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A year–long comparison of particle formation events at paired urban and rural locations

Yun–Seok Jun [1], Cheol–Heon Jeong [1], Kelly Sabaliauskas [1], W. Richard Leaitch [2], Greg J. Evans [1]

[1] *Southern Ontario Centre for Atmospheric Aerosol Research, University of Toronto, 200 College Street, Toronto, Ontario, M5S 3E5, Canada*
[2] *Science and Technology Branch, Environment Canada, 4905 Dufferin Street, Toronto, Ontario, M3H 5T4, Canada*

ABSTRACT

Ultrafine particle size distribution data were collected in downtown Toronto and rural Egbert from May 2007 to May 2008. Particle formation events were observed in both locations and contributed to increased concentrations of particles less than 25 nm in diameter. These events were more frequent in spring and fall and rarely occurred in winter. Stronger solar radiation and drier air were correlated with the occurrence of formation events at both locations. Nucleation events occurred simultaneously at both sites on 10% of the days, and these events involved a shared air mass. Half of these simultaneous events were associated with northern air masses and only a quarter with southerly air masses. The higher loading of aged particles in southerly air masses transported from upwind industrial sectors appeared to limit the occurrence of nucleation events. Formation events occurred less frequently in downtown Toronto than at the rural site, and the frequency was lower on weekdays. It is hypothesized that vehicular emissions were responsible for the suppression of nucleation events in downtown Toronto.

Keywords: *Particle formation, ultrafine particles, traffic emissions, particle nucleation and growth, condensation sink*

Corresponding Author:
Greg J. Evans
☎ : *+1-416-978-1821*
🖷 : *+1-416-978-8605*
✉ : *greg.evans@utoronto.ca*

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1. Introduction

Atmospheric particles exert considerable climate influence and affect human health. In the global troposphere, aerosol particles influence the Earth's radiation budget by directly absorbing or scattering solar radiation and indirectly acting as cloud condensation and ice nuclei. Particles also serve as an interface where heterogeneous reactions occur (Seinfeld and Pandis, 2006). Further these particles can reduce visibility and adversely impact human health. Epidemiological studies have linked cardiovascular or respiratory morbidity and mortality to particulate matter exposure (Peters et al., 1997; Oberdorster et al., 2002). In order to estimate and predict the environmental and health impacts of aerosol particles, it is essential to understand their genesis and evolution in the atmosphere. One of the key processes in this regard is the formation of ultrafine particles and their subsequent growth through nucleation events. These events can produce sharp increases in the number concentration of particles and have been observed in a range of environments throughout the globe. Specifically, new particle formation events have been seen in regions spanning sub–Arctic Lapland (Vehkamaki et al., 2004), boreal forest in Finland (Kulmala et al., 1998; Dal Maso et al., 2005), and urban areas in Europe (Alam et al., 2003; Hamed et al., 2007; Salma et al., 2011), North America (Jeong et al., 2004; Stanier et al., 2004; Jeong et al., 2006; Qian et al., 2007), and Asia (Wehner et al., 2004; Monkkonen et al., 2005). Nevertheless, the mechanisms underlying these events have not been fully elucidated, mainly due to the challenges in directly measuring particles with diameter around 1.0 nm and analyzing the chemical composition of these newly formed particles.

Insight into these mechanisms has been gained through laboratory experiments and field studies. Sulfuric acid is considered a key nucleation precursor due to its low equilibrium vapor pressure in the atmosphere (Seinfeld and Pandis, 2006). Laboratory–based studies have often focused on connecting the concentration of precursor gases, such as sulfuric acid, to nucleation rate (Sipila et al., 2010). Moreover, the role of ammonia and organics have been studied through a number of experiments since binary nucleation of sulfuric acid and water failed to reproduce the nucleation rate measured in the field (Metzger, et al., 2010; Benson et al., 2011). In field studies, researchers have examined the atmospheric conditions favoring nucleation events. Boy and Kulmala (2002) analyzed the influences of meteorological parameters and reported that new particle formation was correlated with solar radiation and anti–correlated with relative humidity (RH). The observation of nucleation events was also found to be negatively correlated with high concentrations of pre–existing particles in field measurements (Weber et al., 1997).

Field studies conducted at multiple locations, either simultaneously or consecutively, have examined the influence of local meteorology, air masses, geography, and anthropogenic emissions. Vana et al. (2004) found that nucleation events at multiple locations in northern Europe were associated with cold Arctic air masses. An extensive field measurement campaign was conducted at 12 locations with varying environments in Europe, and nucleation at different sites was found to follow different seasonal patterns (Manninen et al., 2010). Paasonen et al. (2010) further reported that a correlation between the nucleation rate and the concentration of precursor gases varied between locations,

suggesting that different chemical compounds might contribute to nucleation at different locations.

Jeong et al. (2010) analyzed three weeks of particle number (PN) concentrations and size distributions obtained at five urban and rural locations in southern Ontario, Canada. These authors found that both anthropogenic and biogenic sources contributed to nucleation and growth of particles at locations situated close to industrial districts, and that these sources play an important role in determining aerosol population at both rural and urban sites. These findings pointed to the need for a longer–term study, to further resolve the extent to which differing emissions contribute to particle formation and growth at urban and rural locations. In this follow–up study, particle size distribution measurements were collected simultaneously for one year (May 2007–2008) in downtown Toronto and rural Egbert. These data were used to compare particle nucleation and growth events at these sites. It was hypothesized that examining nearby sites with differing mixes of anthropogenic and biogenic emissions would help elucidate the effects of these emissions, and shared parameters such as meteorology and air mass origin, on the occurrence of particle formation.

2. Experimental Methods

2.1. Monitoring sites and data sources

Toronto. Ultrafine particle number concentrations were measured in ambient air sampled at the laboratory of the Southern Ontario Centre for Atmospheric Aerosol Research (SOCAAR). SOCAAR is located at the Wallberg Building at the University of Toronto in downtown Toronto, Ontario, Canada (43.66° N, 79.40° W), and surrounded by multi–story buildings (Figure 1). The inlet is 15 m away from College Street, which experiences a traffic volume of ~20 000 vehicles per day. Particle size distributions were measured by a Scanning Mobility Particle Sizer (SMPS, TSI, St. Paul, MN) equipped with a nano– Differential Mobility Analyzer (DMA, TSI 3085, St. Paul, MN) and Ultrafine Water–based Condensation Particle Counter (UWCPC, TSI 3786, St. Paul, MN). The SMPS detected particles with mobility diameters of 3 to 106 nm every 2 minute. In addition, a TSI Fast Mobility Particle Sizer (FMPS) was employed to obtain particles with mobility diameters of 6 to 560 nm every second (Table 1). The FMPS data were used when the SMPS data were not available for Toronto. The FMPS data were corrected due to multiple charging of particles from 8 to 100 nm (Jeong and Evans, 2009). Also, the size distributions of particles larger than 100 nm were corrected based on polystyrene latex (PSL) calibration particles and a comparison with the SMPS equipped with a long DMA (TSI 3081, St. Paul, MN) used for Toronto. The SMPS and FMPS data were well–correlated after the FMPS data were corrected (Jeong and Evans, 2009).

A SmartEye Traffic Data Sensor (TDS) was employed to measure traffic volume along College St. (four–lane street). The TDS was set up on the roof of the Gage building situated 150 m west of the SOCAAR site. The TDS uses edge–detection to count the number of vehicles across all four lanes. The TDS continuously recorded traffic volume every five minute. The traffic data used here were collected between June and December 2010, several years after the ultrafine particle data was collected. Further the data from this traffic sensor had known limitations, including undercounting at night. However, despite these limitations, this traffic data was sufficiently representative of diurnal and seasonal traffic patterns in downtown Toronto to meet the needs of this study (Sabaliauskas et al., 2012).

Trace gas concentrations were obtained from the Ontario Ministry of the Environment (MOE) downtown site, situated approximately 850 m northeast of the SOCAAR sampling site (MOE, 2012). This MOE site provided hourly averaged concentrations of sulfur dioxide (SO_2), nitric oxide (NO), nitrogen dioxide (NO_2), carbon monoxide (CO), ozone (O_3), and mass concentrations of fine particulate matter ($PM_{2.5}$). The meteorological data were obtained from Environment Canada (EC) at the Pearson International Airport located approximately 20 km west of the SOCAAR site. This EC site provided hourly temperature (T), relative humidity (RH), wind speed (WS), and wind direction (WD). Solar radiation data were taken from the University of Toronto Mississauga Campus' meteorological station. Though this site is situated 25 km west of the SOCAAR site, its solar radiation data were the most consistently available throughout the campaign.

Egbert. The rural data were collected near Egbert Ontario, at Environment Canada's Centre for Atmospheric Research and Experiment (CARE). CARE is located approximately 80 km north of the Toronto site (44.23° N, 79.78° W) and is surrounded by mixed forest and farmland (Figure 1). The nearest road to the sampling, located 75 m away, experiences only a few vehicles per hour. Particle size distributions between 10 and 400 nm were detected every 15 minute by a SMPS equipped with a long DMA (TSI 3081, St. Paul, MN) and CPC (TSI 3025, St. Paul, MN). The centre also provided meteorological and traces gas concentration data except $PM_{2.5}$ data; $PM_{2.5}$ data were obtained from Barrie, a nearby city 15 km northeast of Egbert. While the sampling location in Toronto was heavily influenced by anthropogenic emissions, such as vehicle exhaust, Egbert experienced minimal local emissions. However, both locations were at times impacted by air masses from the south and southwest, containing outflow from industrialized regions in southwestern Ontario and mid–western United States.

Figure 1. *Map of Toronto and Egbert. Egbert is located 80 km north of Toronto and experiences minimal anthropogenic emissions.*

Table 1. *A summary of instrumentation for particle size and number distributions, air pollutant concentrations, and meteorological parameters*

Location	Data	Sampling Site	Instrument	Size Range	Time Resolution
Toronto	Size Distribution and Particle Number	SOCAAR	SMPS	3–100 nm	2 minute
			FMPS	6–560 nm	1 second
	Traffic Volume	Gage	SmartEye Traffic Data Sensor		5 minute
	Meteorological Data (T, RH, WS, WD)	EC: Pearson International Airport Meteorological Station			1 hour
	Solar Radiation	U of T Mississauga			1 hour
	Pollutant Concentrations (NO, NO_2, CO, O_3, $PM_{2.5}$, SO_2)	Ontario Ministry of Environment: Downtown Toronto Site			1 hour
Egbert	Size Distribution and Particle Number	EC: CARE	SMPS	10–400 nm	15 minute
	Meteorological Data (T, RH, WS, WD, Solar radiation)	EC: CARE			1 hour
	Pollutant Concentrations (NO, NO_2, CO, O_3, $PM_{2.5}$, SO_2)	EC: CARE			1 hour

2.2. Event classification

All days were reviewed and classified visually into categories based on their variations of particle number (PN) concentrations and geometric mean diameter (Jeong et al., 2010). Any day showing a distinct and continuous increase in the particle size and number concentration of 10 to 25 nm particles for more than one hour between 8:00 a.m. to 4:00 p.m. was designated as a particle formation event day. Non–event days with no formation event, or a formation event that occurred either before 8:00 a.m. or after 4:00 p.m. were classified as "Class N" days. As the focus of this study was regional formation events, the criteria applied to identify event days was fairly stringent; most days with particle formation from local point sources and plumes were included in the "Class N" days. The event days were further classified as Class I days if the event showed a distinct appearance of nucleation mode particles for more than 2 hours along with an increase of geometric mean diameter (GMD). Class I represented days with strong and potentially regional–scale formation events. These types of events have been observed at other sites (Stanier et al., 2004; Dal Maso, 2005; Qian et al., 2007). If an event was associated with an abrupt increase of SO_2 concentration and no subsequent growth of newly formed particles, the day was classified as Class II. Class II events usually showed a rapid increase in PN concentrations over a short period of time. These events have previously been observed near industrial regions and attributed to local–scale formation occurring in a plume (Jeong et al., 2010).

It was not always possible to distinguish between Class I or Class II events due to unclear formation events or unclear growth events. Any day with an event that could not be clearly resolved, due to ambiguous evidence, was classified as Class U (unclear event day). For example, if a day showed either a sporadic occurrence of particle formation or growth for particles larger than 25 nm without the presence of newly formed small particles it was categorized as Class U. Further, any increase of PN concentration that failed to exceed 3 000 cm^{-3} was not classified as a formation event, even if it showed other indications of particle formation, since this concentration was much lower than that typically observed during formation events in this region. A few events in Egbert were excluded for this reason. Days that could not be classified due to gaps in the data as a result of instrument failure or calibration were referred to as missing.

2.3. Condensation Sink (CS)

The CS is a parameter that quantifies the ability of the particle surface area to scavenge condensable vapors in the atmosphere. The higher the CS, the more rapidly condensable vapors will condense onto pre–existing particles. The CS was calculated by integrating over the size distribution:

$$CS = 2\pi D \int D_p \beta_M(D_p) n(D_p)\, dD_p \quad (1)$$

$$= 2\pi D \sum_i D_{pi} \beta_{Mi} N_i \quad (2)$$

where, D is the diffusion coefficient of condensing vapor, β_M is the transitional regime correction factor, D_{pi} is the particle diameter of size channel i, and N_i is the PN concentration in size channel i (Kulmala et al., 2001). The measured mobility diameter was used to describe the particle diameter and the particles were assumed to be spherical. The transitional correction factor can be estimated from (Fuchs and Sutugin, 1971):

$$\beta_M = \frac{Kn+1}{1.33\alpha^{-1}Kn^2 + 1.33\alpha^{-1}Kn + 0.38Kn + 1} \quad (3)$$

$$= \frac{Kn+1}{1.33Kn^2 + 1.71Kn + 1} \quad (4)$$

where, Kn is the Knudsen number, and α is the sticking coefficient, assumed to be unity. The Knudsen number is

$$Kn = \frac{2\lambda}{D_p} \quad (5)$$

where, λ (~6.64×10^{-8} m) is the mean free path of the gas molecules under standard conditions (Hinds, 1999). The properties of the condensing vapors are assumed to be very similar to sulfuric acid.

2.4. Potential Source Contribution Function (PSCF)

The PSCF provides a probability field that identifies upwind geographic locations associated with high concentrations of a pollutant at a receptor site based on air mass back trajectories (Ashbaugh et al., 1985). Forty eight–hour back trajectories arriving at the sampling sites at a height of 500 m above ground level were calculated by the HYbrid Single–Particle Lagrangian Integrated Trajectory (HYSPLIT) model based on 40 km gridded data from the Eta Data Assimilation System (EDAS; Draxler and Hess, 1997). The region of interest was gridded with a grid size of 75 km. The PSCF for each grid cell was calculated by counting the number of back trajectories that passed over the cell. The total number of trajectories that crossed the ij^{th} grid cell was denoted as n_{ij}, and the number of trajectories crossing the same grid cell, associated with pollutant concentrations at the receptor site surpassing a threshold criterion, was denoted by m_{ij}. The PSCF for each grid cell was

calculated as:

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}} \quad (6)$$

In this study, the PSCF was employed to investigate the regions that might be the sources of pollutants leading to simultaneous formation events. Therefore, m_{ij} was the number of trajectories associated with days when formation was observed at both sites. Very often, a weighting function, $W(n_{ij})$ is added to the PSCF calculation to reduce the uncertainty that might result from small values of n_{ij}. A weighting function was not applied in this study because the number of days with simultaneous formation events at both sites was already quite low. Therefore these PSCF results were interpreted with this uncertainty in mind.

3. Results and Discussion

3.1. Influence of particle formation on diurnal patterns

Particle number (PN) concentrations in Toronto were higher than in Egbert over the entire size range regardless of the occurrence of formation events (See the Supporting Material, SM, Figure S1). This was presumably due to the greater anthropogenic emissions in the city from vehicles, heating, and industry. At both sites, the occurrence of formation events increased the number concentration of particles less than 25 nm, clearly altering the appearance of the particle size distributions.

Formation events altered the diurnal patterns of PN concentrations in Toronto (Figure 2) and Egbert (Figure 3). This effect was strong for the small 10–25 nm particles but much smaller for the larger 25–293 nm. In Toronto, PN concentrations typically rise on weekdays between 5:00 a.m. and 8:00 a.m. due to rush hour. On Class I days, the concentration of these small 10–25 nm particles continued to increase after 8:00 am and showed a further steep rise between 11:00 am and 12:00 pm (Figure 2a); no such rise was seen on the non–event days (Figure 2b). Clearly, formation events can play an important role in increasing PN concentrations in cities on some days, producing an early afternoon peak, well after rush hour.

During Class I days at Egbert, the diurnal pattern for the 10–25 nm particles (Figure 3a) was similar to that observed in Toronto (Figure 2a); strong increases were observed between 11:00 and 12:00, reaching a peak in the early afternoon. In Egbert, PN concentrations of the small 10–25 nm particles were initially lower than those of the larger particles. On Class I days the PN concentration of the smaller particles rose to exceed that of the larger particles while on non–event days the larger particles dominated throughout the day (Figure 3b). These patterns were consistent with the low local anthropogenic emissions of ultrafine particles in Egbert. Typically, most small particles at this site come from nearby formation events while larger particles are older, having undergone growth during transport from more distant sources.

3.2. Events statistics

Particle formation events were observed at both locations, but more frequently in Egbert. Formation events were identified on 58 days in Toronto as compared to 122 days in Egbert. Formation events were not detected on 196 days in Toronto, and 186 days at Egbert (Table 2). The formation events in Toronto were often simultaneously observed in Egbert, yet numerous formation events detected in Egbert were not observed in Toronto. This suggested that particle formation events could be suppressed in downtown Toronto. A lower frequency of formation in urban areas has previously been reported in several studies. For example, Vana et al. (2004) measured aerosol size distributions at three locations, and the frequency of nucleation bursts was lowest where the background particle number concentration was highest. Similarly, the suppression of formation events in Toronto appeared to be associated with pre–existing particles, suggesting that scavenging of condensable vapors was limiting particle formation and growth (Kulmala et al., 2001).

Further classification of events showed that Class I events dominated over Class II events at both locations. All the formation events observed in Toronto were classified as Class I, and only one Class II event was observed in Egbert. Class II events might have occurred rarely because both the sampling sites were located far from major SO_2 point sources. Previously, Class II events were frequently observed in other sites in southern Ontario, such as Harrow, Ridgetown, and Bear Creek, which are located closer to major industry and power plants in the mid–western United States, and experience frequent plumes with elevated SO_2 and have higher average SO_2 concentrations (Jeong et al., 2010). However, no Class II events were observed in Egbert and Toronto in this earlier study.

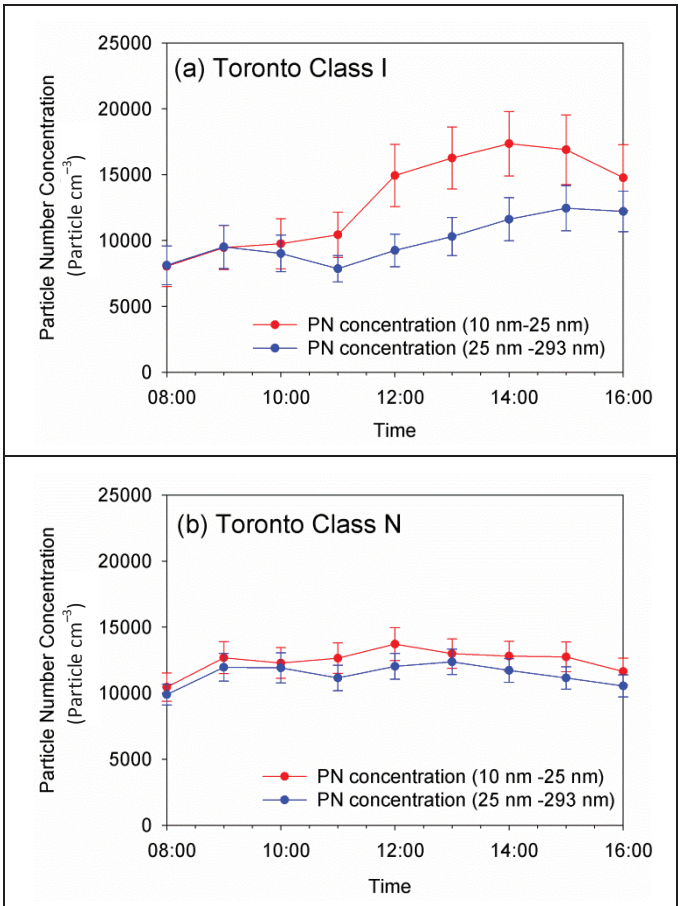

Figure 2. *Temporal variation of size–resolved particle number (PN) concentrations for Class I formation event days* ***(a)*** *and Class N non–event days* ***(b)*** *in Toronto. Averaged PN concentrations between 10 and 25 nm for Class I increased after 8:00 and showed a steep rise between 11:00 and 12:00 (Figure 2a). This suggested that the substantial increase during the day was due to nucleation. PN concentrations remained constant during the day when formation was not observed (Figure 2b). An earlier rise in PN concentration due to traffic typically occured from 5:00 a.m. to 8:00 a.m. on weekdays in Toronto.*

There was a distinct seasonality in the occurrence of formation events; the frequency peaked in spring and fall and decreased in winter at both sites (see the SM, Figure S2). This seasonal pattern has been found in other urban and rural locations (Jeong et al., 2006; Charron et al., 2007; Qian et al., 2007). These studies suggested that nucleation was positively associated with solar irradiance and possibly related to the onset of biogenic activity, especially in rural areas (Dal Maso et al., 2005). In addition,

nucleation events in both locations usually occurred several days in a row rather than being evenly spread out. This clustering of events was observed throughout the year, and was more apparent in spring and fall.

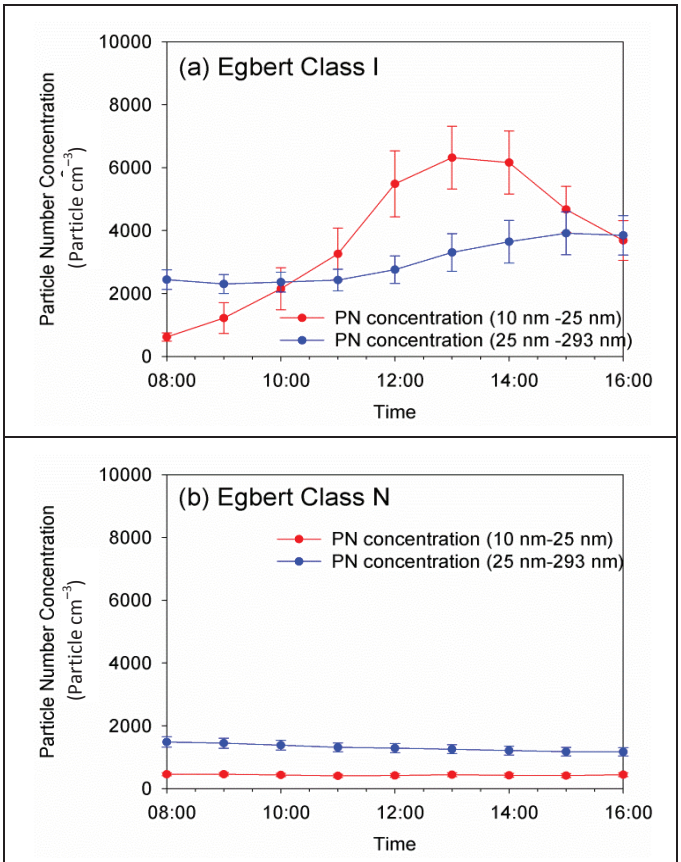

Figure 3. *Temporal variation of size–resolved particle number (PN) concentrations for Class I formation event days* ***(a)*** *and Class N non–event* ***(b)*** *in Egbert. The averaged PN concentrations between 10 and 25 nm for Class I (Figure 3a) exhibited a pattern matching that observed in Toronto (Figure 2a).*

3.3. Comparison of the event and non–events days

Hourly data including solar radiation, temperature, RH, wind speed, wind direction, mass concentrations of $PM_{2.5}$, and SO_2 concentrations were compiled for times between 8:00 a.m. and 4:00 p.m. and averaged every day. These daily averaged parameters were grouped and compared between the Class I and Class N days (see the SM, Table S1).

Solar radiation, RH, and average temperature differed significantly between the event days and non–event days (p<0.05). The solar radiation, RH, and average temperature for Class I days were 200 W m^{-2} higher, 15–16% lower, and 15–16 °C higher, respectively, than on Class N days. These meteorological parameters are all interrelated and associated with seasonality and air mass origin. For example, most formation events occurred in spring to fall, when temperature and solar radiation were higher. No significant difference was found in wind speed, SO_2, or $PM_{2.5}$ between the event and non–event days. However, the absence of a statistically significant association does not necessarily mean that these parameters had no influence on the occurrence of particle formation events. Particle formation events require conditions characterized by a complex combination of conditions rather than any individual parameter.

3.4. Simultaneous events

Greater insight into the parameters associated with the occurrence of formation events was obtained by comparing and contrasting the event days at the two sites. Formation events were simultaneously observed in both Toronto and Egbert on thirty four days, 10% of the days throughout the year. These 34 events suggested that formation was at times occurring regionally, influencing aerosol population across both rural and urban areas. The simultaneous events generally occurred at about the same time at the two sites, despite their 80 km separation: 32 simultaneous events occurred within two hours of one another, and 21 of these 32 events took place within an hour of each other. The concurrent events comprised 59% of the total events in Toronto while only accounting for 28% of all events in Egbert.

On these 34 days, the events in Egbert lasted for a longer period of time, five hours on average, as compared to three hours in Toronto. This may have been due to the more pristine conditions at the rural site. The condensation sink was typically lower at Egbert, which would have sustained the concentrations of condensable gases needed to grow new particles. Conversely, it is possible that it was the source rather than sink that differed between the sites, if particle formation was primarily driven by biogenic gases, which would be more abundant in Egbert.

The role of air mass origin was investigated to evaluate the influences of upwind sources. The air mass path for each day was determined by classifying HYSPLIT back trajectories extracted through the NOAA website (Draxler and Rolph, 2013; Rolph, 2013), as North, South, East, West, and Detoured. Most of the days fell into the North or South categories so these days were directly compared as they had contrasting characteristics. Typically, North represented days when the air masses originated from northern Canada and experienced minimal emissions on route. South represented days with air masses from the mid–western United States that had passed over several industrial and urban areas.

Table 2. *The classification of days based on formation events in Toronto and Egbert from May 2007-2008*

	Toronto	%	Egbert	%
Class I [a]	58	15.8	121	32.9
Class II [b]	0	0	1	0.3
Class U [c]	17	4.6	17	4.6
Class N [d]	196	53.3	186	50.5
Missing [e]	97	26.3	43	11.7
Total	368	100	368	100

[a] *strong event*
[b] *weak event*
[c] *unclear distinctions between class I and II*
[d] *non–event days*
[e] *days with inadequate data*

The PSCF showed the origins of air masses that impacted the site on days that events occurred simultaneously at both locations. The PSCF was calculated twice, once with each location set to be the receptor site; the possible source areas thereby identified were similar to one another (see the SM, Figure S3). This suggested that formation at both sites was very often influenced by identical sources. The potential source regions identified spanned vast areas north of the two sampling sites including regions in central Ontario to south–west Quebec as well as south–eastern areas in the United States. Further, a careful review of each back trajectory on every day revealed that most of the simultaneous events (94%) involved identical air masses arriving at the two sites. The northerly and southerly air masses prevailed, and northerly winds (50%) dominated over southerly winds (28%). Southerly winds were likely less conducive to formation events because these winds usually bring warm and humid air, along with higher loadings of pollutants accumulated by the air mass en route. However, strong regional events were still sporadically observed for air masses from the south, but only on relatively clean days. In contrast, northern air masses are usually clean as there are far fewer emission sources in northern Canada. The northern air is also often cooler and drier, which provides favorable ambient conditions to initiate nucleation. Close association of regional events with northern air masses was previously revealed in southern Ontario (Jeong et al., 2010) and northern Europe (Hussein et al., 2009).

The shape of the particle size distributions during formation events also differed between the sites, and the origin of the air masses (Figure 4). Particles formed through nucleation were superimposed upon preexisting larger particles, and those from local sources such as traffic. The contributions of local sources were quite substantial in Toronto and more evident than in Egbert (see the SM, Figure S1). Further, the presence of larger particles was evident at both sites when the air masses were from the south. In Toronto, the concentrations of the smaller particles, presumably from nucleation, were higher for air masses from the north than from the south. Apparently, the conditions associated with air masses from the north promoted stronger events in Toronto or those for south suppressed formation; higher concentrations of pre–existing particles could weaken nucleation through scavenging of condensable vapors. A sink due to pre–existing particles could also have scavenged newly–formed particles through coagulation before they grew large enough to be detectable. It should be noted that this difference in small particles between northern and southern air masses was not evident in Egbert, despite the presence of higher concentrations of larger particles, with a mode at ~100 nm, in air masses from the south. Presumably the concentration of these large particles in Egbert was too small to have an impact.

3.5. Effects of vehicular emissions

The frequency of formation events that occurred on weekdays and weekends were compared to investigate the anthropogenic influences on particle formation in downtown Toronto. The ratio of Class I to Class N days in Toronto showed a substantial variation between weekdays and weekends while there was little difference in Egbert (Table 3). Several key parameters thought to impact formation were compared. As expected, the meteorological factors considered to have substantial influences on formation did not differ between weekdays and weekends at both locations. For example, solar irradiance and RH were the same on weekdays vs. weekends in Toronto and Egbert.

In contrast, the condensation sink (CS) was significantly higher on weekdays than weekends in Toronto ($p<0.05$). This metric describes the effective first order rate constant for deposition of condensable vapors onto the available particulate surface area. Thus, higher CS on weekdays provides a credible explanation for the observed suppression of formation events on weekdays. The temporal patterns of the CS matched that for traffic in Toronto: the weekend/weekday ratio for traffic count was 0.8 while that for CS was 0.7. The CS also exhibited diurnal patterns (Figure 5) consistent with that of the traffic patterns (see the SM, Figure S4). Qualitatively, the CS was higher on weekdays and showed a significant increase between 6:00 and 9:00 a.m., consistent with traffic emissions during rush hour. Quantitatively, the weekday CS and traffic count patterns were highly correlated ($r=0.87$). The CS also showed a good correlation with traffic related pollutants, such as NO_2 ($r=0.53$) and CO ($r=0.48$). Overall, the temporal trend of CS and its correlation with traffic–related pollutants strongly supports the hypothesis that local traffic played an important role in increasing the CS and thereby suppressed formation events on weekdays in downtown Toronto.

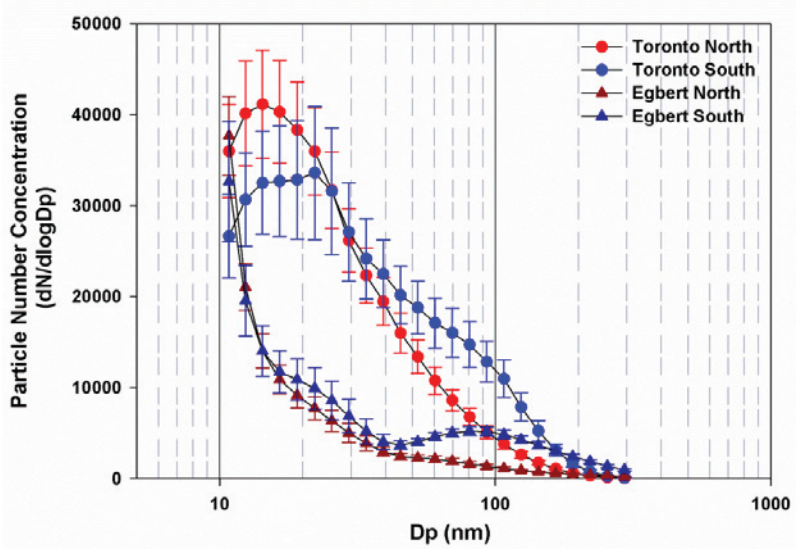

Figure 4. *Average size distributions for 34 simultaneous formation events sorted by the directional origin of air masses arriving at each sites. Only size distributions measured during the formation events were included in the averages. Error bars represent 95% confidence intervals. Concentrations of particles less than 25 nm were higher in Toronto during events associated with air masses from the north. Southerly air masses transported aged particles from upwind industrial sectors, resulting in higher concentrations of larger particles.*

Table 3. *Selected characteristics for weekdays and weekends at both locations. The condensation sink and meteorological parameters were averaged for 8:00 to 16:00 over the period May 2007–08. 95% confidence intervals were included*

		Class I Class N	Solar Radiation (W m^{-2})	RH (%)	Condensation Sink ($1x10^{-3}$ s^{-1})
Toronto	Weekdays	0.26	342±25.2	64±1.7	10.3±0.63
	Weekends	0.41	353±41.7	62±3.0	7.1±0.93
Egbert	Weekdays	0.67	364±24.6	70±1.9	3.2±0.32
	Weekends	0.60	380±41.0	68±3.1	2.5±0.47

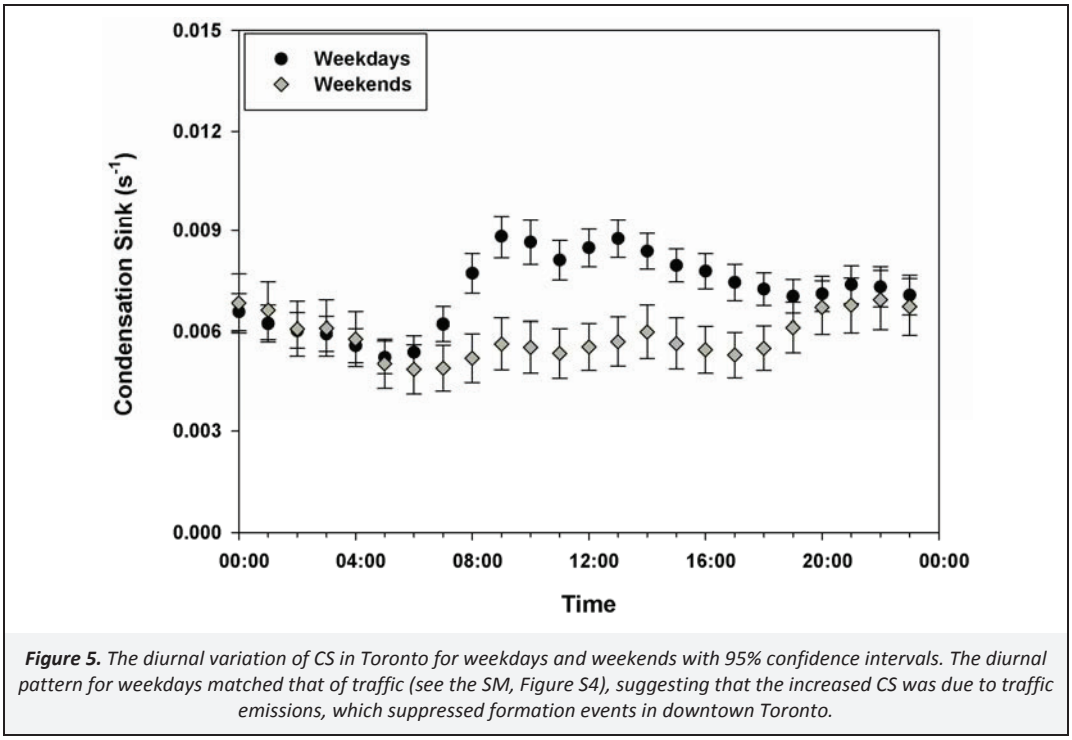

Figure 5. *The diurnal variation of CS in Toronto for weekdays and weekends with 95% confidence intervals. The diurnal pattern for weekdays matched that of traffic (see the SM, Figure S4), suggesting that the increased CS was due to traffic emissions, which suppressed formation events in downtown Toronto.*

4. Conclusion

Particle size and number distribution data simultaneously collected in downtown Toronto and Egbert from May 2007–2008 were investigated to compare formation and growth at urban and rural sites. Formation events were frequently observed during the day and contributed to increasing the concentrations of particles smaller than 25 nm at both locations. The seasonality and influences of meteorological parameters on events were consistent at both sites. Formation events were detected half as often at the urban as at the rural site, and occurred simultaneously at both locations on 10% of the days. These simultaneous regional events shared the same air masses with northern air masses promoting more frequent formation events. The lower frequency of formation events associated with southerly winds was attributed to a higher condensation sink due to pre–existing particles transported from upwind industrial regions. The frequency of formation events was lower in downtown Toronto than in Egbert, particularly for weekdays as compared to weekends. It is likely that local traffic emissions suppressed formation by providing a large condensation sink that consumed condensable precursor gases needed to promote particle formation or growth.

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Supporting Material Available

Selected meteorological parameters with respect to classification of particle formation events at both locations (Table S1), Average size distributions of formation event (Class I) and non–event (Class N) in Toronto and Egbert (Figure S1),The seasonal patterns of new particle formation in Toronto and Egbert for May 2007 to May 2008 (Figure S2), PSCF plot for the days that formation events occurred at both sites simultaneously (Figure S3), The PSCF was calculated with Toronto (a) and Egbert (b) serving as the receptor site, respectively, The temporal variation of traffic counts on College St. at the Toronto site with 95% confidence intervals (Figure S4). This information is available free of charge via the Internet at http://www.atmospolres.com.

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