum around 600-800 m from the shore. Local landform and subsequent ozone production regime are connected to ozone gradients as they increased in steepness from urban to rural, -15.4 ± 6.7 (1 standard deviation) ppb/km in Toronto, -23.5 ± 8.5 (1 standard deviation) ppb/km in Oshawa, and -37.6 ppb/km in Sandbanks Provincial Park (Blanchard & Aherne, 2019). A slight urban-rural ozone gradient was also observed in summer with ozone levels increasing towards more urban regions.

The seasonal changes in the lakeshore ozone gradient in Oshawa and Toronto suggest that the lake-edge removal effect is less strongly associated with lake breeze circulation than previously assumed. Average ozone gradients decreased in winter in Oshawa while they remained similar in Toronto. In addition, the gradient remained present in winter despite the lack of lake breeze and there was no correlation with local wind speed in winter in both cities. The strong seasonal difference in Oshawa but not Toronto provides support that the effects of vegetation on ozone loss rate may be related to the lake-edge removal effect. In Toronto, elevated $NO_x$ emissions and NO titration may be the dominant nearshore loss mechanism for ozone. Further studies to co-monitor $O_3$ and $NO_x$ gradients perpendicular to the shore could provide support for the connection of NO titration to the lake-edge removal effect.

Ground-level ozone can vary dramatically in a small scale at the lake-land boundary. The photochemical differences between urban and rural environments and their interaction with lake-breeze circulation has a strong influence on the observed trends in the lake-edge removal effect.

## Data availability

The supplemental material and all data used in this paper can be obtained at https://doi.org/10.5683/SP3/KETM5Z.

## Author contributions

All authors designed the field campaign and YH carried out the field measurements. YH completed the data analysis, and all authors discussed the data and findings. YH prepared the draft manuscript. All authors reviewed manuscript and approved the final version of the manuscript.

## Competing interests

The authors declare that they have no conflict of interest.

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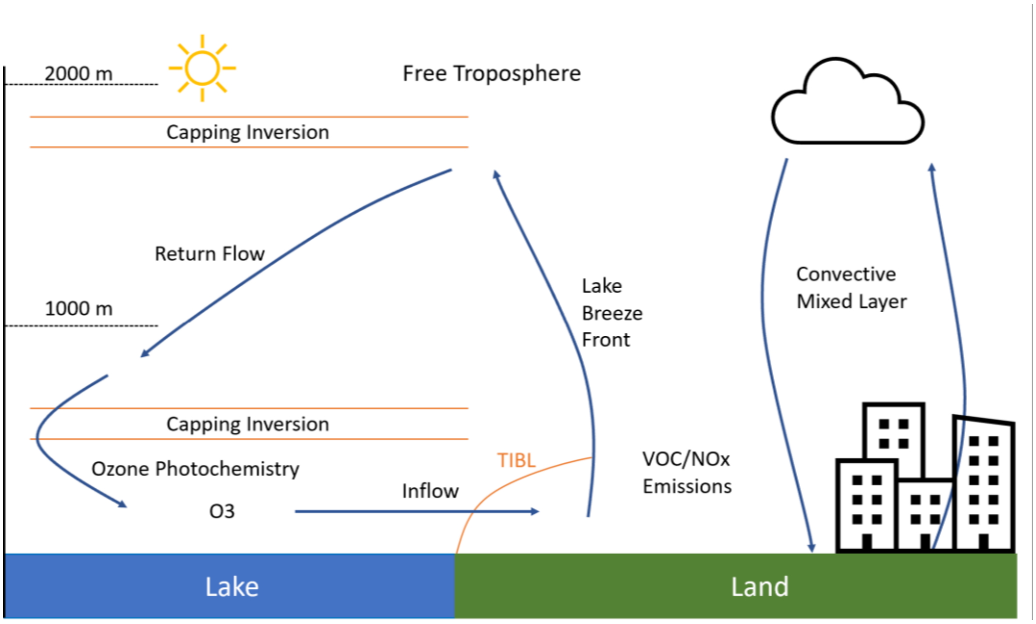

385 **Figure 1: Simplified model of the connection between lake breeze circulation and ozone. Ozone precursors are trapped within the stable inversion layer over the water and react in the day to produce O3 that is moved inland by lake breeze. Arrows depict motion of air masses. The thermal internal boundary layer (TIBL) is shown in orange and grows in height with distance inland until it reaches the height of the convective mixed layer. Adapted from Wentworth et al. (2015) and Stroud et al. (2020).**

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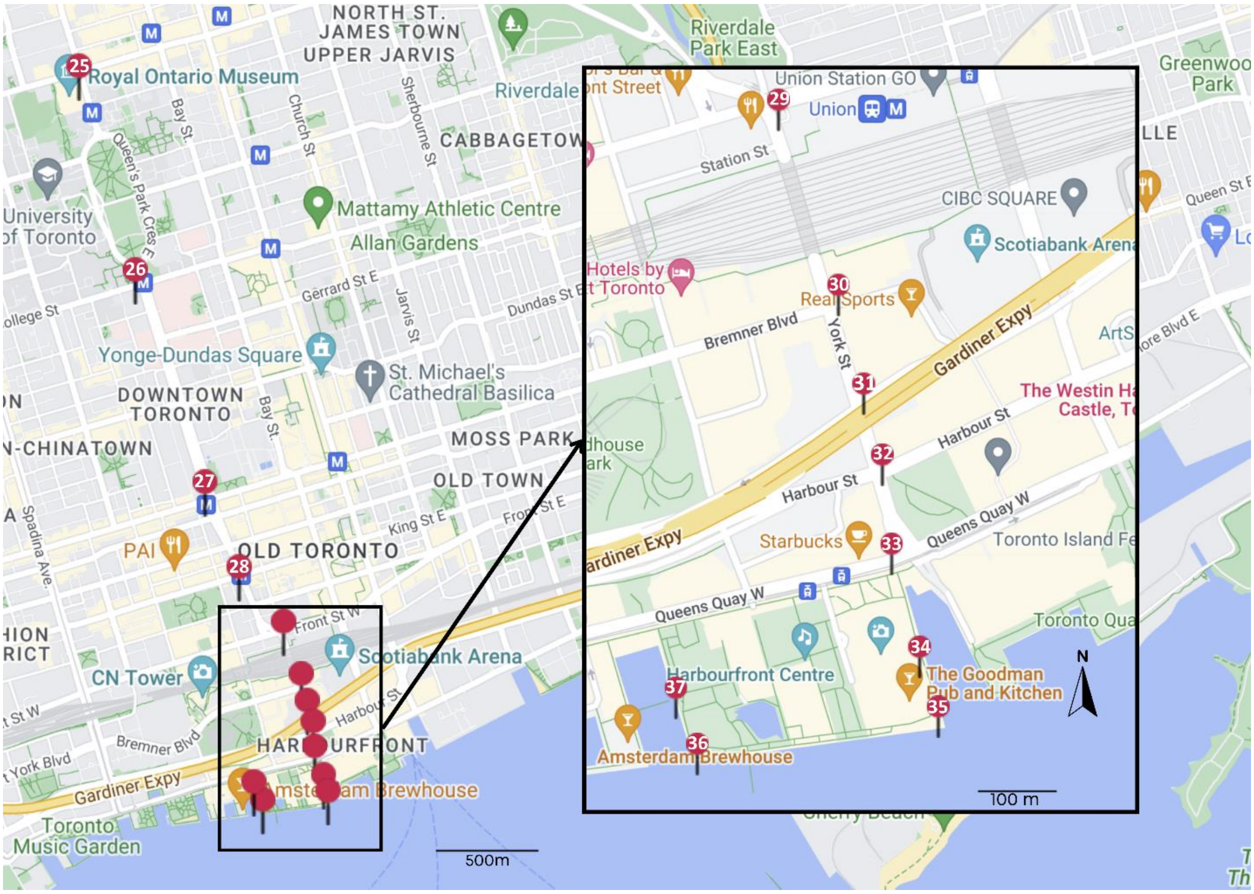

**Figure 2: Ozone sampling locations in Toronto for transects perpendicular to shore. © Google Maps 2023.**

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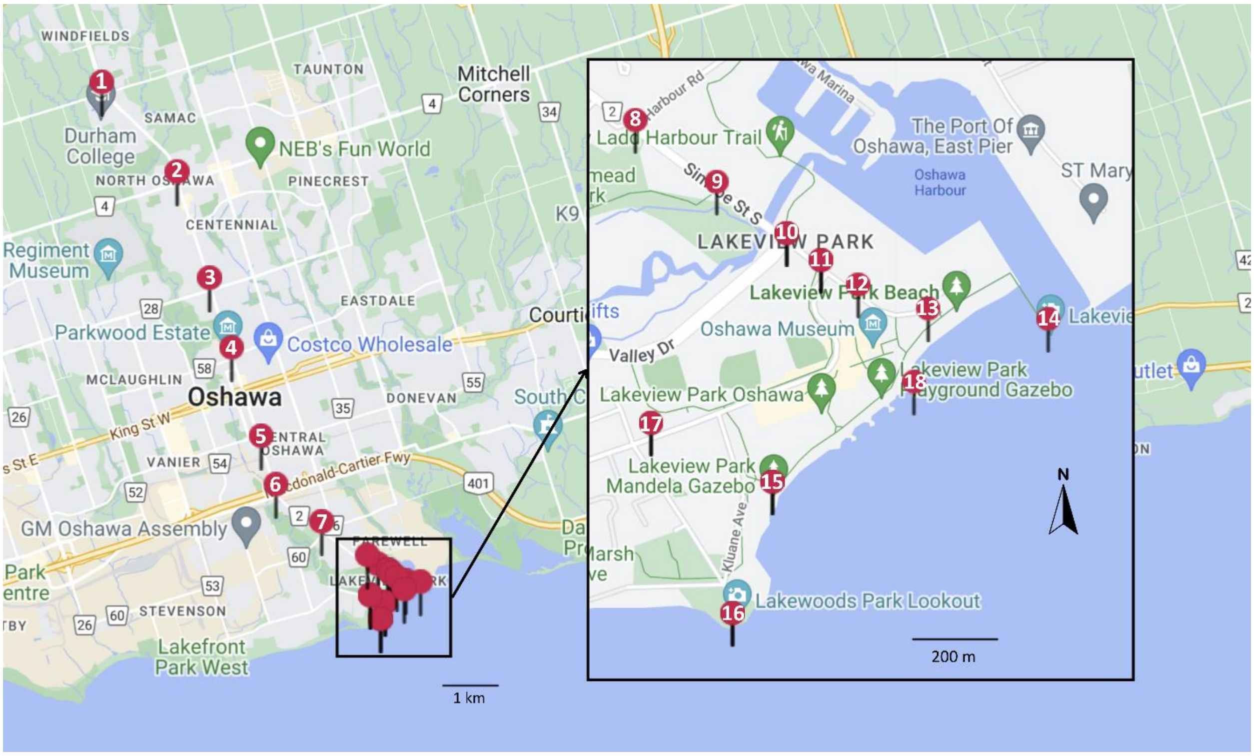
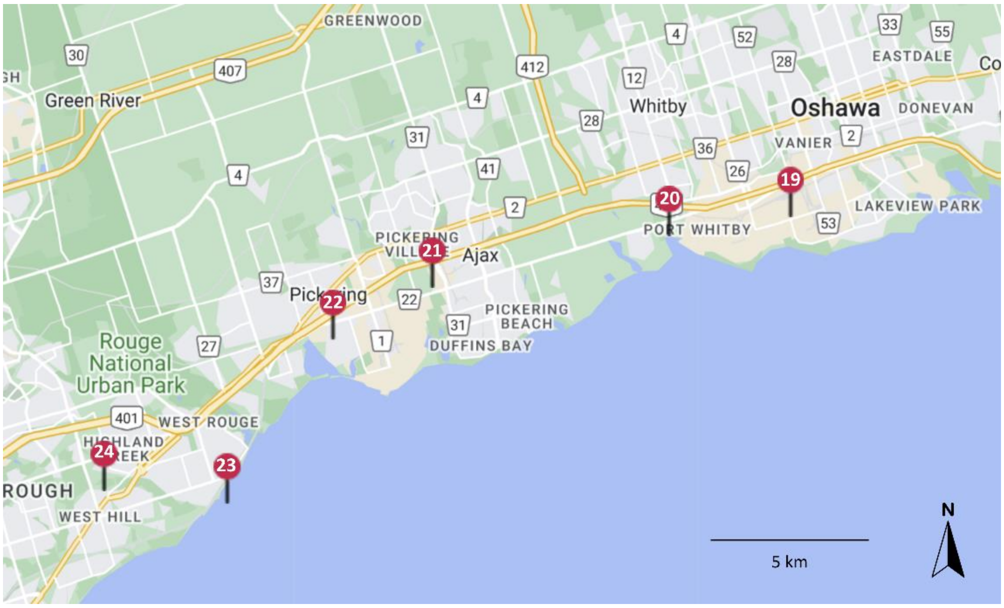


Figure 3: Ozone sampling locations in Toronto for transects perpendicular to shore. © Google Maps 2023.



395 Figure 4. Ozone sampling sites in summer 2022 for parallel transect. © Google Maps 2023.

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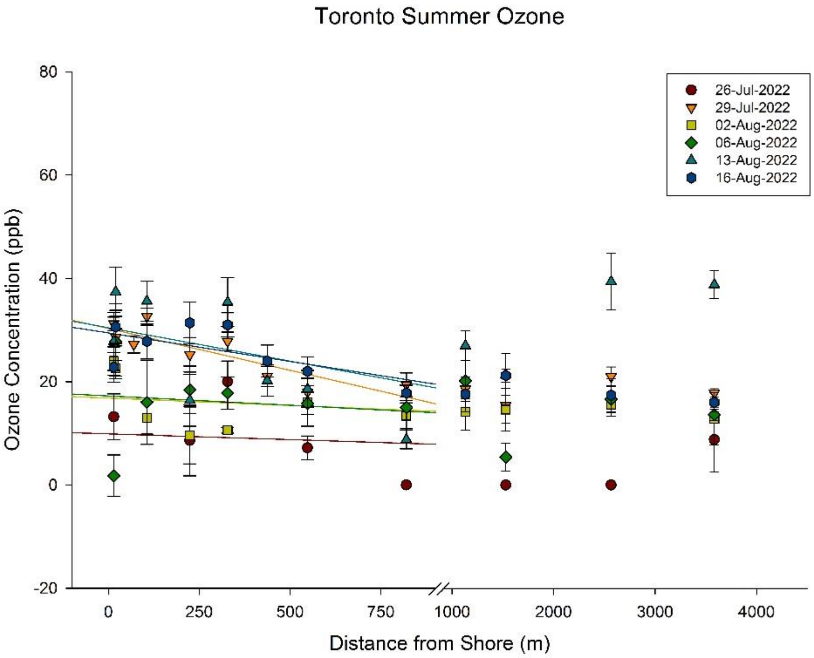


**Figure 5. Scatter plot of average $O_3$ (ppb) to distance from the shore of Lake Ontario (m) in Toronto summer with linear regression within 1 km. Error bars represent ± 1 standard deviation from the mean of five consecutive 1 min measurements.**

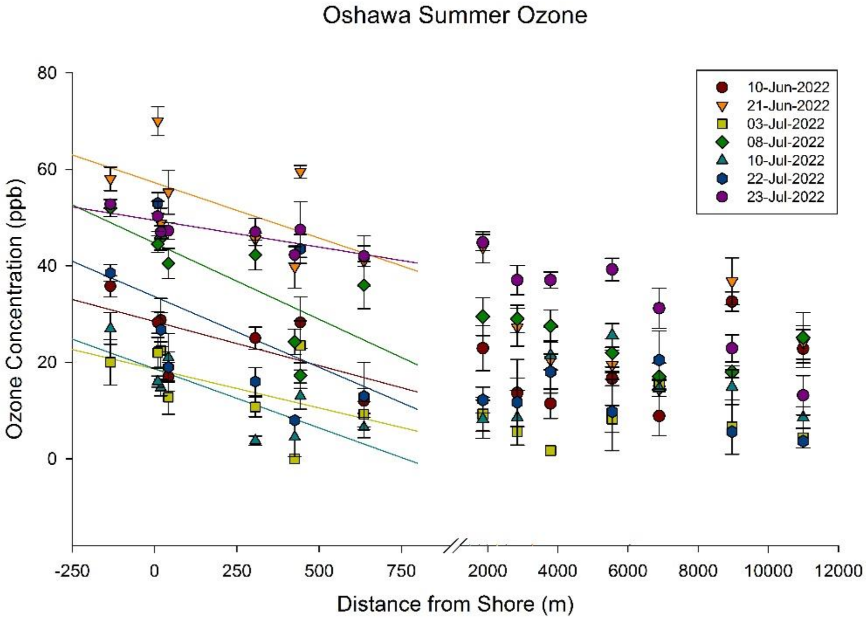
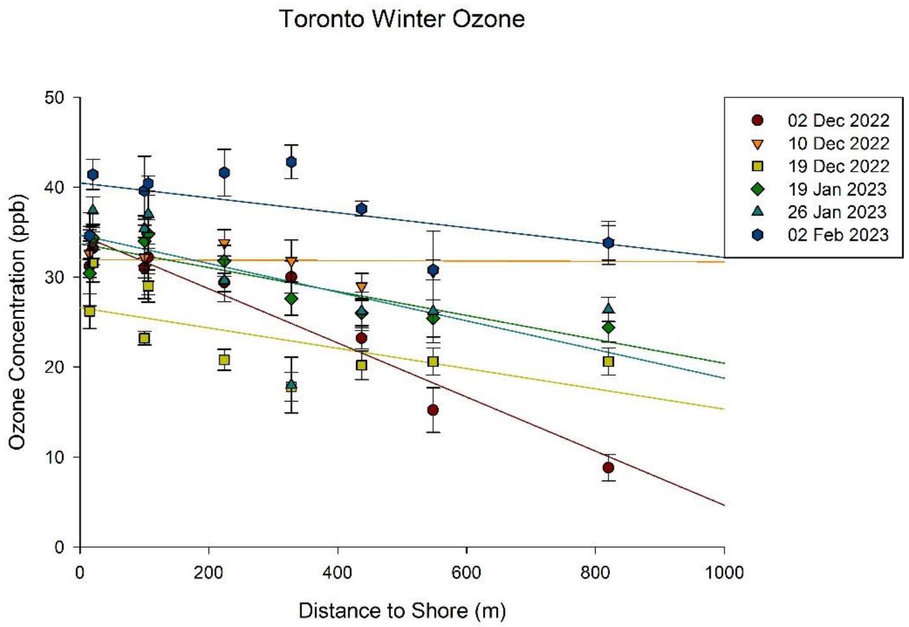


**Figure 6. Scatter plot of average $O_3$ (ppb) to distance from the shore of Lake Ontario (m) in Oshawa summer with linear regression within 1 km. Error bars represent ± 1 standard deviation from the mean of five consecutive 1 min measurements.**



405 **Figure 7. Scatter plot of average $O_3$ (ppb) to distance from the shore of Lake Ontario (m) in Toronto winter with linear regression within 1 km. Error bars represent ± 1 standard deviation from the mean of five consecutive 1 min measurements.**

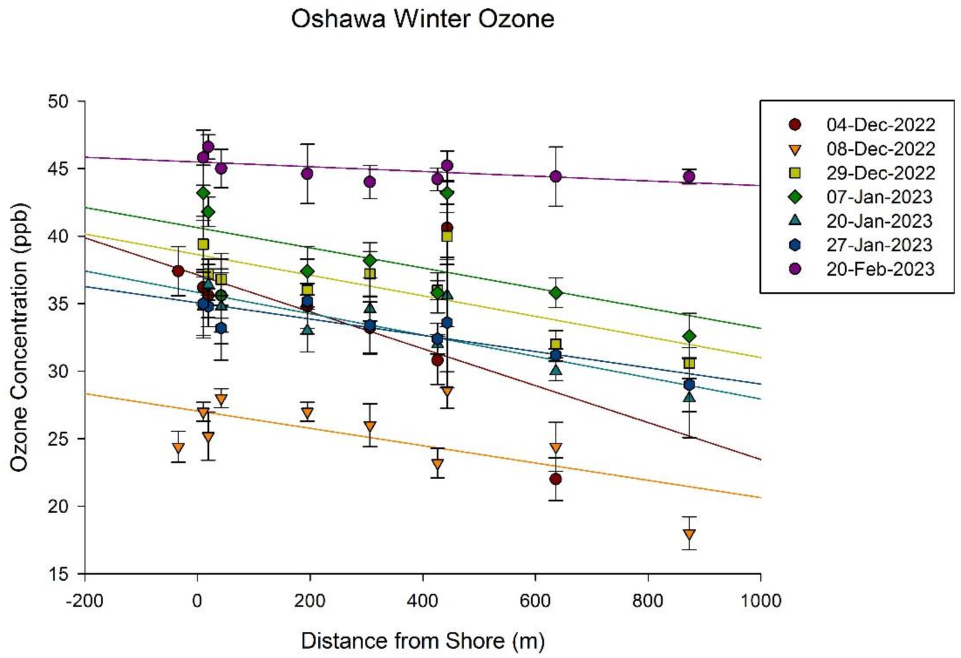


**Figure 8. Scatter plot of average $O_3$ (ppb) to distance from the shore of Lake Ontario (m) in Oshawa winter with linear regression within 1 km. Error bars represent ± 1 standard deviation from the mean of five consecutive 1 min measurements.**

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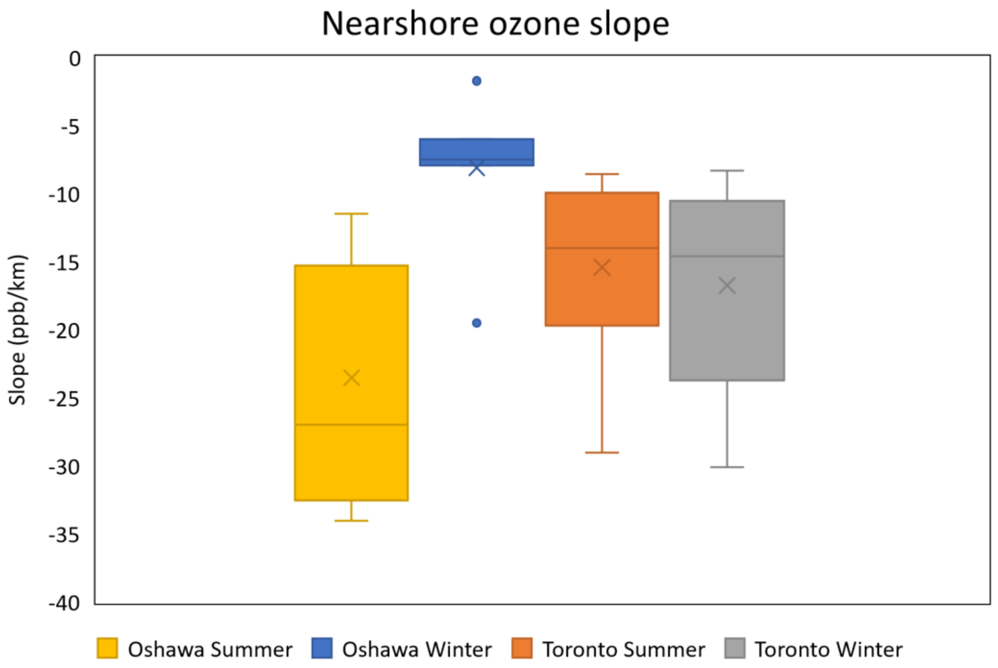
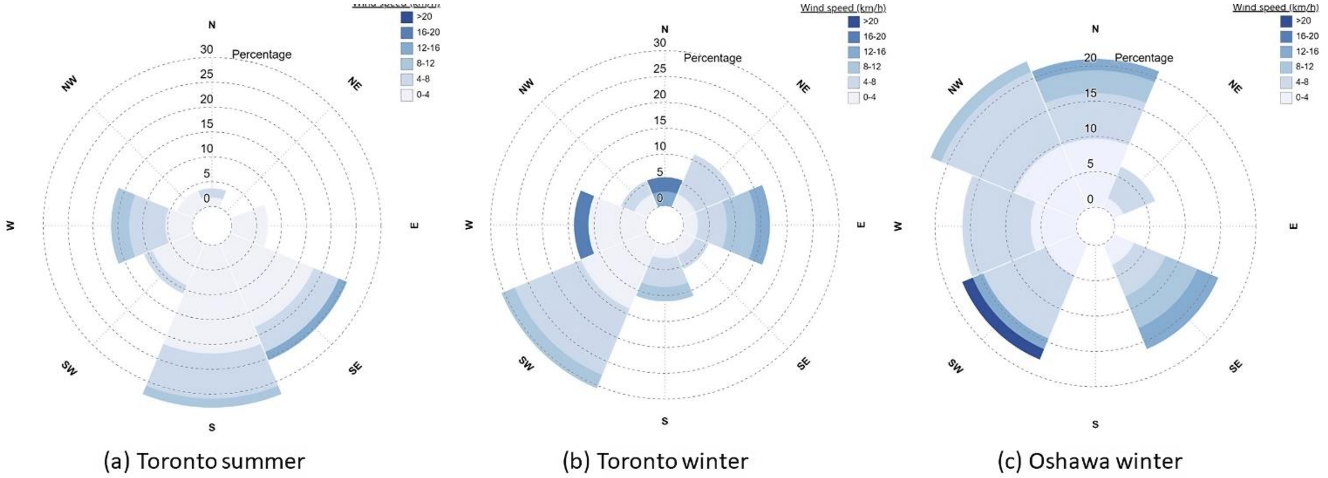


**Figure 9. Box-and-whisker plot of median nearshore slopes in Oshawa and Toronto in two seasons, summer (Jun-Aug) and winter (Dec-Feb). The edges of the box represent the interquartile range, the median of the upper and lower half of the data exclusive of the median. The error bars represent the maximum and minimum values. The horizontal line within the box shows the value of the median and the x symbol shows the mean. Individual dots represent outliers.**



(a) Toronto summer

(b) Toronto winter

(c) Oshawa winter

**Figure 10. Wind rose plots displaying the relative frequencies of wind direction (cardinal direction) and speed (km/h) at sampling sites in (a) Toronto summer, (b) Toronto winter, and (c) Oshawa Winter. Data was not collected during Oshawa summer. Made with www.WindRose.xyz.**