Comparison of Nucleation and Growth at Paired Urban and Rural Locations

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
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Abstract

The number and size distributions of particles between 10 and 400 nm were measured in Toronto and rural Egbert during May 2007 to May 2008 to compare nucleation and growth at paired urban and rural locations. Particle formation and growth were observed in Egbert more frequently than in Toronto, and simultaneous events occurred on 34 out of 368 days. In contrast, formation and growth rates were both higher in Toronto. Further, a linear regression analysis suggested that compounds contributing to nucleation and growth processes were different in Toronto and Egbert. Vehicular emissions seemed to suppress particle formation in downtown Toronto. Nucleation also appeared to be suppressed by long-range transported pollutants originating from industrial regions in southwestern Ontario and northern Ohio in the United States. A Nucleation Indicator (NI) was developed by combining relevant parameters, and it was found to provide a reasonable measure of the probability of nucleation events occurring.
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1. Introduction

An aerosol is defined as a suspension of liquid or solid particles in air (Seinfeld and Pandis, 2006). Atmospheric aerosols can stem from either natural sources, such as windblown dust, sea spray, and volcanoes, or anthropogenic emissions, such as combustion of fossil fuels. These aerosols are ubiquitous in the atmosphere with concentrations varying with location by orders of magnitude. The number of particles per cubic centimeter of air varies by several orders of magnitude between pristine locations and urban areas. For example, in polar regions, concentrations of tens of particles per cubic centimeter are common. In contrast, many urban areas have particle number concentrations in the thousands (Riipinen, 2008).

Particles in the atmosphere can be categorized into primary or secondary aerosols depending on the way they are formed. While primary aerosols are introduced directly into the atmosphere from a source, secondary particles are formed in the atmosphere by gas to particle conversion processes. Once present in the atmosphere, aerosol particles may change their size and composition by numerous processes, such as condensation or evaporation of gas molecules, and coagulation with other particles (Seinfeld and Pandis, 2006).

Atmospheric particles affect climate and human health. Aerosols impact climate either directly by scattering or absorbing solar radiation or indirectly by serving as cloud condensation nuclei (Seinfeld and Pandis, 2006). Moreover, a number of epidemiological studies have observed positive associations between particulate matter exposure and cardiovascular or respiratory disease mortality and morbidity (Peter et al., 1997; Oberdörster et al., 2002; Pope et al., 2004).
It has been recognized that limitations on predicting climate change are due in part to uncertainties in radiative forcing initiated by atmospheric aerosols (Riipinen, 2008), yet the spatial and temporal variation of aerosol concentrations have not been entirely elucidated. Particle formation and growth in the atmosphere plays a significant role in changing aerosol characteristics. Although many studies have observed particle formation and growth events, the extent to which biogenic and anthropogenic emissions influence these events has yet to be determined. Understanding the contribution of biogenic and anthropogenic sources to nucleation will represent a significant step towards understanding the impact of aerosols on climate change.

The objective of this study was to quantify the impacts of anthropogenic emissions on particle formation and growth in the atmosphere by comparing nucleation and growth events at paired urban and rural locations in Southern Ontario. The size distributions of particles were measured in downtown Toronto and rural Egbert by particle instruments, such as a Scanning Mobility Particle Sizer (SMPS) or a Fast Mobility Particle Sizer (FMPS).

In this thesis, the main analysis is organized into three sections: 5.1: Identification of New Particle Formation, 5.2: Event Characteristics and 5.3: Underlying Causes. The Identification of New Particle Formation section compares the frequency of nucleation at the two locations and discusses the spatial scales and seasonal trends of nucleation. The Event Characteristics section includes a characterization of nucleation by formation and growth rates and a regression analysis carried out to infer relative contributions of chemical compounds to formation and growth. Finally, the Underlying Causes section discusses the impacts of meteorological parameters, vehicular emissions, and regional-scale transported pollutants in order to understand what influenced nucleation at each location.
2. Literature Review

This section reviews the relevant literature to provide the reader with background on the nucleation of atmospheric particles required to understand the analysis presented in this study. Included in this section are the influences of particulate matter, an introduction to the instruments essential to study atmospheric particles, the global atmospheric observations, and key components for nucleation.

2.1. Influences of Aerosol Particles

Aerosols in the atmosphere have a significant influence on climate through direct and indirect effects. The direct effects include the scattering and absorption of solar radiation by aerosols. Aerosols can have either warming or cooling effects depending on their chemical composition. For example, sulphate particles and organic aerosols scatter solar radiation causing a reduction in the amount of solar radiation reaching the Earth’s surface. On the other hand, carbonaceous particles, such as Black Carbon (BC) absorbs the outgoing solar radiation at the top of the atmosphere, resulting in warming effects. The overall net effect of aerosols is cooling (Ramanathan et al., 2001; Seinfeld and Pandis, 2006).

The indirect effects are associated with the role of aerosols as cloud condensation nuclei. A rise in the number of aerosol particles may lead to increased water droplet number concentrations. More droplets results in greater reflection of solar radiation to space, resulting in climate cooling. Also, the droplet diameter could decrease due to the increase in the aerosol number concentrations. The diameter of droplets is dependent on the amount of moisture and the number of nuclei inside a cloud. If the number of nuclei increases while the amount of moisture remains constant, the droplet diameter will be reduced. Precipitation can be reduced by these smaller droplets in contaminated clouds. Moreover,
increased particle number can increase the lifetime and consequently cloud coverage, which will further lead to reduction in the solar radiation at the surface (Ramanathan et al., 2001).

In addition, atmospheric aerosols have been associated with adverse health effects. A number of epidemiological and exposure studies have shown a positive association between cardiovascular and respiratory diseases and exposure to particulate matter (Peter et al., 1997; Oberdörster et al., 2002; Pope et al., 2004). Particle exposure has been shown to increase the risk of having heart attack or stroke, alter heart rhythms, increase blood pressure, and trigger asthma attacks in susceptible populations.

2.2. Instrumentation

Nucleation mode or ultrafine particles are defined as particles with diameters less than 100nm. In order to investigate nucleation of aerosol particles, it is essential to detect the evolution of nucleation mode particles as a function of number, size and chemical composition. It is also very important to measure the concentrations of gas precursors that are believed to contribute to particle formation. The size distributions of particles are often measured by a Differential Mobility Analyzer (DMA), and the number concentrations of mono-dispersed particles are counted by a Condensation Particle Counter (CPC). The characteristics of these instruments are briefly introduced in this section.

2.2.1. DMA

The size distributions of airborne particles are widely detected by a DMA. The DMA often comprises the main section of a particle sizer, such as Scanning Mobility Particle Sizer
(SMPS), which was used for this study. The DMA separates particles with respect to their electrical mobility, which is one measure of particle size. In brief, aerosol particles are first exposed to a pool of ions in which the number of positive ions is equal to the number of negative ions. Colliding with these ions, particles will lose their initial charges as they are attracted to the oppositely charged ions. This neutralizing process will eventually lead to an equilibrium charge state, often called the Boltzmann equilibrium charge distribution. The Boltzmann equilibrium charge distribution provides the fraction of particles carrying a particular charge at given size (Hinds, 1999).

These particles are then introduced along the centerline between the two concentric cylinders that maintain an electric field, and the particles deposit along the collecting cylinder due to the electrical attraction. The distance that particles travel within the cylinder will depend on their electrical mobility, and therefore particles with different size will impact on different sections of the cylinder.

During this process, only the charged particles will be collected. However, from the Boltzmann equilibrium charge distribution, the entire aerosol size distribution with uncharged particles can be calculated. Once the particles have been size segregated according to their electrical mobility, the number concentration of these separated particles can be measured by drawing a selected size fraction into a CPC or a Faraday cup aerosol electrometer (Curtius, 2006). The detailed operating principles are discussed in the Methodology section.

2.2.2. CPC

The number concentrations of particles are often determined by a CPC. Particles with diameter less than 100 nm cannot be optically detected because these particles are smaller
than the wavelength of the light. Therefore, these particles first need to grow by condensation until they are optically observable.

The CPC first saturates the aerosols by exposing the particle flow to a supersaturated vapour. The saturated vapour condenses onto the particles as the sample flow cools down. Supersaturation is achieved by either an adiabatic expansion or heat transfer between the warm flow and the wall of the condenser maintained at ~ 10°C (McMurry, 2000). The particles will eventually grow to sizes bigger than 1 μm and will be detected by appropriate optical techniques (Curtius, 2006).

In order to study nucleation of atmospheric particles, it is very important to measure the particles just after they are produced by nucleation. However, the freshly formed particles (~1nm in diameter) are not directly measured by current instruments due to their detection limit (~3nm), and this often challenges study of atmospheric nucleation. CPCs need to be further developed so as to count freshly formed particles, allowing direct observation of nucleation.

### 2.3. Atmospheric Observations

The development of a nano-DMA and CPC has enabled observation of the number and size distributions of ultrafine particles down to ~10 nm in diameter, and nucleation of new aerosol particles and subsequent growth in the atmosphere has been identified at various locations in the Earth’s atmosphere (Weber et al., 1997; Alam et al., 2003; Birmili et al., 2003; Staneir et al., 2004; Dal Maso, et al., 2005; Mönkkönen et al., 2005; Hussein et al., 2008; Manninen et al., 2010). These locations include the boreal forest in northern Europe, urban areas in Europe and North America, and coastal environments in Europe. Although a nucleation
event is usually observed on a sunny and comparatively clean day, the seasonal occurrence of events and their characteristics such as formation and growth rate vary significantly with locations. For example, a typical seasonal trend of nucleation events, a maximum in spring and fall with a minimum in winter, has been observed at many locations, such as the boreal forest in Finland (Dal Maso et al., 2005), urban sites in Eastern America (Stanier et al., 2004; Jeong et al., 2006) and metropolitan areas in Europe (Hussein et al., 2008; Salma et al., 2011). However, these seasonal trends were not found in coastal environments (O’Dowd et al., 2002; Manninen et al., 2010) where particle formation events were observed to occur throughout the year without a distinct trend.

Fig. 1. A typical evolution of particle size distribution for a nucleation event day observed in Hytiäälä in Finland. (Curtius, 2006)(©Elsevier)

The observed nucleation is often characterized by formation and growth rates, which typically range from 0.01 to 10 cm$^{-3}$s$^{-1}$ and from 1 to 20 nmhr$^{-1}$, respectively in the boundary layer (Kulmala et al., 2004). These measured rates often exhibit spatial and seasonal variances. For instance, formation rates observed in industrial areas were as high as 100 cm$^{-3}$s$^{-1}$ and in coastal environments the rates were about $\sim$10$^4$-10$^5$ cm$^{-3}$s$^{-1}$ (Kulmala et al., 2004).

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Furthermore, the growth rates also show a considerable variation with location, ranging from as low as 0.1 nm/hr\(^{-1}\) in polar regions (Kulmala et al., 2004) to as high as 11.6 to 18.1 nm/hr\(^{-1}\) in heavily polluted cities in Asia (Mönkkönen et al., 2005). Thus, it is likely that particle growth is dictated by the availability of condensable vapours and thus will differ in rural and urban environments.

The significant variations in seasonal frequency of nucleation events as well as formation and growth rates can result from numerous factors, such as the fluctuation of meteorological parameters with season. Moreover, they could be due to diverse chemical species participating in nucleation processes since the type and quantity of nucleating and condensing agents presumably vary with season and locations, as inferred from a number of observations. Therefore, different chemical species might account for nucleation events in different circumstances, further indicating that nucleation mechanism can differ with environments.

While sulphuric acid has been considered to be key to nucleation of particles in the atmosphere, a few other chemical species, such as ammonia, amines, and organics compounds, also have been proposed to participate in the atmospheric nucleation, and the corresponding mechanisms, such as binary nucleation of H\(_2\)SO\(_4\) and H\(_2\)O or ternary nucleation of H\(_2\)SO\(_4\), H\(_2\)O, and NH\(_3\), have been suggested. In order to understand and quantify the atmospheric nucleation, it is desirable to reproduce the atmospheric level of ultrafine particle concentrations by such mechanisms in the laboratory experiments. Nevertheless, laboratory studies have not duplicated the field observations. There still exists a discrepancy between field observations and laboratory experiments. A few key nucleating species with corresponding mechanisms are briefly reviewed, and the field measurements have been compared with the laboratory studies.
2.4. Comparison of Laboratory Studies with Atmospheric Observations

Along with sulphuric acid, a few other species have been proposed to account for nucleation: ammonia, and organic species including amines. The mechanisms including these species are briefly reviewed, and the laboratory experiments in the presence of these species are compared with atmospheric observations.

2.4.1. Sulphuric Acid: Binary Homogeneous Nucleation of H₂SO₄ and H₂O

Gas-phase sulphuric acid is recognized as an essential precursor gas to nucleation in the atmosphere (Sihto et al., 2006; Riipinen et al., 2007; Sipilä et al., 2010) due to its very low vapour pressure of ~10⁻⁴ Pa at ~400 K (Ayers et al., 1980). Gas-phase sulphuric acid can be produced by the reaction of SO₂ with hydroxyl radical (Stockwell and Calvert, 1983). The H₂SO₄ and H₂O molecules will collide with each other, forming clusters if they do not encounter pre-existing particles. The clusters may grow by condensation depending on the atmospheric conditions. Once the clusters reach the critical size for thermodynamic stability, they can nucleate to form a new particle from the gas-phase (Curtius, 2006). This process is called binary homogenous nucleation of H₂SO₄ and H₂O because two substances (H₂SO₄ and H₂O) are involved in the reaction and the nucleation takes place without any other external substances that provides a surface for nucleation.

It is important to connect the gas phase concentration of H₂SO₄ and the ultrafine particle concentration produced by nucleation to understand the role of sulphuric acid. This often requires resolving the initial concentration of H₂SO₄ that initiates nucleation and the number of H₂SO₄ molecules in the critical cluster. According to the nucleation theory (Kashchiev, 1982), the number of precursor molecules in the critical cluster can be drawn from the correlation between the nucleation rate and the concentrations of key chemical
species. For instance, the slope of the nucleation rate versus the H$_2$SO$_4$ concentrations in the atmosphere indicates the number of sulphuric acid molecules in the critical cluster.

![Diagram of nucleation and growth](image.png)

Fig. 2. The schematic of binary homogenous nucleation of H$_2$SO$_4$ and H$_2$O. In this system, organics vapours participate in growth process (Curtius, 2006). (© Elsevier)

The number of H$_2$SO$_4$ molecules in the stable cluster and the threshold H$_2$SO$_4$ concentrations initiating nucleation have been estimated from field observations. According to Sihto et al. (2006) and Riipinen et al. (2007), the slope of the nucleation rate versus the H$_2$SO$_4$ concentrations was found to be between 1 and 2, and nucleation events were observed at a H$_2$SO$_4$ concentration of $10^6$ to $10^7$ molecules per cubic centimeter (cm$^3$). However, this has not been duplicated by laboratory experiments. Higher concentrations of H$_2$SO$_4$ were required to explain the concentrations of new particles produced by nucleation in the atmosphere (Ball et al., 1999; Zhang et al., 2004; Young et al., 2008). For instance, Ball et al. (1999) estimated the onset H$_2$SO$_4$ concentrations produced from a liquid reservoir to be $\sim 10^9$ cm$^3$, and Young et al. (2008) reported that nucleation took place at H$_2$SO$_4$ concentrations of $\sim 10^8$ cm$^3$ formed from the in situ reaction of SO$_2$ with OH. However, in

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some laboratory studies, nucleation was observed at close to ambient H$_2$SO$_4$ concentrations of $\sim$10$^7$ produced in situ (Berndt et al., 2005; Benson et al., 2010; Sipilä et al., 2010).

Nevertheless, the number of H$_2$SO$_4$ molecules in the critical cluster, represented by the slope of the nucleation rate versus H$_2$SO$_4$ concentrations, has never been shown definitively to be between 1 and 2 in laboratory experiments (Ball et al., 1999; Berndt et al., 2005; Berndt et al., 2006; Young et al., 2008; Benson et al., 2010) except Sipilä et al. (2010). This failure has motivated the idea that a third chemical species, such as ammonia, amines, and organic compounds, might be required to explain the observed nucleation rate.

Only Sipilä et al. (2010) has reported binary nucleation taking place at ambient H$_2$SO$_4$ concentrations of $\sim$10$^6$ with a slope of approximately 1.5. However, there is a variation between different studies at the present time, and a number of laboratory studies still show a slope bigger than 2 (Benson et al., 2010, 2011). Sipilä et al. (2010) suggested that the failure of experiments conducted to date could be due to a deficiency in particle counting. Also, since H$_2$SO$_4$ alone produced the ambient level of new particles, the other sulphur-containing compounds, such as HSO$_5$, would play a minor role in nucleation processes. Further they pointed that although the measured growth rate from H$_2$SO$_4$ in this work showed good agreement with the theoretical value, it was low as compared to the ambient growth rate. This also supports the hypothesis that other compounds are likely taking part in the early growth of new particles (Sipilä et al., 2010).

2.4.2 Ammonia: Ternary Nucleation of H$_2$SO$_4$, NH$_3$, and H$_2$O

While the binary nucleation of sulphuric acid and water has been assumed to be the primary mechanism, particle formation rates measured in the field are too high to be explained by
binary nucleation alone (Weber et al., 1997). This has motivated researchers to search for a third component participating in nucleation. Ammonia was considered as the most likely species taking part in the process since the vapour pressure of sulphuric acid above a solution considerably decreases in the presence of ammonia (Kulmala et al., 2000).

Ammonia is ubiquitous in the Earth’s atmosphere with its mixing ratio ranging from 0.1 to 10 ppb (Seinfeld and Pandis, 2006). The dominant sources of ammonia include animal waste, synthetic fertilizers, and industrial emissions. Because ammonia is easily dissolved into water, the residence time of ammonia is about 10 days in the atmosphere (Seinfeld and Pandis, 2006).

In theory, the presence of NH$_3$ enhances the nucleation rate because NH$_3$ stabilizes the critical cluster by releasing extra free energy (Kulmala et al., 2000). The predicted nucleation rate in ternary nucleation theory is higher than in binary nucleation by several orders of magnitude (Korhonen et al., 1999). However, laboratory studies have only shown nucleation rate to increase by a few orders of magnitude increase in the presence of ammonia (Ball et al., 1999; Fangqun Yu, 2006; Benson et al., 2009). For example, Ball et al. (1999) and Benson et al. (2009) showed that the nucleation rate in a ternary system was increased by approximately one of magnitude as compared to binary nucleation, which was lower than the theoretical prediction.

Moreover, the concentration of sulphuric acid required to achieve ambient concentrations of ultrafine particles are lower than that required in a binary system (Kulmala et al., 2000). However, Benson et al. (2011) showed that the threshold concentration of sulphuric acid for a nucleation rate of 1 cm$^3$s$^{-1}$ was consistent both in binary and ternary nucleation systems although the nucleation rate was higher in ternary systems. This indicates that the nucleation process is still governed by sulphuric acid, and ammonia seems
to increase the nucleation rate although the enhancement was weaker at a low level of sulphuric acid.

It was also believed that in ternary nucleation systems the number of sulphuric acid molecules in the critical cluster should be close to 1 or 2, which is drawn from atmospheric observation. However, none of the laboratories studies have succeeded in reproducing this observed number of sulphuric acid molecules in the cluster (Benson et al., 2009; 2011). Benson et al. (2009) reported that the estimated number of sulphuric acid in the cluster was about 6~8, which is still greater than that observed in the atmosphere. Therefore, the addition of ammonia into the binary nucleation system does not fully resolve the discrepancy between the atmospheric observation and the laboratory studies although the nucleation rate is enhanced.

2.4.3. Organic Compounds

Organic compounds have also been proposed to explain the observed formation and growth rate which cannot be clarified by binary homogenous nucleation alone. Organic species including amines are reviewed here.

2.4.3.1. Amines

Recently, the contribution of amines to particle nucleation and growth has received increased attention as they have been found in nanoparticles in the atmosphere (Smith et al., 2008). Wang et al. (2010) also reported that organics enhanced the growth of nanoparticles by creating non-volatile oligomers and polymers, and alkylaminium sulphates.

Being organic offshoots of ammonia, amines are basic compounds containing a
nitrogen atom with a lone pair of electron (McMurry, 2008). Amines can be directly emitted into the atmosphere by a variety of natural and anthropogenic sources. Natural sources include ocean, biomass burning, and vegetation while anthropogenic sources comprise animal husbandry, combustion, and vehicle exhaust (Ge et al., 2011). Since animal husbandry is the largest source of amines, the concentrations of amines are highest near regions with a high density of livestock (Berhein et al., 2011). Global amine emissions are approximately two orders of magnitude smaller than that of ammonia (Ge et al., 2011).

Amines have been found in nanoparticles during nucleation events in the atmosphere (Smith et al., 2008 and 2010). Smith et al. (2008) directly measured the chemical composition of particles between 10 and 33 nm formed by atmospheric nucleation using a Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS), and found that about 40 percent of major ions detected were amines. It was also found that aminium ions are the major constituents of smaller particles sized from 8 to 10 nm that are observed at other locations including urban site in Atlanta and boreal forest in Hytyiälä, Finland (Smith et al., 2010), indicating that amines play an important role in growth process of newly formed particles.

It is generally understood that amines can react with organic or inorganic acids to form salts, resulting in producing extremely low volatility compounds within particles. However, it is unclear whether the formation of organic salt can entirely explain the growth by organic compounds as organics salt formation only accounted for 23% and 47% of measured growth rate in Hytyiälä and Tecamac, respectively (Smith et al., 2010). Therefore, further investigation is required to comprehend how organics apportion to particles.

Recently, laboratory experiments investigating the effect of trimethylamine (TMA) on binary nucleation of sulphuric acid and water have been conducted by Erupe et al. (2011).
The effects of TMA were very similar to that of ammonia; the threshold sulphuric acid concentration was \(~10^6\) to \(10^7\) cm\(^{-3}\) and the number of sulphuric acid molecules in the cluster was estimated to be 4-6, which was consistent with a parallel experiment for ammonia (Erupe et al., 2011). However, the enhancement of nucleation rate due to TMA was increased with decreasing RH while the effect of ammonia on nucleation rate was unrelated to RH, meaning that TMA may have a greater impact on increasing nucleation rate than ammonia under dry atmospheric conditions (Erupe et al., 2011). These laboratory studies and atmospheric observations have suggested that the role of amines should be included in atmospheric nucleation studies.

2.4.3.2. Other Organic Compounds

Organic species have been proposed to account for atmospheric nucleation and growth processes (Bonn et al., 2002; 2003; Zhang et al., 2004; Metzger et al., 2010). Bonn et al. (2003) suggested that products from ozonolysis of biogenic volatile organic compounds (VOCs) make contributions to particle formation and growth. For instance, the sesquiterpene emitted by vegetation reacts with ozone forming a primary ozonide, and the primary ozonide instantaneously decomposes to the Criegee Intermediate (CI), which is further stabilized (sCI) by colliding with unreactive air molecules, such as nitrogen (Bonn et al., 2008). The sCI is able to react with most trace gases in the atmosphere, such as water, carbon monoxide, carbonyl compounds, and sulphuric acid. While the reaction with either carbonyl compounds or sulphuric acid results in new particle formation, the reaction with water vapour does not lead to nucleation (Bonn et al., 2008). The latter reaction is prevalent due to abundant amount of water vapour in the atmosphere. This mechanism elucidated the anti-correlation of new particle formation with increasing RH (Boy and Kulmala, 2002).
Furthermore, Zhang et al. (2004) showed that the nucleation rate could be enhanced in the presence of organic acids, such as benzoic, \( p \)-toluic, and \( m \)-toluic acids. The nucleation rate was increased by a factor of 5-13 depending on the concentration of such acids ranging from 0.1 to 0.3 ppb. This implies that the nucleation rate in urban areas can be greater than that in rural areas since these organic acids are produced from photochemical reaction of aromatic hydrocarbons emitted by automobiles.
3. Theoretical Principles

This section provides a theoretical background of aerosol nucleation processes. The classical nucleation theory based on an equilibrium approach is presented.

3.1. Classical Nucleation Theory

Although a number of theories have been proposed to explain atmospheric nucleation processes, the classical nucleation theory, introduced about 80 years ago, still forms the basis of the thermodynamic fundamentals of these processes. It should be noted that the classical nucleation theory considers homo-molecular case, which assumes that only one chemical species is involved in the nucleation for simplicity.

The classical nucleation theory describes the change of Gibbs free energy that accompanies the transition of gas-phase molecules to a bulk-phase of liquid or solid. This theory begins by considering a substance, A, in gas phase with a vapour pressure of \( p_A \) in a system. The homogeneous nucleation takes place when the substance is supersaturated, where the saturation ratio of \( S \),

\[
S = \frac{p_A}{p_A^s}
\]

(1)
is larger than 1 (\( p_A^s \) is the saturation vapour pressure of substance A). The system is metastable under supersaturated conditions, and the gas molecules of A tend to go through a phase transition, leading to the formation of single drop of A with a radius of \( R_p \) if the vapour molecules do not encounter any surface to condense on to. This formation of a new drop of liquid or solid is spontaneous because the Gibbs free energy is decreased due to the lower chemical potential of the bulk liquid. The change of Gibbs free energy is expressed as
\[ \Delta G = G_{\text{droplet}} - G_{\text{vapour}} \]
\[ = n (g_l - g_v) + 4\pi R_p^2 \sigma \]

where \( n \) is the number of molecules in the droplet, \( g_l \) and \( g_v \) are the Gibbs free energy of the molecules in the liquid and vapour phase, respectively. The last term of the RHS of the equation relates the interface of the new droplet with a surface tension \( \sigma \). The surface tension is the energy needed to increase the area of a surface (Seinfeld and Pandis, 2006). Therefore, \( 4\pi R_p^2 \sigma \) is the amount of energy required to maintain the interface of the new droplet, and the free energy change associated with the surface tension is positive. The \( n \) can be expressed as

\[ n = \frac{4\pi R_p^3}{3 v_l} \]

where \( v_l \) is the volume of new droplet in liquid phase. Thus, the equation above can be written as

\[ \Delta G = \frac{4\pi R_p^3}{3 v_l} (g_l - g_v) + 4\pi R_p^2 \sigma \]

The variation in the Gibbs free energy per molecule in the liquid and vapour states \((g_l - g_v)\) should be assessed. The change of the Gibb free energy in the system with respect to temperature and pressure is expressed by (Seinfeld and Pandis, 2006)

\[ dG = -SdT + Vdp + \sum_{i=1}^{k} \mu_i dn_i \]

where \( S \) is the entropy of the system, \( T \) is the system temperature, \( V \) is the volume of the system, \( p \) is the system pressure, and \( \mu_i \) is chemical potential of species \( i \), and \( n_i \) is the number of moles of chemical species \( i \). Applying this equation at constant temperature and because there is no change in number of moles of \( i \) \((dn_i = 0)\), the equation can be written as \( dg = vdp \)
or

\[ g_l - g_v = (v_l - v_v) dp \]  

(7)

Since the volume of vapour is relatively much greater than that of liquid, the equation is further reduced to

\[ g_l - g_v = -v_v dp \]  

(8)

The vapour state is presumed to be ideal, so

\[ v_v = \frac{kT}{p} \]  

(9)

Substituting in and integrating,

\[ g_l - g_v = -kT \int_{\frac{\rho_A}{\rho_A^s}}^{\rho_A} \frac{1}{p} dp \]  

(10)

\[ = -kT \ln \frac{\rho_A}{\rho_A^s} \]  

(11)

Combining this with the equation (5), the following expression is obtained:

\[ \Delta G = -\frac{4}{3} \pi R_p^2 \frac{kT}{\nu_l} \ln S + 4\pi R_p^2 \sigma \]  

(12)

When the system is not supersaturated, both terms in the RHS of the equation are positive, and nucleation will not occur. However, when a vapour is supersaturated, there is a competition between the two terms depending on \( R_p \), since the first term will be negative while the last term will be positive. In the beginning of the nucleation process the surface tension term dominates over the first term, meaning that the increase in surface energy from the new droplet formed will be greater than the energy decrease by the phase transition of gas molecules to a condensed phase. Therefore, the droplet will evaporate off the molecules rather than growing by condensation since creating a new particle does not cause the Gibbs
free energy to decrease for small $R_p$. This situation implies that there is a nucleation barrier in regards to $R_p$ that inhibits nucleation of new droplets even if a vapour is supersaturated. Once a droplet reaches the critical radius, $R_p^*$, the first term in the RHS of the equation will govern, and further growth of the particle will lower the Gibbs free energy. Therefore, a thermodynamically stable droplet will be formed once a molecular cluster grows bigger than $R_p^*$. The variation of Gibbs free energy with the particle radius, $R_p$, is described below (Curtius, 2006).

![Diagram showing the change in Gibbs free energy with the cluster radius. $\Delta G$ is the nucleation barrier, and $R_p^*$ is the corresponding critical radius of the cluster (Curtius, 2006). (© Elsevier)](image)

Fig. 3. The change in Gibbs free energy with the cluster radius, $R_p$. $\Delta G$ is the nucleation barrier, and $R_p^*$ is the corresponding critical radius of the cluster (Curtius, 2006). (© Elsevier)

Although in most cases clusters will not overcome the nucleation barrier, there exists a statistical chance that a cluster will accumulate enough molecules and reach the critical radius, $R_p^*$, ending up surmounting the nucleation barrier.

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By differentiating the equation (12), the $R_p^*$ can be expressed as

$$R_p^* = \frac{2\sigma v_l}{kT \ln S}$$  \hspace{1cm} (13)

Substitution of this into the equation (12) gives the height of the free energy barrier as follows.

$$\Delta G^* = \frac{4\pi}{3} \sigma R_p^* \frac{2}{3}$$  \hspace{1cm} (14)

$$= \frac{16\pi v_l^2 \sigma^3}{3(kT \ln S)^2}$$  \hspace{1cm} (15)

It should be noted that both the critical radius and the nucleation barrier are related to the saturation ratio; a higher saturation ratio reduces both the size of critical droplet and the nucleation barrier. Therefore, the more supersaturated a vapour is, the greater the chance of nucleation.

The nucleation rate, $J$, is defined as a rate at which the number of clusters grow beyond the critical radius per time and is associated with the height of the nucleation barrier as

$$J = C \exp \left( \frac{-\Delta G^*}{kT} \right)$$  \hspace{1cm} (16)

where $C$ is the pre-exponential factor.

While classical nucleation theory provides plausible conceptual fundamentals to comprehend the nucleation process in the atmosphere, it is not entirely sufficient; there are discrepancy between the theory’s predictions and actual measurements (Curtius, 2006).

In the classical nucleation theory, the properties of a cluster, especially the density and surface tension, are assumed to be identical to the bulk phase of liquid and this is called the capillarity approximation (Seinfeld and Pandis, 2006). However, the properties of clusters
composed of only a few molecules significantly deviate from the bulk phase, and it is very challenging to quantify the properties of such clusters. Accordingly, a few modified theories, such as molecular theory and density functional theory, have been proposed to correct shortcomings of the classical theory while maintaining the essential perception of the nucleation process. Nevertheless, none of these modifications have succeeded in elucidating nucleation clearly, and various aspects of nucleation remain ambiguous.
4. Methodology

This section presents a description of the monitoring sites and instruments used for this study. Also, the criteria for the classification of nucleation and the calculation of formation and growth rates are discussed in detail.

4.1. Sampling Locations

The ambient air was sampled in downtown Toronto and rural Egbert. Included are descriptions of each of the sampling locations.

4.1.1. Toronto

Ambient air has been continuously sampled at the laboratory of Southern Ontario Centre for Atmospheric Aerosol Research (SOCAAR) since 2006. 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. Toronto is one of the largest cities in North America, with a population of approximately 5 million (Statistics Canada). The inlet is 15 m away from College Street, which experiences a traffic volume of 25,000 vehicles per day.

Trace gas concentrations were obtained from the Ontario Ministry of Environment downtown site, situated approximately 850 m northeast of the SOCAAR sampling site. This MoE (Ontario Ministry of Environment) site provided hourly averaged concentrations of sulphur dioxide (SO$_2$), nitric oxide (NO), nitrogen dioxide (NO$_2$), carbon monoxide (CO), ozone (O$_3$), and mass concentration of fine particulate matter (PM$_{2.5}$).

The meteorological data were obtained from Environment Canada at the Pearson International Airport located approximately 20 km west of the SOCAAR site. This EC
(Environment Canada) 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.

![Map of SOCAAR, Ontario Ministry of Environment (MoE) gas monitoring site, and Environment Canada (EC) meteorological site.](image)

**Fig. 4.** Map showing the locations of SOCAAR sampling site, the Ontario Ministry of Environment (MoE) gas monitoring site, and the Environment Canada (EC) meteorological site.

### 4.1.2. Egbert

Egbert is the rural-background site of the rural/urban pair, and the Egbert data were obtained from the Environment Canada’s Centre for Atmospheric Research and Experiment (CARE). This site provided size distribution data as well as meteorological and traces gas concentration data. CARE is located at Egbert, Ontario, Canada (44.23 °N, 79.78 °W), approximately 70 km north of Toronto, and surrounded by mixed forest and farmland. The nearest road to the sampling, located 75 m away, experiences only a few vehicles per hour. While the sampling location in Toronto is heavily influenced by anthropogenic emissions,
such as vehicle exhaust, Egbert experiences minimal local emissions. However, both locations can be impacted by urban outflow of industrialized regions in Southwestern Ontario and mid-western United States when influenced by southerly winds.

![Map of Toronto and Egbert](image)

**Fig. 5.** Map of Toronto and Egbert (red stars), and the surrounding area. Major cities are marked with blue circles, and coal-fired power plants are shown with black diamonds.

### 4.2. Instrumentation

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) in Toronto, and with a long DMA (TSI 3081, St. Paul, MN) and Condensation Particle Counter (CPC, TSI 3025, St. Paul, MN) in Egbert. While the SMPS with a long DMA used at Egbert detected particles varying from 10 to 400 nm every 15 minute, the other
SMPS with a nano-DMA for Toronto measured particles between 3 and 100 nm every 2 minute.

In Toronto, 6 to 560 nm particles were also measured by a TSI 3091 Fast Mobility Particle Sizer (FMPS), which provided size distributions every second. The FMPS data were used when the SMPS data were not available for Toronto. Owing to distortions in detecting particles from 8 to 100 nm by the FMPS, measured particles in that range were corrected as suggested by Jeong and Evans (2009). Also, the size distributions of particles bigger than 100 nm measured by FMPS were corrected based on polystyrene latex (PSL) calibration particles and a comparison with the SMPS used for Toronto. The SMPS and FMPS data were well correlated after the FMPS data were corrected (Jeong and Evans, 2009). The operating principles of particle sizers used in this study are detailed in Table 1.
<table>
<thead>
<tr>
<th>Location</th>
<th>Data</th>
<th>Sampling site</th>
<th>Instrument</th>
<th>Size range</th>
<th>Time resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toronto</td>
<td>Size distribution and Particle number</td>
<td>SOCAAR</td>
<td>SMPS</td>
<td>3-100 nm</td>
<td>2 minute</td>
</tr>
<tr>
<td></td>
<td>Meteorological Data (T, RH, WS, WD)</td>
<td></td>
<td>FMPS</td>
<td>6-560 nm</td>
<td>1 second</td>
</tr>
<tr>
<td></td>
<td>Solar radiation</td>
<td></td>
<td></td>
<td></td>
<td>1 hour</td>
</tr>
<tr>
<td>Teckton</td>
<td>Trace gas concentrations (NO, NO₂, CO, O₃, PM₂.₅, SO₂)</td>
<td>Ontario</td>
<td></td>
<td></td>
<td>1 hour</td>
</tr>
<tr>
<td>Egbert</td>
<td>Size distribution and Particle number</td>
<td>EC: CARE</td>
<td>SMPS</td>
<td>10-400 nm</td>
<td>15 minute</td>
</tr>
<tr>
<td></td>
<td>Meteorological Data (T, RH, WS, WD, Solar radiation)</td>
<td>EC: CARE</td>
<td></td>
<td></td>
<td>1 hour</td>
</tr>
<tr>
<td></td>
<td>Trace gas concentrations (NO, NO₂, CO, O₃, PM₂.₅, SO₂)</td>
<td>EC: CARE</td>
<td></td>
<td></td>
<td>1 hour</td>
</tr>
</tbody>
</table>

**4.2.1. Scanning Mobility Particle Sizer (SMPS)**

A SMPS consists of an Electrostatic Classifier, a DMA, and a CPC. The aerosol first enters the impactor mounted on the outside of the Electrostatic Classifier. The impactor is composed of a nozzle that accelerates the aerosol flow and a plate that forms a perpendicular bend to the flow. While the larger aerosols with high inertia fail to follow the streamline and impact on the plate, the smaller particles avoid a collision and exit the impactor. Thus, the impactor removes particles bigger than the instrument’s size range to prevent
contamination or clogging of the instrument.

The aerosols are then introduced into the Electrostatic Classifier which neutralizes the poly-dispersed particles by exposing them to highly concentrated bipolar ions. The neutralized aerosols flow into the DMA that contains two concentric metal cylinders. The inner cylinder is maintained at a negative voltage while the outer is electrically grounded, and an electric field is generated between the two cylinders. Depending on the particle’s electrical mobility, the positively charged particles impact along the wall of the inner cylinder. The smaller particles with high electrical mobility impact on the upper part of the collector rod while the larger particles with low electrical mobility impact along the lower part of the rod. The particles that fall in the narrow range of electrical mobility of interest will exit through a small slit located at the bottom of the collector rod. The remaining particles are removed from the DMA through the excess air flow.

Fig. 6. Schematic of the DMA (Chen et al., 1998) (© Elsevier)\(^4\)

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The size-aggregated particles collected are transferred to the CPC to determine their concentration. The CPC first grows the mono-dispersed particles through condensation of a working fluid on the particles. Once the particles are grown to a detectable size, they can be counted by a laser and optical detector that senses the light scattered by the particles.

![Diagram of the UWCPC](image)

**Fig. 7. Schematic of the UWCPC (Hering et al., 2005) (©Taylor and Francis)**

### 4.2.2. Fast Mobility Particle Sizer (FMPS)

While the working principle of FMPS is similar to that of SMPS, the FMPS exhibits a faster time resolution (1 second) than the SMPS (minimum 30 seconds). The description of the FMPS will be discussed in this section.

The FMPS begins operating by first removing the particles larger than the detection limit. The neutralization of aerosols is done by two unipolar diffusion chargers, rather than the bipolar charger within a SMPS. The charged particles then are fed into the sizing region, fashioned by the space between the two concentric cylinders. Unlike the DMA in the SMPS

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which impacts the positively-charged particles along the inner negatively-charged cylinder, the inner rod in the FMPS is connected to a positive voltage repelling the positively-charged particles to the outer cylinder equipped with a stack of sensing electrodes. The sensing electrodes are able to detect the particle size and concentrations instantaneously, and hence the separated CPC is not included in the FMPS. This significantly improves the time resolution. The particles moving toward the outer cylinder transmit their charge to the sensing electrodes, and the transferred current is amplified by the electrometers and interpreted in real time to obtain a particle size distribution every second.

4.3. Event Classification Criteria

It is essential to classify nucleation and growth events in order to study nucleation and the atmospheric settings that initiate nucleation. All days of the sampling period were categorized into a few classes based on the type of nucleation and growth events observed on a given day.

A number of criteria have been employed for the classification of nucleation events at many other locations. For example, particle formation events in the boreal forest in Finland have been categorized using criteria suggested by Dal Maso et al. (2005). This method is based on the distinct appearance of nucleation mode particles followed by a subsequent growth over several hours. This method is more applicable to areas where new particle formation is observed on a regional scale.

Particle formation events in Southern Ontario, including Toronto and Egbert, have previously been classified using the criteria suggested by Jeong et al. (2010a). These criteria are based on temporal variations in the number concentration of particles between 10
and 25 nm, which provides an objective approach to categorize nucleation events. This number concentration-based method formed the basis for the particle formation event criteria applied in this study. In addition, since the contour plots of size distribution provide a detailed picture of particle evolution, they were also reviewed to make sure that nucleation increased the number of particles. There exist a number of other sources that could increase the particle number, and the influences of such sources could be identified by examining the contour plots.

Nucleation events in Toronto and Egbert were classified based on their strength and persistence as suggested by Jeong et al. (2010a). Any day showing a continuous increase in concentration of particles sized between 10 and 25 nm for more than an hour between 8:00 to 16:00 was identified as a particle formation event (Jeong et al. 2010a). Any formation event that occurred either before 8:00 or after 16:00 was excluded.

A formation event was classified as Class I if it showed a distinct appearance of nucleation mode particles for more than 2 hours followed by a subsequent increase of Geometric Mean Diameter (GMD). Class I events represented strong and potentially regional-scale nucleation events. These types of events have been observed at other sites (Stanier et al., 2004; Dal Maso et al., 2005; Qian et al., 2007).
Fig. 8. Typical variations of the particle number concentrations (cm$^{-3}$), geometric mean diameter (nm), and SO$_2$ concentrations (ppb) during a Class I event day.

If an event was closely associated with an abrupt increase of SO$_2$ concentration and no subsequent growth of newly formed particles, it was considered to be a Class II event. Class II events usually show a rapid increase in number particle concentrations over a short period of time, and are frequently observed near industrial plumes since these events are correlated with a local-scale nucleation occurring in a plume (Jeong et al., 2010a).
Fig. 9. Typical trends of particle number concentrations (cm$^{-3}$), geometric mean diameter (nm), and SO$_2$ concentrations (ppb) during a Class II event.

It was not possible to classify certain days into either of the classes described above due to their unclear appearance. Any day that could not be clearly resolved based on the available weak evidence was classified as “unclear” (Class U). For example, if a day showed either a sporadic occurrence of particle formation or later phase of particle growth bigger than 25 nm without the presence of newly formed small particles, it was categorized as Class U. Further, any increase of particle number concentration that failed to exceed a maximum concentration of 3,000 cm$^{-3}$ was not classified as a nucleation event, even if it showed other indications of particle formation, since this concentration is too low as compared to typical nucleation events. A few events in Egbert were not included in Class I due to this reason. Days showing no evidence of particle formation events were grouped into Class N (Non-event days).
4.4. Formation Rate, Growth Rate, and Condensation Sink

In this section, the methods for calculation of formation and growth rates, and condensation sink are described.

4.4.1. Formation and Growth Rate.

Nucleation events can be characterized by the formation rate and the growth rate. These two parameters indicate the extent of influence of nucleation on the aerosol population. The formation rate signifies how many particles are formed per given time during the event and depends on the participating chemical species and surrounding atmospheric conditions. This is one of the most important parameters that should be included in climate-prediction modeling (Paasonen et al., 2010). Moreover, freshly formed particles grow to larger mode particles by condensation. The growth rate shows how rapidly the new particles will grow to Aitken or accumulation mode particles. Therefore, the growth rate also is a crucial parameter because the larger mode particles are very likely to participate in cloud formation processes (Mönks et al., 2009).

A variety of methods have been developed to calculate these formation and growth rate, from the measured size distribution data (Lehtinen and Kulmala, 2003; Dal Maso et al., 2005). Formation and growth rates of nucleation events observed in Southern Ontario have been previously determined using the approach suggested by Jeong et al. (2010a). Since this method copes well with the data obtained from both urban and rural sites, it was applied in this study.

Formation rate was calculated using the minimum and maximum number concentrations of 10 and 25 nm particles during the nucleation period. Thus, the formation rate was estimated by
where $N_{\text{max}}$ and $N_{\text{min}}$ are the minimum and maximum number concentrations of particles between 10 and 25 nm during the event, and $t_2$ and $t_1$ are the corresponding times for the maximum and minimum number concentrations, respectively.

The observed growth rate was estimated by utilizing the temporal evolution in the Geometric Mean Diameter (GMD) of each size distribution and fitting it over the period of time that demonstrated a linear increase of GMD. The GMD is calculated by (TSI, 2005)

$$\ln(d_g) = \frac{\sum_{i=m}^{n} \Delta N_i \ln(d_i)}{N}$$

where $d_g$ is the GMD, $d_i$ is the midpoint diameter of size channel $i$, $N$ is the total number concentration, $\Delta N_i$ is the concentration within the channel $i$, $m$ is the first channel, and $n$ is the last channel.

### 4.4.2. Condensation Sink

A condensation sink is a parameter that quantifies the ability of the size distribution to scavenge condensable vapour in the atmosphere. The higher the condensation sink, the more rapidly condensable vapour will condense onto pre-existing particles. The condensation sink (CS) is calculated by integrating over size distribution:

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

$$= 2\pi D \sum_i D_p i \beta_{M_i} N_i$$
where $D$ is the diffusion coefficient of condensing vapour, $\beta_M$ is the transitional regime correction factor, $D_{pi}$ is the particle diameter of size channel $i$, and $N_i$ is the particle number concentration in size channel $i$ (Kulmala et al., 2001). The transitional correction factor can be estimated by (Fuchs and Sutugin, 1971)

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

$$= \frac{Kn + 1}{1.33 Kn^2 + 1.71 Kn + 1}$$

where $Kn$ is the Knudsen number, and $\alpha$ is the sticking coefficient which is usually assumed to be unity. The Knudsen number is

$$Kn = \frac{2\lambda}{D_p}$$

where $\lambda$ is the mean free path of the gas molecules under standard conditions. Practically, the property of the condensing vapour is assumed to be very similar to sulphuric acid, which is believed to have a very low vapour pressure at the surface of pre-existing particles.
5. Results and Discussion.

This section will present a comprehensive comparison of particle formation and growth events in Toronto and Egbert.

5.1. Identification of New Particle Formation

This section focuses on occurrence of nucleation and growth events at each site. Spatial and temporal variations of nucleation events are presented.

5.1.1 Occurrence of New Particle Formation

The size particle distributions found from 368 days of data from each location were investigated to identify nucleation and growth events according to the criteria described in section 4. The number of days with missing data was 97 in Toronto, and 43 in Egbert. New particle formation was frequently observed at both locations, and Class I events dominated over Class II events at both locations. All nucleation events observed in Toronto were classified as Class I, and only one Class II event was observed in Egbert. Class II events are associated with local-scale nucleation occurring in plumes and have been frequently observed in other sites in Southern Ontario, such as Harrow, Ridgetown, and Bear Creek, which are about 30~50 km away from major power plants (Jeong et al., 2010a). However, Class II events were rarely observed in both Toronto and Egbert.

The onset time of Class I events were compiled and averaged with respect to seasons. Nucleation mostly occurred within an hour before noon at both locations, and the time for the onset of nucleation was similar at both sites. Class I events appeared to take place earlier in summer probably due to the increased hours of daylight.
Fig. 10. Seasonal average time for the onset of Class I events in Toronto (black) and Egbert (red).

A considerable difference in the frequency of new particle formation was observed between the two locations. The frequency of nucleation events in Toronto was significantly lower than in Egbert. While 58 days were classified as Class I in Toronto, 121 days were categorized as Class I in Egbert (Table 2). Also, the ratio of event days to non-event days in Toronto was 0.30, whereas it was 0.65 in Egbert. This suggests that particle formation events take place much more frequently in rural sites as compared to urban sites. A lower frequency of nucleation in urban areas, as compared to rural areas, has also been reported in several studies. Vana et al. (2004) measured aerosol size distribution at three locations, and the frequency of nucleation bursts was lowest where the background number particle concentrations were highest. Moreover, clearer particle formation events were detected more frequently in clean rural areas than in urban areas in Finland (Hussein et al., 2008).
Table 2. The classification of nucleation events in Toronto and Egbert from May 14, 2007 to May 15, 2008.

<table>
<thead>
<tr>
<th></th>
<th>Toronto</th>
<th></th>
<th>Egbert</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>days</td>
<td>%</td>
<td>days</td>
<td>%</td>
</tr>
<tr>
<td>Event days</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Class I</td>
<td>58</td>
<td>16</td>
<td>121</td>
<td>33</td>
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<tr>
<td>Simultaneous events</td>
<td>34</td>
<td>9</td>
<td>34</td>
<td>9</td>
</tr>
<tr>
<td>Local events</td>
<td>24</td>
<td>7</td>
<td>87</td>
<td>24</td>
</tr>
<tr>
<td>Class II</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.3</td>
</tr>
<tr>
<td>Non-event days</td>
<td>196</td>
<td>53</td>
<td>186</td>
<td>51</td>
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<tr>
<td>Unclear days</td>
<td>17</td>
<td>5</td>
<td>17</td>
<td>5</td>
</tr>
<tr>
<td>Days with missing data</td>
<td>97</td>
<td>26</td>
<td>43</td>
<td>12</td>
</tr>
<tr>
<td>Total days</td>
<td>368</td>
<td>368</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Throughout the year, 34 days showed simultaneous nucleation events in Toronto and Egbert. The simultaneous events appeared to occur close to each other in time. For example, 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 percentage of simultaneous events out of total events was 59% in Toronto while simultaneous events accounted for 28% of all events in Egbert, consistent with the larger total number of nucleation events detected in Egbert. This suggests that nucleation events in urban areas may be suppressed, possibly by anthropogenic emissions. The suppression in Toronto might be associated with the role of pre-existing particles which scavenge condensable vapours contributing to particle formation and growth (Kulmala et al., 2001). The condensation sink, the parameter of loss of condensable sources onto pre-existing particles, seems to be one important underlying reason for the significant difference between the two sampling locations, and was, therefore, used to interpret a number of observations from this study. The influences of background aerosol on new particle formation are discussed in section 5.3.2.
The 34 simultaneous events suggest that nucleation events in Southern Ontario can span a large area. In fact, regional-scale nucleation has been reported in several studies (Tunved et al., 2005; Dal Maso et al., 2007; Hussein et al., 2009; Stanier et al., 2004; Vana et al., 2004; Wehner et al., 2007). Nilsson et al. (2001) found that nucleation occurred concurrently over a large area spanning 1,000 km sharing the same air mass. Moreover, Jeong et al. (2010a) observed a regional-scale nucleation event occurring simultaneously at five sites in Southern Ontario. The distance between the furthest sites, which was about 350 km, indicates that regional-scale nucleation event can occur over a large area in Southern Ontario (Jeong et al., 2010a). In this study, the air mass at both sites was found to be shared and have the same origin for 32 days of the 34 simultaneous nucleation events. Therefore, it appears that regional-scale nucleation in Southern Ontario generally involves a shared air mass.

5.1.2. Seasonal Trends of New Particle Formation in Toronto and Egbert

New particle formation at both sites exhibited a clear seasonal trend as shown in Fig. 11. Nucleation events peaked in spring and fall and occurred least frequently in winter. Although the summer suppression was not as clear for Toronto as for in Egbert, it is evident that the seasonal trend of particle formation in Toronto is similar to the trend in Egbert. In addition, events were observed to occur clustered for several days in a row rather than spread out. This clustering of events was observed throughout the year, and was more apparent in spring and fall.

The seasonal pattern, maximum in spring and fall and minimum in winter, has been found in other rural areas as well as urban locations (Dal Maso et al., 2005; Charron et al.,
Dal Maso et al. (2005) found that nucleation events in the Finnish boreal forest exhibited a clear seasonal pattern for eight years of measurement, and Hussein et al. (2008) also revealed a similar tendency at an urban site in Helsinki. These studies suggested that nucleation is positively associated with solar irradiance and possibly related to the onset of biogenic activity, especially in rural areas (Dal Maso et al., 2005). The further discussion of the impacts of meteorological parameters is provided in section 5.3.1.

![Graphs showing seasonal patterns of new particle formation in Toronto and Egbert](image)

**Fig. 11.** The seasonal patterns of new particle formation in Toronto (A) and Egbert (B) for May 2007 to May 2008. The nucleation events occurred most frequently in spring and fall and least frequently in winter at both locations. The graphs with n/a days excluded are provided in Appendix A.

Particle formation is positively correlated with solar intensity yet, the frequency of nucleation events was lower in summer than in spring and fall. This apparent contradiction requires additional explanation. Jeong et al. (2006) reported that this could be attributed to the varying intensity of the condensational sink with season. According to Pirjola (1999) and Birmili et al. (2000), rising temperatures as well as falling Relative Humidity (RH) increases the influence of condensation sink on particle formation. It is also possible that increased photochemistry due to stronger solar radiation in summer promotes particle growth thereby increasing the surface area of pre-existing particles (Qian et al., 2007). Therefore,
higher temperatures and greater background aerosol surface area in summer could limit the occurrence of nucleation by increasing the condensation sink.

5.2 Event Characteristics

This section focuses on analyzing characteristics of nucleation events in Toronto and Egbert. All identified nucleation and growth events were characterized by formation and growth rate based on the method described in section 3.1.2. The table 3 shows the average formation and growth rate during new particle formation at each site. In brief, both formation and growth rate appeared to be higher in Toronto than in Egbert.

Table 3. The averaged formation and growth rate of all events in Toronto and Egbert with the 95% confidence intervals.

<table>
<thead>
<tr>
<th></th>
<th>Formation rate (cm$^3$s$^{-1}$)</th>
<th>Growth rate (nm hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>mean</td>
</tr>
<tr>
<td>Toronto</td>
<td>0.8</td>
<td>3.9 ± 0.7</td>
</tr>
<tr>
<td>Egbert</td>
<td>0.2</td>
<td>1.7 ± 0.2</td>
</tr>
</tbody>
</table>

5.2.1 Formation Rate

The formation rates obtained from two locations showed a significant variation (p<0.05). In Toronto, the formation rate varied from 0.8 to 11.2 with a mean of 3.9 cm$^3$s$^{-1}$, whereas the formation rate in Egbert ranged from 0.2 to 6.0 with a mean of 1.7 cm$^3$s$^{-1}$. The formation rate in Toronto was higher than in Egbert by a factor of 2.
The greater formation rate in urban sites have been reported in several studies (Kulmala et al., 2004; Salma et al., 2011; Hussein et al., 2008; Mönkkönen et al., 2005; Qian et al., 2007). Salma et al. (2011) found that the formation rate in urban Budapest ranged from 1.65 to 12.5 cm$^{-3}$s$^{-1}$ which is comparable to those measured in Toronto, and Mönkkönen et al. (2005) reported a higher formation rate varying from 3.3 to 13.9 cm$^{-3}$s$^{-1}$ in New Delhi. Furthermore, Hussein et al. (2008) stated that the formation rate measured in urban Helsinki appeared higher than the formation rate measured in rural Hyytiälä by more than a factor of 2.

![Graph showing comparison of formation rates between Toronto and Egbert and other urban and rural sites.](image)

**Fig. 12.** Comparison of formation rates between Toronto and Egbert and other urban and rural sites. The left three locations (coloured by grey) are urban, whereas the right three locations (coloured by green) are rural sites.

The mean formation rates measured in Toronto and Egbert were compared with other studies as illustrated in Fig.12. Studies with sampling periods of more than a year were selected for comparison. It should be noted that different size ranges were used to calculate the formation rates for different studies. For instance, Salma et al. (2011) used the particles
sized from 6 to 25 nm while Dal Maso et al. (2005) selected the particles between 3 and 25 nm. Therefore, some of the differences between the locations could be due to using different size ranges.

The higher formation rate in urban air could result from a number of factors. Hussein et al. (2008) argued that the formation rate estimated in metropolitan areas includes not only production of particles by regional nucleation but also other production of particles from sources, such as local traffic or industrial plumes.

Kulmala et al. (2004) suggested that even though pre-existing particles are thought to decrease the concentrations of condensable molecules, the concentrations of background aerosol might be positively associated with the formation rate if the condensable gases and pre-existing particles originate from the same sources, as possibly could be true in plumes. This means that a higher concentration of condensable vapours could coincide with a high concentration of pre-existing particles.

In addition, Zhang et al. (2004) reported that the formation rate was enhanced in the presence of organic acids, such as benzoic and toluic acids. These acids are products of photochemical disintegration of aromatic hydrocarbons from vehicular emissions. Therefore, organic compounds emitted in the urban atmosphere could enhance the formation rate.

5.2.2 Growth Rate

The growth rates calculated from size distribution data measured in Toronto were higher than the rates from data obtained in Egbert (p<0.05). The mean growth rate in Toronto was 4.8 nm/hr, with a minimum and a maximum of 1.2 and 11.2 nm/hr, respectively. The growth
rates measured in Egbert showed a mean of 3.5 nmhr\(^{-1}\), ranging from 0.5 to 10.5 nmhr\(^{-1}\).

![Graph comparing growth rates between different locations]

**Fig. 13.** Comparison of growth rates between Toronto and Egbert and other urban (Budapest and Helsinki) and rural sites (Hyytiälä and Hohenpeissenberg).

Higher growth rate coupled with higher formation rate in urban atmospheres is a typical phenomenon that has been observed at a number of other urban measurement sites (Kulmala et al., 2004; Salma et al., 2011; Qian et al., 2007; Hussein et al., 2008; Mönkkönen et al., 2005; Kulmala et al., 2005; Jeong et al., 2006). Hussein et al. (2008) compared the growth rate for simultaneous events observed in urban Helsinki and the rural boreal forest in Hyytiälä. The growth rate was higher in Helsinki ranging from 2.25 to 4.42 nmhr\(^{-1}\) than at the rural site where the growth rate varied from 1.67 to 3.62 nmhr\(^{-1}\). Moreover, the growth rate can be much higher in highly polluted cities. For example, Dunn et al. (2004) reported growth rates ranging from 0.5 to 9.0 nmhr\(^{-1}\) for Mexico City, and Mönkkönen et al. (2005) reported growth rates varying from 11.6 to 18.1 nmhr\(^{-1}\) in New Delhi.
Greater growth rate in urban sites could result from a number of factors. Hussein et al. (2008) stated that high concentrations of ultrafine particles in urban sites could participate in growth by coagulation, which leads to a higher growth rate than in rural areas. Furthermore, Kulmala et al. (2005) suggested that the contribution of sulphuric acid to particle growth is considerably larger in urban areas than in clean locations. For instance, Boy et al. (2005) estimated that sulphuric acid accounted for 3 to 17% of particle growth, whereas Stanier et al. (2004) reported that ground level sulphuric acid concentration was responsible for almost 100% of particle growth in an urban city.

However, growth rate is often much higher than can be explained only by the contribution of sulphuric acid alone; other species are required to account for observed growth rate. Smith et al. (2008) found that nucleated particles of 10-33 nm in size were composed mostly of organics, nitrate and sulphur species in Tecamac, Mexico. The organics included oxidized organics and nitrogen-containing organics. Therefore, low-volatile condensable organic vapours emitted by traffic or industrial plumes could make a significant contribution to particle growth in an urban area, possibly including Toronto.

In fact, the participation of organics in growth is not limited to urban sites. Weber et al. (1997) estimated the growth rate at a remote continental area and concluded that species other than sulphuric acid accounted for a significant portion of the observed growth rate. Birmili et al. (2003) also found that the condensation of $\text{H}_2\text{SO}_4$, $\text{H}_2\text{O}$, and $\text{NH}_3$ can explain only about 50% of the observed growth rate. The contribution of biogenic organics to particle growth has been observed in the boreal forest in Finland (Kulmala et al., 2004; Dal Maso et al., 2005; Riipinen, 2008). The growth rate peaks in summer, and this is in line with the maximum emissions of biogenic organic vapours in the forest (Riipinen, 2008). One interesting point regarding particle growth is that observed growth rate depends on the
particle size (Kulmala et al., 2004; Hirsikko et al., 2005; Manninen et al., 2010). Although in theory, the growth rate should be higher for smaller particles (Seinfeld and Pandis, 2006), the measured growth rate was higher for larger particles (Riipinen, 2008). Hirsikko et al. (2005) measured the growth rate from three different particle size classes including 1.3 – 3, 3 – 7, and 7 – 20 nm, and the growth rate of the 7-20 nm particles was highest. Further the 7-20 nm particles showed a clear seasonal pattern of maximum in summer. In contrast, the growth rate of 1.3 – 3 nm particles did not show any seasonal trend. This implies that biogenic organics may preferentially contribute to particle growth of larger particles in summer.

5.2.3 Seasonal Trends of Formation and Growth Rate

The seasonal trends of growth rate as well as formation rate have been reported at both urban and rural locations (Kulmala et al., 2004; Qian et al., 2007; Salma et al., 2011). Formation rate often corresponds to the frequency of particle formation; it peaks in spring and fall (Dal Maso et al., 2005; Hussein et al., 2008; Salma et al., 2011). On the other hand, growth rate usually shows a maximum in summer at both rural and urban sites (Kulmala et al., 2004; Vehkamäki et al., 2004; Dal Maso et al., 2005 and 2007; Qian et al., 2007; Hussein et al., 2008; Salma et al., 2011). This suggests that higher concentrations of condensable vapours due to increased photochemistry as well as greater emission of biogenic organics make a considerable contribution to particle growth in summer (Salma et al., 2011). The different seasonality of formation rate and growth rate might indicate that different chemical compounds are responsible for each process. This also supports the poor correlation between formation and growth rate found in this study, which will be discussed in section 5.2.4.
Nevertheless, the formation and growth rates in Toronto and Egbert did not show any seasonal pattern. This could be due to a shortage of data; one year of data may not be sufficient to reveal seasonal trends. Dal Maso et al. (2005) and Hussein et al. (2008) found seasonal trends based on 8 years and 9.5 years of measurement, respectively. Hence, the estimation of formation and growth rates over a longer period may help to resolve any seasonal trends in Toronto and Egbert.

5.2.4 Regression Analysis of Formation and Growth Rate

Regression analysis was employed to further discern any relationship between formation and growth rate. Formation of particles sized from 10 to 25 nm and growth of particles between 10 to 80 nm in size were regressed at both locations as depicted in Figure 14. A strong association would suggest that nucleation and growth were linked to the same pre-cursor compounds (Kulmala et al., 2004, Sipila et al., 2010). The correlation between the formation and growth rates was statistically significant in Egbert (p<0.05) and almost significant in Toronto (p=0.06). However, the formation rate showed a weak correlation with the growth rate at both locations (r < 0.35). Further, $r^2$ value ranged from 0.08 to 0.10, meaning that only 8–10% of variation in the growth rate could be explained by the variation of the formation rate. Therefore, different chemical compounds might be contributing to nucleation and growth, producing this weak association. In addition, the positive y-intercept values may indicate the presence of compounds that are contributing to growth but not formation.
The linear regression analysis showed a higher y-intercept in Toronto. The y-intercept for Toronto was 3.6 nmhr\(^{-1}\) while it was 2.6 nmhr\(^{-1}\) in Egbert. Also, minimum growth rate was greater in Toronto than in Egbert. The growth rate in urban sites may need to be higher than in rural sites to overcome the greater effects of coagulation by a higher load of pre-existing particles. Since the formation rate was measured for particles between 10 and 25 nm, newly formed particles needed to grow fast enough to avoid removal by pre-existing particles in order to reach the detectable size range of 10 and 25 nm. Thus the observed formation rate of 10-25 nm particles differs from the initial nucleation of new 1-2 nm particles, in that formation requires initial nucleation followed by growth. If new particles fail to grow to larger particles, the nucleation event will not be observed because all the newly-formed particles will be scavenged by coagulating onto pre-existing particles (Kerminen et al., 2001). This means that since the level of background aerosol is much higher in Toronto, a higher growth rate of new particles is essential to overcome the greater
rate of coagulation in this urban atmosphere. New particle formation followed by slow
growth, which fails to overcome the influences of coagulation, would not be observed in
Toronto. Therefore, in theory the formation rate should be related to the growth rate, even if
different compounds are contributing to nucleation and growth.

5.3 Underlying Causes

This section details underlying causes that influence new particle formation in Toronto and
Egbert. The influences of meteorological parameters, pre-existing particles, and air masses
are described. The nucleation parameter, a parameter predicting the probability of a
nucleation event will also be discussed.

5.3.1. Influences of Meteorological Parameters

Hourly meteorological data including solar radiation, temperature, relative humidity, wind
direction, wind speed, mass concentrations of PM$_{2.5}$, and SO$_2$ concentrations were compiled
for times between 8:00 and 16:00 for everyday and averaged. These daily averaged
parameters were grouped based on the occurrence of nucleation events (Table 4).

As illustrated in Table 4, solar radiation differed significantly between event days and
non-event days (p<0.05). The solar radiation for Class I days was approximately 73%
greater than Class N. This positive association of solar irradiance with new particle
formation has been previously reported (Harrison et al., 2000; Boy and Kulmala, 2002;
Birmili et al., 2003; Alam et al., 2003; Stanier et al., 2004; Vehkamäki et al., 2004; Jeong et
al., 2010a; Salma et al., 2011). Solar radiation induces the production of hydroxyl radicals
formed by photolysis of ozone, and the hydroxyl radicals are essential to producing less
volatile compounds that can contribute to aerosol nucleation or growth (Alam et al., 2003).
Therefore, the observed association of nucleation events with solar intensity was consistent with the theoretical understanding of the underlying role of photochemistry in new particle formation.

Table 4. Selected meteorological parameters with respect to classification of nucleation events at both locations. Observations between 8:00 and 16:00 were included.

<table>
<thead>
<tr>
<th>Location</th>
<th>Solar Radiation (W/m²)</th>
<th>Temperature (°C)</th>
<th>Relative Humidity (%)</th>
<th>Wind Speed (Km/hr)</th>
<th>SO₂ (ppb)</th>
<th>PM2.5 (μg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toronto</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Class I</td>
<td>487</td>
<td>16</td>
<td>52</td>
<td>17</td>
<td>2.6</td>
<td>6.1</td>
</tr>
<tr>
<td>Class N</td>
<td>281</td>
<td>9</td>
<td>67</td>
<td>17</td>
<td>2.2</td>
<td>8.0</td>
</tr>
<tr>
<td>Class U</td>
<td>504</td>
<td>14</td>
<td>56</td>
<td>17</td>
<td>1.5</td>
<td>5.9</td>
</tr>
<tr>
<td>na</td>
<td>363</td>
<td>12</td>
<td>64</td>
<td>18</td>
<td>1.8</td>
<td>8.8</td>
</tr>
<tr>
<td>Egbert</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Class I</td>
<td>485</td>
<td>11</td>
<td>60</td>
<td>12</td>
<td>1.6</td>
<td>7.8</td>
</tr>
<tr>
<td>Class N</td>
<td>281</td>
<td>8</td>
<td>76</td>
<td>14</td>
<td>1.4</td>
<td>7.3</td>
</tr>
<tr>
<td>Class U</td>
<td>452</td>
<td>10</td>
<td>60</td>
<td>13</td>
<td>1.0</td>
<td>4.4</td>
</tr>
<tr>
<td>na</td>
<td>395</td>
<td>11</td>
<td>71</td>
<td>14</td>
<td>1.3</td>
<td>6.7</td>
</tr>
</tbody>
</table>

The average temperature was higher on event days both in Toronto and Egbert (p<0.05). This was due to the positive correlation of temperature with solar radiation, but was only apparent in spring and fall. In contrast, the temperature on event days was lower than non-event days in summer and winter in both locations. Jeong et al. (2010a) compared the average temperature between event days and non-event days in Southern Ontario during summer, and the temperature was lower by 3-5°C for event days. The preference of nucleation for cooler temperature in summer could be related to air masses or to cooler temperatures promoting condensation and thereby growth. The influence of air mass is further discussed in section 5.3.3. In winter, the heavy and dense cold air was likely to suppress cloud formation, which introduced more solar radiation on colder days.

One unexpected result is the variation of mass concentration PM₂.₅ with respect to the
classification of nucleation and sampling locations. In Toronto, average PM$_{2.5}$ was lower on Class I than on Class N days (p=0.06), as anticipated because PM$_{2.5}$ should suppress nucleation owing to its role in removing condensable vapours by condensation. However, the mass concentration of PM$_{2.5}$ of Class I in Egbert was no different than for Class N events (p=0.5). Also, the average PM$_{2.5}$ mass concentration in Egbert over the whole period of study was 7.2 μg/m$^3$ while the corresponding PM$_{2.5}$ concentration of Toronto was 7.8 μg/m$^3$. The difference between two locations was insignificant (p=0.28), despite the higher level of urbanization in Toronto. This could in part be as a result of using PM$_{2.5}$ data from Barrie, a city 15 km northeast of Egbert with a population of 185,900 (Statistics Canada, 2007), due to the lack of PM$_{2.5}$ data from Egbert. More importantly, PM$_{2.5}$ in Ontario tends to be a regional pollutant with transportation from southwest regions accounting for a significant portion of the PM$_{2.5}$ mass concentration along the Windsor to Montreal corridor (Jeong et al., 2010b). Therefore, it is probable that this regional PM$_{2.5}$ would also affect Egbert. Further PM$_{2.5}$ is not a direct indicator of particle surface area, the parameter that actually governs condensation rate. Overall, PM$_{2.5}$ mass concentrations seem to play a minor role in differentiating the frequency of nucleation events between Toronto and Egbert.

The average Relative Humidity (RH) was significantly different between event days and non-event days (p<0.05). On average, the RH was approximately 28% higher on non-event days compared to event days in both locations, indicating that high RH might have inhibiting influences on new particle formation. The negative effects of RH have been studied (Weber et al., 1997; Birmili and Wiedensohler, 2000; Harrison et al., 2000; Bonn et al., 2002; Boy and Kulmala, 2002; Bonn and Moortgat, 2003; Vehkamäki et al., 2004; Jeong et al., 2006; Charron et al., 2007; Boy et al., 2008). A number of factors could result in the anti-correlation of RH with nucleation. Weber et al. (1997) proposed that aerosol surface
area could be increased by uptake of water vapour, which could inhibit new particle formation. Harrison et al. (2000) also explained that nucleation bursts often coincide with increased solar radiation, which also heats the lower atmosphere, thereby reducing RH. The lower RH could reduce the surface area of hygroscopic aerosols. However, the association with RH may just be as a result of lower RH being associated with higher temperatures or increased solar irradiation. Also, increased RH could reduce solar radiation by increasing scattering or contributing to cloud formation.

Alternatively, it has been proposed that new particle formation is initiated by Criegee Intermediates (CIs) produced by ozonolysis of biogenic organics, such as monoterpenes (Bonn et al., 2002) and sesquiterpenes (Bonn and Moortgat, 2003). The CIs can further react with either carbonyl compounds, which also originate from ozone reaction of organic molecules, or water vapour. While the reaction with carbonyl compounds results in producing secondary ozonides (SOZ) thought to effectively initiate nucleation, the majority of CIs are lost by reacting with water vapour due to a high concentration of water vapour in the atmosphere (Bonn and Moortgat, 2003). The CIs can also disintegrate into more volatile and less reactive products by reacting with water molecules (Boy et al., 2008). In summary, high RH was found to suppress new particle formation at both the urban and rural locations and multiple explanations remain as to the underlying reason.

The average SO$_2$ concentrations were slightly higher on event days than non-event days. However, the difference between the event and non-event days was not significant (p>0.3) even though SO$_2$ is often regarded as a pre-cursor gas, through its oxidation to produce sulphuric acid. Kulmala et al. (2000) proposed that nucleation is taking place almost everywhere in the atmosphere producing a reservoir of Thermodynamically Stable Clusters (TSCs), which are not detected as they are smaller than the detection limit of
available particle instruments (3 nm). These TSCs can grow to observable size ranges or even larger under certain circumstances. One condition is a low concentration of pre-existing particles. This would allow self-coagulation of TSCs to dominate over scavenging by other particles, leading TSCs to grow to a detectable size. Another condition is the presence of an adequate concentration of condensable vapours including organics, inorganic acids and ammonia, which condense on TSCs to allow growth into larger mode particles. Moreover, neutral clusters with diameter of less than 3 nm have been actually observed by recently developed instruments, such as Neutral clusters Air Ion Spectrometer (NAIS), and these clusters are concluded to be present at all times (Kulmala et al., 2007). Therefore, observation of nucleation is likely to be influenced by a number of factors, and a high concentration of SO$_2$ alone should not necessarily be directly indicative of new particle formation.

While no substantial difference in wind speed was observed between Class I and Class N events (p>0.5) in Toronto, significant difference was found in Egbert (p<0.05). In Egbert, the average wind speed was lower on event days than on non-event days by 14%. It is, however, unclear why wind speed should physically influence nucleation.

Also, no significant dependence on average of wind direction, in azimuth degree, was detected (p>0.5). However, these local wind direction measurements do not provide a good indication of the origin of air masses. Further analysis of wind direction regarding air masses suggested that nucleation events are associated with air mass origin in Southern Ontario. This is described in section 5.3.3.
5.3.2. Influences of Pre-existing Particles

This section discusses the influences of pre-existing particles on nucleation. The average condensation sink from Toronto was compared with that from Egbert. Selected characteristics of weekdays and weekends were compared within Toronto and Egbert. Also, temporal variation of the condensation sink was detailed to see its influences on nucleation.

5.3.2.1. Suppression of New Particle Formation in Toronto

As discussed in section 5.1, the frequency of nucleation events in Toronto was lower than in Egbert, and a number of nucleation events observed in Egbert were not detected in Toronto. A lower frequency of nucleation in urban sites has been attributed to a higher concentration of background aerosol, usually due by primary emissions, which leads to a greater surface area (Alam et al., 2003; Vana et al., 2004; Dal Maso et al., 2007; Stanier et al., 2004). The surface area of pre-existing aerosols affects the condensation sink, a parameter that determines how rapidly vapour will condense onto background particles (Pirjola et al., 1999). The occurrence of nucleation events in the atmosphere is often negatively correlated with condensation sink (Hyvönen et al., 2005).
As shown in figure 15, the average condensation sink in Toronto was greater than in Egbert by a factor of 3. This higher level of background aerosols in Toronto may have suppressed particle formation in Toronto by scavenging potential condensable sources. A comparison of weekdays and weekends, described below, also supported the role of suppression by background aerosol from anthropogenic emissions.

5.3.2.2. Comparison of Weekdays and Weekends

In order to investigate the contribution of local traffic, the 368 days of data were grouped into weekdays and weekends. The table below describes selected characteristics of weekdays and weekends.
Table 5. 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.

<table>
<thead>
<tr>
<th></th>
<th>Class I</th>
<th>Formation rate (cm$^{-1}$$s^{-1}$)</th>
<th>GR (nmhr$^{-1}$)</th>
<th>C.Sink (1e-3s$^{-1}$)</th>
<th>Solar Radiation (W/m$^2$)</th>
<th>Temperature ($°C$)</th>
<th>PM$_{2.5}$ (ug/m$^3$)</th>
<th>SO$_2$ (ppb)</th>
<th>RH (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toronto</td>
<td>Weekdays</td>
<td>0.26</td>
<td>4.1</td>
<td>4.9</td>
<td>10.3</td>
<td>342</td>
<td>11</td>
<td>8.4</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>Weekends</td>
<td>0.41</td>
<td>3.6</td>
<td>4.6</td>
<td>7.1</td>
<td>353</td>
<td>10</td>
<td>6.3</td>
<td>1.7</td>
</tr>
<tr>
<td>Egbert</td>
<td>Weekdays</td>
<td>0.67</td>
<td>1.7</td>
<td>3.7</td>
<td>3.2</td>
<td>364</td>
<td>10</td>
<td>7.8</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>Weekends</td>
<td>0.60</td>
<td>1.6</td>
<td>3.0</td>
<td>2.5</td>
<td>380</td>
<td>9</td>
<td>5.9</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The ratio of event days to non-event days in Toronto shows a substantial variation with respect to weekdays and weekends (0.26 vs. 0.41) while there was no difference at Egbert (0.67 vs. 0.60). This suggests that local anthropogenic emissions influenced nucleation in Toronto but not Egbert, given that anthropogenic emissions are higher in Toronto on weekdays than weekends in Toronto. As expected, the meteorological factors considered to have substantial influences on nucleation did not differ between weekdays from weekends at both locations. For example, solar irradiance, temperature, and RH were all consistent regardless of weekdays or weekends at Toronto and Egbert; meteorology should not be strongly influenced by greater anthropogenic emissions on weekdays. However, the condensation sink, the rate of loss of condensable vapours onto background aerosols, showed a significant difference between weekdays and weekends in Toronto (p<0.05). This implies that a lower frequency of new particle formation on weekdays in metropolitan sites is due to the higher condensation sink resulting from anthropogenic emissions. Further, the condensation sink showed temporal patterns that are consistent with traffic patterns. The average traffic count on College St. was about 20,000 during weekdays and about 16,000 during weekends. The ratio of this weekend/weekday traffic, 0.8, is slightly greater than the weekend/weekday ratio of 0.7 for the condensation sink in Toronto. Moreover, the
condensation sink showed a diurnal pattern similar to a traffic pattern during weekdays. The peak in the morning for weekdays is likely to be caused by vehicular emissions. Therefore, the condensation sink in Toronto is likely related to vehicle exhaust.

![Figure 16](image1.png)

**Fig. 16.** The temporal variation of traffic counts on College St. at the Toronto site with 95% confidence intervals.

![Figure 17](image2.png)

**Fig. 17.** The diurnal variation of condensation sink in Toronto with 95% confidence intervals. The diurnal trends for weekdays are similar to that of traffic counts (Fig 16), suggesting that vehicular emissions affect condensation sink.
5.3.3 Air Mass Influences

The air masses arriving daily at the locations were classified and compared to investigate the dependence of new particle formation on them. The classification of air masses was based on the back trajectories acquired by running the National Oceanic and Atmospheric Administration (NOAA) HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model. The archive trajectories were computed for 48 hours starting at 15:00 p.m. (UTC), at a height of 500 m above ground level (Draxler and Rolph, 2003).

Depending on the origin and the path of the winds, all days were categorized into North, South, East, West, and n/c (not classified). It should be noted that “North” included northwesterly, northerly, and northeasterly winds (i.e. 315° to 45°) because air masses from these directions are usually cleaner and cooler as they pass closer to the Arctic and encounter few sources of pollutants in transit. Thus, “North” represents cooler air masses that generally contain fewer pre-existing particles, other than during the occurrence of major forest fires. In contrast, air masses from the southwesterly, southerly, and southeasterly directions (135° to 225°) were grouped together as “South” since these masses often contain higher levels of pollutants, such as SO$_2$ or PM$_{2.5}$ due to the numerous coal-fired power plants situated near Detroit, Windsor, and Northern Ohio. Hence, “South” represents highly polluted air masses impacted by urbanized and industrial regions in Southwestern Ontario and mid-western United States. Figure 5 shows the locations of power plants and major cities near Toronto and Egbert. Days where the origin of the air mass was unclear, due to extreme detours, were classified as n/c. The table 6 describes selected characteristics of air masses landing in Toronto and Egbert.
Since Toronto and Egbert are only 80 km apart from one another, both locations appeared to be impacted by almost the identical air masses throughout the year, and northerly winds were dominant for both sites. It also appeared that both locations are rarely influenced by easterly winds mainly due to Prevailing Westerly in the middle latitude.

Northerly winds show the highest frequency of nucleation in Egbert and possibly Toronto; the significance of the elevated occurrence rate with easterly winds in Toronto was unclear due to the low number of associated days. The higher frequency of nucleation for northern air masses was attributed to clean and cold conditions favouring new particle formation. The positive correlation of northerly winds with nucleation has been reported in many locations (Nilsson et al., 2001; Dal Maso et al., 2007; Hussein et al., 2009). Jeong et al. (2010a) suggested that nucleation is likely to be caused by the arrival of northerly winds that contain few pre-existing particles. Also, the average temperature on event days was lower compared to non-event days, consistent with the association of nucleation with
northerly winds (Jeong et al., 2010a). Therefore, it is concluded that air masses from Northern Canada provide appropriate conditions that favour new particle formation in Southern Ontario.

In contrast, the PM$_{2.5}$ concentrations, SO$_2$ concentrations, and the condensation sink were higher, and the frequency of new particle formation dropped significantly during the days impacted by southerly and westerly winds. Therefore, it can be said that air masses containing regional-scale pollutants suppress nucleation events in Southern Ontario.

### 5.3.4 Nucleation Indicator

Since no existing theory can definitively predict the occurrence of nucleation events, it would be useful to establish a stochastic indicator that predicts whether a nucleation event is likely to take place on a given day by combining various parameters shown to be associated with new particle formation (Hamed et al., 2007). As discussed in section 5.3.1, solar irradiance showed a positive association with nucleation indicating an essential role of photochemistry in particle formation. Although SO$_2$ is the main pre-cursor to the production of sulphuric acid, hypothesized to be vital to new particle formation, only a weak association between SO$_2$ concentration and nucleation type I event days was found for these sites. Nevertheless, SO$_2$ concentrations were included in calculating a nucleation indicator since SO$_2$ was associated with type II events and SO$_2$ has been shown to produce a significant amount of sulphuric acid in the atmosphere in laboratory experiments (Berndt et al., 2005).

The condensation sink was found to clearly suppress nucleation in this study. Moreover, high RH exhibited a negative correlation with nucleation owing to either its reaction with the Cls, transforming them into more volatile compounds, or its contribution to
hygroscopic growth of pre-existing particles, which increases the condensation sink. A nucleation indicator was developed by taking these four parameters into account. This “Nucleation Indicator” was defined as:

\[
\text{NI (Nucleation Indicator)} = \frac{SO_2 \times SR}{CS \times RH}
\]

where \(SO_2\) is the sulphur dioxide concentrations (ppb), \(SR\) is the solar radiation (W/m\(^2\)), \(CS\) is the condensation sink (1/s), and \(RH\) is the relative humidity. These parameters were calculated over a particular time period that a nucleation event is taking place for event days. However, parameters from 8:00 a.m. to 4:00 p.m. were used in calculations for non-event days because nucleation is most likely to occur during that time period. The greater the NI is, the more likely that a nucleation event will be observed for a given day. The purpose of developing the NI was to find the threshold that separates nucleation event days from non-event days for both urban and rural sites.

Table 7. Descriptive statistics for the Nucleation Indicator (NI) of all event days and non-event days regardless of locations

<table>
<thead>
<tr>
<th></th>
<th>Mean</th>
<th>Geo.Mean</th>
<th>Median</th>
<th>Std.Dev</th>
<th>Min</th>
<th>Max</th>
<th>Lower Quartile</th>
<th>Upper Quartile</th>
<th>Percentile 10th</th>
<th>Percentile 90th</th>
</tr>
</thead>
<tbody>
<tr>
<td>Event</td>
<td>9268</td>
<td>5580</td>
<td>5685</td>
<td>13278</td>
<td>475</td>
<td>12767</td>
<td>3064</td>
<td>9650</td>
<td>1544</td>
<td>20353</td>
</tr>
<tr>
<td>Non-event</td>
<td>1779</td>
<td>806</td>
<td>918</td>
<td>5087</td>
<td>28</td>
<td>74554</td>
<td>381</td>
<td>1745</td>
<td>165</td>
<td>3075</td>
</tr>
</tbody>
</table>

The statistics for the nucleation indicator showed a significant difference between event days and non-event days (p<0.05). The geometric mean of the NI (Nucleation Indicator) for event days was 5580, whereas it was 806 for non-event days. Moreover, the lower and upper quartiles for event days were 3064 and 9659 respectively, while these quartiles were
381 and 1745 for non-event days, respectively. This indicates that the NI allows considerable distinction between event days and non-event days.

No threshold NI value that completely separates the event days from non-event days was found. Nevertheless, a reasonable probabilistic relationship was determined. If the NI is below 1500 we can predict with 90% confidence that there will be no nucleation event whereas if it is above 3000 we can be 90% confident that there will be an event. However, there is a risk of incorrect prediction for the intermediate the NI values as these 10th percentile values overlap, and 17.8% of the total days had NI values that fell in this overlapping region. Therefore, there is a risk of using the NI, but it provides a reasonable measure of the probability of an event occurring.

Fig. 18. The distribution of event and non-event days with respect to nucleation parameters. The SO2*SR on the y-axis is driving nucleation while CS*RH on the x-axis is inhibiting particle formation. Therefore, event days are located at the top-left side of the graph, whereas non-event days are placed at the bottom-right side of the graph.
A variety of factors have been previously used to create a nucleation parameter that separates event days from non-event days. Boy and Kulmala (2002) combined UV-A radiation flux, water number density and temperature while Stanier et al. (2004) included SO$_2$ concentration, solar radiation, and condensation sink. A simpler version of the nucleation parameter was tested by integrating condensation sink and relative humidity (Hyvönen et al., 2005). Nevertheless, none of these parameters has succeeded in completely separating event days and non-event days, and neither has the NI in this study. This could be due to the omission of a parameter that has a significant contribution to nucleation. One possible addition is a concentration of condensable organic compounds that accelerate particle growth, leading to growth overcoming coagulation loss to pre-existing particles (Hamed et al., 2007). Furthermore, Boy and Kulmala (2002) suggested a seasonal factor should be added to the nucleation parameter since the relative impact of each component in the nucleation parameter might vary with season. Therefore, the NI might be upgraded by incorporating these factors into the calculation.
6. Conclusion

The primary objective of this study was to compare nucleation and growth of atmospheric particles at paired urban and rural locations in order to understand the impacts of anthropogenic emissions on particle formation. The size and particle number distribution from May 2007-2008 measured in Toronto and Egbert were investigated to compare identification and characterization of events, and the underlying causes. The following conclusions resulted from this study.

1. Nucleation events were observed in Egbert more frequently than in Toronto; 33% of days were identified as nucleation event days in Egbert while 16% of days showed nucleation events in Toronto. This suppression in Toronto could be due to anthropogenic emissions which increase the uptake of condensable vapours onto pre-existing particles. Only 34 days (~10%) showed simultaneous nucleation events, and 32 of them shared the same air mass. This indicates that regional-scale nucleation involving a shared air mass occurs in Southern Ontario but more often events are localized even over a distance of 100 km.

2. The mean formation rate measured in Toronto was higher than that measured in Egbert by a factor of 2, and the mean growth rate measured in Toronto was also greater than in Egbert. These trends were comparable to other urban and rural locations, such as Helsinki and the boreal forest in Hyytiälä, Finland. Also, a regression analysis showed a weak but significant correlation (~R^2=0.1) between formation and growth rates, suggesting that different chemical species contribute to particle formation and growth.

3. Solar radiation and RH showed a clear difference between nucleation event days and
non-event days. The average solar radiation on event days was approximately 70% higher than that on non-event days, consistent with the theoretical understanding of the role of photochemistry in new particle formation. The RH showed a clear anti-correlation with nucleation, corresponding to the explanations that water vapour can increase the surface area of pre-existing aerosols or scavenge biogenic organic compounds contributing to formation and growth.

4. The calculated CS was higher in Toronto than in Egbert by a factor of 3, and the lower frequency of nucleation in Toronto could be partially attributed to this higher CS. This conclusion was further supported by the comparison of weekdays and weekends. The ratio of event days to non-event days in Toronto showed a substantial difference between weekdays and weekends (0.26 vs. 0.41) while no difference was shown in Egbert (0.67 vs. 0.60). Further, the diurnal trend of CS was similar to that of traffic counts in downtown Toronto on weekdays. This suggests that local anthropogenic emissions in Toronto, due to vehicle exhaust, significantly suppress the occurrence of nucleation.

5. Nucleation events in Southern Ontario were influenced by regional-scale pollutants, and this was supported by comparing nucleation frequency with respect to air masses. All days were categorized into North, South, East, and West depending on the origin and the path of the winds, and air mass “North” exhibited the highest frequency of nucleation. Since air masses from the “North” typically encounter few sources of contaminants, they were usually cleaner and cooler than other air masses, providing more appropriate conditions for nucleation. In contrast, the frequency of nucleation for “South” and “West” air masses were substantially lower. These air masses often contained a high level of pollutants emitted from industrial
regions in Detroit, Windsor, and Northern Ohio. Thus, nucleation was likely inhibited by regional-scale transported pollutants during the days impacted by “South” or “West” air masses.

6. A Nucleation Indicator was developed by combining parameters relevant to particle formation, such as solar radiation intensity, SO\(_2\), RH, and CS. Although the Nucleation Indicator did not provide a distinct threshold that unambiguously separates event days from non-event days, it was found to provide a reasonable measure of the probability of a nucleation event taking place. The nucleation indicator might be further refined by adding a parameter, such as a concentration of condensable organics contributing to nucleation.
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Appendix A: Seasonal Trends with n/a Days Excluded

The seasonal trends of nucleation with days of missing data excluded are provided at both locations.

Fig. A. Seasonal trends of nucleation with n/a days excluded at Toronto (a, total days = 271) and Egbert (b, total days = 325)
Appendix B: The Seasonal Variation of Formation and Growth Rates

The formation and growth rates in Toronto and Egbert did not show any seasonal trend as illustrated below.

a) Formation rate

b) Growth rate

Fig. B. Formation (a) and growth rate (b) of nucleation events in Toronto during May 2007 to May 2008
a) Formation rate

b) Growth rate

Fig. C. Formation (a) and growth rate (b) of nucleation events in Egbert during May 2007 to May 2008
Appendix C: Average Time for the Onset of Nucleation

a) Toronto

b) Egbert

Fig. D. Monthly average time for the onset of nucleation in Toronto (a) and Egbert (b) (Mean with 95% confidence intervals). The confidence intervals are excluded for months with less than three nucleation events in Toronto (a).
Appendix D: Calculation of Nucleation Rate

Nucleation rate was calculated by connecting the apparent formation rate and the competition between condensational growth and coagulation loss of particles onto background aerosols (Lehtinen et al., 2007). The nucleation rate of 2nm particles can be calculated by

\[ J_2 = \exp\left(\frac{d_2}{m + 1}\left[1 - \frac{d_{10}}{d_2} \right] \frac{CoagS(d_2)}{GR}\right) \]

where \( J_2 \) is the calculated nucleation rate of 2nm particles, \( J_{10} \) is the apparent formation rate of 10nm particles, \( GR \) is the growth rate of freshly formed particles, \( CoagS(d_2) \) is the coagulation sink of 2nm particle, and \( m \) is calculated by

\[ m = \frac{\log \left[ \frac{CoagS(d_{10})}{CoagS(d_2)} \right]}{\log \left[ \frac{d_{10}}{d_2} \right]} \]

where \( CoagS(d_{10}) \) is the coagulation sink of 10nm particles. The coagulation sink determines how rapidly freshly formed particles are scavenged by pre-existing aerosols and estimated by

\[ CoagS = \sum_j K_{ij} N_j \]

where \( K_{ij} \) is the coagulation coefficient (Kulmala et al., 2001).

The calculated nucleation rate was plotted against growth rate in order to compare the role of chemical compounds contributing to nucleation and growth with laboratory studies. However, no significant relation could be drawn from this analysis.
Fig. E. The nucleation rate (1/cm³s) versus growth rate (nm/hr). No significant relationship was found from the analysis.
Appendix E: The Frequency Distribution of the NI

The distribution of the NI frequency was illustrated below. The locations were not separated in the distribution.

Fig. F. The frequency distribution of the NI.
Appendix F. Condensation Sink versus Particle Diameter

Condensation sink (s\(^{-1}\)) is plotted as a function of particle diameter (nm). The particle number concentrations were averaged over May 2007 to May 2008. This graph showed that calculating condensation sink for particles up to 300 nm particles accounted for the entire condensation sink.

Fig. G. Condensation sink (s\(^{-1}\)) as a function of particle diameter (nm) for Toronto May 2007 to May 2008.