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Impact of urbanization on the ozone weekday/weekend effect in Southern Ontario, Canada

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ABSTRACT

The ozone weekday/weekend effect has been examined for a suite of urban centers in Southern Ontario, Canada using 2010 data to explore the impact of urban size. The magnitude of the weekday/weekend effect was measured by comparing the difference in ozone concentrations at 7 h for weekdays and weekends. The results indicate a statistically significant relationship between this difference and degree of urbanization as measured by population.
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1. Introduction

Ground level ozone is a component of photochemical smog and can cause deleterious health effects (Burnett et al., 1997; OMA, 2001) and structural and agricultural damage (Lee et al., 1996; Wilkinson et al., 2012), which in turn leads to economic loss. Air pollution costs the Canadian Province of Ontario several billion dollars per year and this is expected to increase to almost $10 billion by 2015, the majority being due to ground level ozone and fine particulate matter (OMA, 2005).

In 2000, the Canadian Council of Ministers of the Environment set the Canada wide 8 h standard for ground level ozone at 65 ppb (CCME, 2000). This standard is repeatedly exceeded in the Greater Toronto Area (GTA), with the highest ozone concentrations occurring during afternoons in the summer months (MOE, 2009). In addition, the city experiences several ozone exceedance days each year – days with at least one hour of ground level ozone levels above 80 ppb. Ozone exceedance days in Southern Ontario have ranged from a few to over 30 from the period of 2000–2010 (MOE, 2009).

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Although efforts have been made to remediate this issue, there is evidence that while local emissions of ozone precursors in the City of Toronto have been reduced, there has been no statistically significant change in ground level ozone concentrations over the past 10 years (Geddes et al., 2009). One of the reasons that local emissions reductions in Southern Ontario may not significantly improve air quality is that the area receives large amounts of transboundary pollution, especially from upwind US states along the Ohio River Valley. Several studies have shown that over much of Southern Ontario 50–60% of ground level ozone concentrations are a result of emissions in the United States (Yap et al., 1988; Brankov et al., 2003; MOE, 2005; Galvez, 2007; Johnson et al., 2007).

An understanding of the subtle chemistry of ozone production also explains why remediation efforts appear to have little effect. Ground level ozone is formed through a series of complex chemical reactions, involving its precursors – nitrogen oxides (NO*x*) and volatile organic compounds (VOCs) – and sunlight. Ozone production can be summarized through the following reactions:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (1)$$

$$NO_2 + O_2 + hv \rightarrow NO + O_3 \quad (2)$$

If reactions 1 and 2 occur in equilibrium there is no net gain or loss of ozone and a steady state typically of 10–20 ppb is achieved. However, oxidation of CO and VOCs by OH in the atmosphere generates peroxy radicals (RO_2), which in turn oxidize NO to NO_2, summarized as:

$$OH + VOC + O_2 \rightarrow H_2O + RO_2 \quad (3)$$

$$RO_2 + NO \rightarrow RO + NO_2 \quad (4)$$

This in turn results in a net production of ozone through reaction (2) which also results in additional NO that can repeat the cycle. In contrast, at high NO*x* concentrations, ozone is broken down, a process referred to as ozone scavenging. High NO*x* relative to VOC concentrations can also result in less ozone production as NO_2 outcompetes VOC for OH and suppresses production of the peroxy radicals. This points to two potential precursor states, NO*x* saturated or VOC saturated (Murphy et al., 2006a,b; Geddes et al., 2009). If the atmosphere is NO*x* saturated, remediation efforts need to focus on the reduction of VOCs and vice versa.

1.1. Weekday/weekend effect

One of the most counterintuitive examples of ozone chemistry is the weekday/weekend effect. This is defined as an increase in ground level ozone concentrations on weekends in spite of decreased NO*x* emissions, and is most noticeable during the morning rush hour period. This was first observed in various cities around the world in the 1970s (Cleveland et al., 1974; Lebron, 1975; Elkus and Wilson, 1977; Karl, 1978). Beaney and Gough (2002) observed a weekday/weekend effect in the GTA. They found a depression of ground level ozone concentrations on weekdays between 6 and 7 h, which resulted in overall lower average ozone concentrations by hour and lower maximum ozone concentrations on weekdays compared to weekends. More recently the weekday/weekend ozone effect has been detected in many other regions of the world (Sadanaga et al., 2008; Pudasainee et al., 2010; Pires, 2012; Castell-Balaguer et al., 2012; Im et al., 2013; Wolf et al., 2013).

Observation of the weekday/weekend effect can provide insight into the ozone chemistry of a region and how ozone production will respond to emissions reduction strategies. Because the weekday/weekend effect is usually most prominent during morning rush hour, most studies have attributed the weekend effect to be influenced mainly by vehicular emissions. Generally these emissions are composed of a higher percentage of NO*x* relative to VOCs, and gasoline engines release a higher proportion of NO compared to NO_2 (Yao et al., 2005), which would favour ozone scavenging through reaction (1). The presence of a weekday/weekend effect can also suggest a region is in a NO*x* saturated area of ozone production and reducing NO*x* emissions relative to VOC emissions will therefore lead to an increase in ground level ozone concentrations. Most of the observed weekday/weekend effects around the world have been in larger population centers.

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