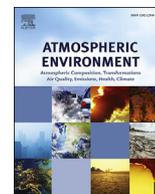


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## Emissions of hydrogen cyanide from on-road gasoline and diesel vehicles



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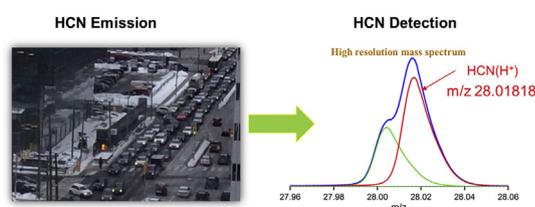
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### HIGHLIGHTS

- HCN emission factors are reported as a function of fuel types and driving modes.
- HCN emissions using diesel and biodiesel fuels are 10 times less than gasoline.
- Gasoline direct injection (GDI) vehicles emit 10 times more HCN than port fuel injection (PFI) vehicles.
- Ambient measurements of HCN were conducted in traffic impacted areas in Toronto.
- Model predictions and ambient measurements of HCN were consistent with each other.
- Exposure to HCN in urban areas is dominated by vehicle emissions.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Hydrogen cyanide (HCN) is considered a marker for biomass burning emissions and is a component of vehicle exhaust. Despite its potential health impacts, vehicular HCN emissions estimates and their contribution to regional budgets are highly uncertain. In the current study, Proton Transfer Reaction-Time of Flight-Mass Spectrometry (PTR-ToF-MS) was used to measure HCN emission factors from the exhaust of individual diesel, biodiesel and gasoline vehicles. Laboratory emissions data as a function of fuel type and driving mode were combined with ambient measurement data and model predictions. The results indicate that gasoline vehicles have the highest emissions of HCN (relative to diesel fuel) and that biodiesel fuel has the potential to significantly reduce HCN emissions even at realistic 5% blend levels. The data further demonstrate that gasoline direct injection (GDI) engines emit more HCN than their port fuel injection (PFI) counterparts, suggesting that the expected full transition of vehicle fleets to GDI will increase HCN emissions. Ambient measurements of HCN in a traffic dominated area of Toronto, Canada were strongly correlated to vehicle emission markers and consistent with regional air quality model predictions of ambient air HCN, indicating that vehicle emissions of HCN are the dominant source of exposure in urban areas. The results further indicate that additional work is required to quantify HCN emissions from the modern vehicle fleet, particularly in light of continuously changing engine, fuel and after-treatment technologies.

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## 1. Introduction

Vehicular emissions are considered the dominant source of air pollution in urban areas and have adverse effects on human health, air quality and the environment (Franco et al., 2013; Karlsson, 2004; May et al., 2014; Vardoulakis et al., 2003; HEI Panel, 2010; Jerrett et al., 2009). Emissions from vehicles depend upon vehicle type, age, maintenance, operation and fuels used, and contain a complex mixture of particles and gaseous pollutants. Most vehicle emission testing has been limited to common pollutants, such as carbon monoxide, nitrogen oxides and selected hydrocarbons (including aromatic compounds) and more recently a range of particle-bound compounds (Zielinska et al., 2004). However, given increased evidence of adverse health effects associated with exposure to traffic-related air pollution (Jerrett et al., 2009; Beckerman et al., 2008; McKeown, 2007), there is a need to identify and quantify emissions of more pollutants which are potentially toxic and may be partly responsible for the observed health impacts (HEI Panel, 2010; McKeown, 2007). Such data will enable better estimates of traffic related air pollutant exposures and assessments of health risks, and potentially help to identify more effective approaches to control their emissions.

Hydrogen cyanide (HCN), along with acetonitrile ( $\text{CH}_3\text{CN}$ ), are the most abundant cyanides in the atmosphere (Singh et al., 2003), yet the atmospheric budget of HCN remains uncertain. Due to its stability and thus long lifetime in the atmosphere (~5 months), HCN has been considered a biomass burning marker. (Bunkan et al., 2013) Numerous satellite and aircraft measurements of HCN (Singh et al., 2003; Crouse et al., 2009; Glatthor et al., 2013; Goode et al., 2000; Shim et al., 2007; Simpson et al., 2011; Viatte et al., 2013; Duflo et al., 2013; Le Breton et al., 2013; Liang et al., 2007; O'Shea et al., 2013; Rinsland et al., 2007, 1999, 2000; Vigouroux et al., 2012; Wiegele et al., 2012), and a few reports from ground based locations (Ambrose et al., 2012; Knighton et al., 2009), suggest that on a global basis, biomass burning (BB) emissions are a large source of HCN to the atmosphere ( $0.1\text{--}3.2 \text{ Tg-N-yr}^{-1}$ ) (Crouse et al., 2009; Glatthor et al., 2013; Viatte et al., 2013; Duflo et al., 2013; Le Breton et al., 2013; O'Shea et al., 2013; Rinsland et al., 2000; Ambrose et al., 2012; Glatthor et al., 2009; Li et al., 2000, 2003, 2009; Lupu et al., 2009).

Although limited measurements have reported HCN in the exhaust of vehicles (Karlsson, 2004; Baum et al., 2007; Keirns and Holt, 1978; Bradow and Stump, 1977; Cadle et al., 1979; Urban and Garbe, 1979; Harvey et al., 1983; Urban and Garbe, 1980; Becker et al., 1999), the exact formation mechanism remains somewhat unclear. While some studies have indicated that HCN is associated with the catalytic reduction of nitric oxides ( $\text{NO}_x$ ) over various catalytic systems (selective catalytic reduction (SCR), silver, alumina, rhodium and platinum) typically used to reduce  $\text{NO}_x$  emissions (Keirns and Holt, 1978; Tamm et al., 2008; Voorhoeve et al., 1975), others have shown that HCN in exhaust is enhanced in the absence of a catalyst (Keirns and Holt, 1978). Despite the fact that HCN is a reduced species which can be created in emission control systems (employing reduction catalysts), the formation of HCN during biomass burning suggests that HCN is also formed directly from fossil fuel combustion sources, which is consistent with the work of Dagaut et al. (2008) who demonstrated that HCN is also an intermediate in the formation of  $\text{NO}_x$  in combustion via both prompt- $\text{NO}$  and fuel- $\text{NO}$  mechanisms (Dagaut et al., 2008). Vehicle emission of HCN is also consistent with the reported variability in the HCN correlation with CO and acetonitrile in biomass burning plumes in the vicinity of urban areas, suggesting that urban sources of HCN are significant (Crouse et al., 2009).

Despite the studies reporting that HCN is emitted from vehicle emissions, no near-road measurements of HCN have been

performed and thus the contribution of vehicle emissions to HCN population exposure in urban areas is unclear. Furthermore, with increased public concern regarding air pollution, energy security, fuel efficiency and climate change, the use of alternative fuels such as biodiesel and advanced engine technologies such as gasoline direct injection (GDI) is increasing (Basha et al., 2009; Di et al., 2009a; Fernando et al., 2005; Shahid and Jamal, 2008; Wang et al., 2000; Chan et al., 2013). While biodiesel fuels are generated from natural and renewable sources (Wang et al., 2000; Pinto et al., 2005; Lapuerta et al., 2005; Sun et al., 2010; Anderson, 2012), and have the potential to reduce emissions of atmospheric pollutants (Di et al., 2009a; Shahid and Jamal, 2008; Wang et al., 2000; Bakeas et al., 2011; Basha and Raja Gopal, 2012; Di et al., 2009b; Peng et al., 2008; Zou and Atkinson, 2003; Karavalakis et al., 2009, 2010), GDI engines offer the promise of reduced  $\text{CO}_2$  emissions arising from increased fuel efficiency (Chan et al., 2013). However, the potential effect of these evolving engine and fuel technologies on HCN emissions has not been characterized. From a health perspective, quantifying urban HCN emissions is important, given the known toxicity and the lifetime of this compound in the atmosphere. HCN is a toxic compound that has negative impacts on human health. While the acute effects for exposure to HCN are known, the sub-chronic and chronic effects for exposures to ambient HCN levels are poorly understood. Cyanide in the form of HCN and  $\text{CN}^-$  at high levels (270 ppmv) is highly toxic and can lead to death if inhaled or ingested (U.S. EPA, 2010; Jackson et al., 2014; Logue et al., 2010; Minakata et al., 2011; Scherer, 2006). Exposure to HCN can contribute to acute and chronic inflammatory lung diseases (Scherer, 2006). In human blood, HCN is converted to thiocyanate ( $\text{SCN}^-$ ) via the enzyme rhodanese in the presence of a sulfur donor group (Logue et al., 2010). A large number of medical studies have documented the adverse effects of thiocyanate in humans, with most of these studies having focused on cigarette smoking as the source of exposure to HCN (Jackson et al., 2014; Logue et al., 2010; Minakata et al., 2011; Scherer, 2006; Rickert and Robinson, 1981; Vinnakota et al., 2012; Hauth et al., 1984).

The emission of HCN from vehicles has been documented in a number of publications, the majority of which are relatively old (1978–1983; 2004–2007) (Karlsson, 2004; Baum et al., 2007; Keirns and Holt, 1978; Cadle et al., 1979; Urban and Garbe, 1979; Harvey et al., 1983; Urban and Garbe, 1980; Rickert et al., 1980). With the improvement of vehicle technology with respect to engines, catalysts, ignition systems and quality/types of fuel, the emission of HCN will likely have changed and hence HCN exhaust emission factors from modern in-use vehicles would be useful for emission inventories, source appointment and exposure studies. In the current study, emission factors (mg/kg of fuel consumed) of HCN from various light duty vehicles (LDVs) are derived as a function of fuel type (diesel, bio-diesel, gasoline) and driving mode, and with vehicles utilizing emerging engine and exhaust after-treatment technologies. We demonstrate via a combination of laboratory experiments, ambient measurements and air quality model predictions that vehicular emissions are the dominant source of urban ambient HCN, representing a potentially important HCN exposure pathway.

## 2. Experiments and methods

### 2.1. PTR-TOF-MS

Measurements were performed using proton reaction time-of-flight mass spectrometry (PTR-TOF-MS, Ionicon Analytik GmbH, Austria). The operating principles of the PTR-MS are described in detail by Jordan et al. (2009) and Graus et al. (2010). In brief, the PTR-MS uses a chemical ionization technique in which hydronium

ions ( $\text{H}_3\text{O}^+$ ) are used as reagent ions to protonate analyte molecules via R1. The chemical ionization reaction by  $\text{H}_3\text{O}^+$  is considered a soft process relative to electron impact, resulting in comparatively little fragmentation. A number of papers have reported molecular fragmentation with the PTR-ToF-MS depending on the operating conditions and sampled matrix (HEI Panel, 2010; Ambrose et al., 2010; Kaser et al., 2013; Kim et al., 2009; Tani et al., 2003; White et al., 2009). Hydronium ions are generated by passing water vapor through a hollow cathode ion source. The reagent ion and the sample gas enter a drift tube, which was maintained at 2.15 mbar and at a temperature of 60 °C. The drift tube operated at an E/N of 140 Td where species (X) with a proton affinity greater than that of water (165 kcal/mol) are protonated according to reaction (R1).



The product ions are then detected with a high resolution Time-of-Flight (HR-TOF) mass spectrometer (mass resolution >3000; Tofwerk AG, Switzerland). Data analysis was performed with the TOFWARE software package (Tofwerk AG). This software performs high resolution peak fitting that is able to accurately integrate and separate the peaks from each other.

PTR-MS signals for HCN and other VOC species (benzene, toluene, xylenes and acetonitrile) were calibrated with standard gas cylinders (HCN standard from Air Liquide at  $5.5 \pm 0.275$  ppm in  $\text{N}_2$ ; VOC standards from IONIMED Analytik) through a gas calibration unit (GCU, Ionicon, Analytik GmbH, Austria). Given that the proton affinity of HCN (170.4 kcal/mol) is only slightly greater than that of water, the PTR-TOF-MS response to HCN is dependent on the relative humidity in the sample air stream (Knighton et al., 2009). To address this issue, relative humidity dependent calibrations for HCN were performed and the resulting response factor-relative humidity relationship was applied to subsequent data (Fig. S1). The water dependence of the response to HCN (Knighton et al., 2009),  $\text{H}_2\text{S}$  (Li et al., 2014) and HCHO (Vlasenko et al., 2010) in the PTR-MS has been reported previously.

## 2.2. Engine exhaust experiments

### 2.2.1. Diesel and biodiesel engine dynamometer experiment

A turbo diesel injection (TDI), removed from a 2001 Volkswagen Jetta, was operated on an engine dynamometer. The engine was equipped with a diesel oxidation catalyst (DOC) and was operated on ultralow sulfur diesel (ULSD), three pure biodiesels (B100) reformulated from soy, canola, and tallow/waste fry oils, respectively, and three blends (B5, B20, B50) of each biodiesel with ULSD. B5, B20 and B50 represent the 5%, 20% and 50% by volume mixed blends with ULSD, respectively. During the experiments, the engine was operated in four steady state modes, including idle and three other conditions derived based upon average speed and engine torque for the associated transient driving cycle: a) idle, b) US06 (Supplemental Federal Test Procedure, aggressive driving mode), c) HWFET (Highway Fuel Economy Driving Schedule, highway driving mode) and d) FTP75 (U.S. Federal Test Procedure 75, city driving mode). The engine exhaust delivery and experimental setup have been described previously. (Li et al., 2011; Wentzell et al., 2013) In brief, the PTR-ToF-MS sampled from a constant volume sampler (CVS) dilution tunnel where HEPA filtered and charcoal filtered room air was used to dilute the raw exhaust. The dilution factor used in the CVS ranged from 15 to 80 depending upon the operation mode. In addition to the PTR-ToF-MS measurements, concentrations of CO,  $\text{CO}_2$  (both with non-dispersive infrared analyzers),  $\text{NO}_x$  (chemiluminescence) and total hydrocarbons (THC, flame ionization detector) were measured in the CVS (Table S1).

### 2.2.2. Gasoline vehicle chassis dynamometer studies

During this study, several gasoline light duty vehicles (LDVs) with different engine and after-treatment technologies were configured on a chassis dynamometer for emission testing. The vehicles were a 2011 Hyundai Sonata equipped with a wall-guided stoichiometric gasoline direct injection (GDI) engine, a 2010 Volvo S40 and a 2008 Silverado light-duty truck (LDT) equipped with a port fuel injection (PFI) engine. All vehicles were equipped with three way catalytic converters (TWCs). The Sonata (GDI-LDV) and the Volvo (PFI-LDV) are certified as Tier 2 vehicles which operated on EPA Tier 2 certified gasoline. The transient driving cycles used in this study were the US06, steady state 50 miles per hour (SS 50mph) and LA4 (urban driving). A subset of the emission experiments were performed when the GDI vehicle was equipped with a gasoline particulate filter (GPF). The GPF used in this study has been described in detail by Chan et al. (2012, 2013, 2014) and was provided by the Manufacturers of Emission Control Association (MECA). Each test day began with two back to back LA4, followed by the 50 miles per hour steady state, followed by two back to back US06 drive cycles. The raw exhaust from the vehicle was directed and diluted using a full-flow CVS dilution tunnel, which is described in detail by Chan et al. (2012, 2013) (Chan et al., 2012, 2013). Diluted exhaust was continuously sampled from the CVS over the entire driving cycle by the PTR-ToF-MS. Concentrations of CO,  $\text{CO}_2$  (Horiba instruments AIA-210 and AIA210LE, respectively),  $\text{NO}_x$  (California Analytical Instruments, 400-HLCD) and THC (California Analytical instruments, 300HFID) were also monitored (Table S2). Fuel-based emission factors (EFs) were calculated using Equation (1), where [A] and [ $\text{CO}_2$ ] are mass concentrations in  $\mu\text{g}/\text{m}^3$  for species of interest and  $\text{CO}_2$  respectively and  $W_c$  is the carbon mass fraction of the fuel of interest (Wentzell et al., 2013). CO and VOCs are not included in the equation because they account for <1% of the carbon in the fuel. HCN, VOCs and  $\text{CO}_2$  were background corrected using zero air, prior to being used in the emission factors calculations.

$$EF(\text{mg}/\text{kgfuel}) = \frac{[A]}{[\text{CO}_2]} \times \frac{MW_{\text{CO}_2}}{12.01} \times W_c \quad (1)$$

## 2.3. Ambient measurements

Ambient measurements of HCN, acetonitrile, benzene, toluene and xylenes were performed in Toronto, Ontario, Canada between June 28th and July 19th, 2013 at an urban location approximately 100 m from a major roadway. Another sampling period was conducted between September 10th and September 17th, 2014 where the PTR-ToF-MS was deployed in the Canadian Regional and Urban Investigation System for Environmental Research (CRUISER) mobile laboratory (Beckerman et al., 2008). Latitude and longitude were measured using a GPS (GARMIN, GPMap 176C). On most days driving started at approximately 10:00 a.m., continued through the afternoon and ended between 5:00–7:00 p.m. for a total of 20 h of driving over the study period.

Ambient air in both cases was sampled through a perfluoroalkoxy (PFA) tube by a diaphragm pump at a flow rate of 2–4 L/min of which 100 sccm was sampled by the PTR inlet maintained at 60 °C. Instrument background measurements were performed for 5 min every hour using a platinum catalyst heated at 350 °C.

In addition to the PTR measurements in the 2013 campaign, parallel ambient measurements were performed using a chemical ionization mass spectrometer (CIMS) with iodide as the reagent ion (Le Breton et al., 2013, Wentzell et al., 2013). HCN was detected as  $\text{CN}^-$  ( $m/z$  26) and  $\text{HCN.I}^-$  ( $m/z$  154) as described elsewhere (Le

Breton et al., 2013).

#### 2.4. Air quality emission modelling

HCN predictions over Toronto for September 2014 (to coincide with mobile measurements), were performed with Environment Canada's operational air quality model (GEM-MACH) (Makar et al., 2015a, 2015b), to coincide with the mobile measurements. The air quality prediction system was run in an off-line configuration with the meteorology driven by Environment Canada's operational weather forecast model (GEM). For this study, GEM-MACH was run in a nested configuration down to a 2.5-km grid spaced domain over Southern Ontario in which Toronto is located. HCN was added to the modelling system as an emitted, transported and chemically reactive species, and the model was run to test the sensitivity of HCN ambient levels to vehicle emission (on-road and off-road gasoline and diesel). Other anthropogenic emissions (e.g. NO<sub>x</sub>, CO, VOCs) were based on the 2008 US EPA and 2006 Canadian emission inventories (NPRI). The incorporation of HCN and emission inventories in GEM-MACH is described in details in SI.

### 3. Results and discussion

#### 3.1. Gasoline emission studies

Fig. 1 shows the dilution-corrected concentration profiles for benzene, toluene and HCN for the duration of each transient driving mode for a GDI vehicle with no GPF. The Figure shows that the concentrations of HCN, benzene, and toluene in the exhaust were 10 fold higher in the full cold start cycle than when compared to the hot start cycle. HCN emissions from the exhaust correlated with emissions of other traffic markers such as benzene and toluene and were on the same order of magnitude as the aromatic compounds measured. Table 1 provides a summary of the 22 min average fuel-based emission factors for HCN, benzene, toluene and acetonitrile for the different driving cycles. For the GDI vehicle, the fuel based emission factors for HCN were 2 times higher for cold start modes compared to the equivalent hot start mode. The highest emission factor was obtained during the first US06 (aggressive) cycle followed by the LA4 (urban) cold drive cycle. The effect of engine and/or catalyst temperature on HCN EFs was even more pronounced in the PFI vehicle, where the EFs were 30 and 3 times higher for LA4 and US06 cold start compared to the equivalent hot starts, respectively.

A comparison of HCN emission factors (mg/km) from the exhaust of different vehicles used in literature is shown in Table 2. There is clearly a wide range of HCN EFs reported in the literature which is due to the fact that exhaust emissions of HCN are known to vary greatly with operation, engine, maintenance, age and control technology of the engine. Consequently, these variables make direct comparison of HCN emissions from this study to other studies difficult. This is further exacerbated by the limited number of vehicles used in this study (three gasoline vehicles) compared to other studies, by the different driving cycles which were used here compared to other studies, and by the fact that the three vehicles used in this study have newer technology relative to others reported in the literature.

Despite the aforementioned caveats, the EFs obtained in this study fall within the same range of some of the EFs reported in literature. For instance, Karlsson (2004) was the only study from Table 2 that reported emissions of HCN from an LA4 transient cycle. Qualitatively, the average LA4 fuel-based EF for HCN (Table 1) for the GDI engine equipped with GPF is 6.65 mg/kg (~0.5 mg/km), which is on the same order of magnitude compared to the ~1.2 mg/km EF reported by Karlsson (2004). However, the average LA4 EF for

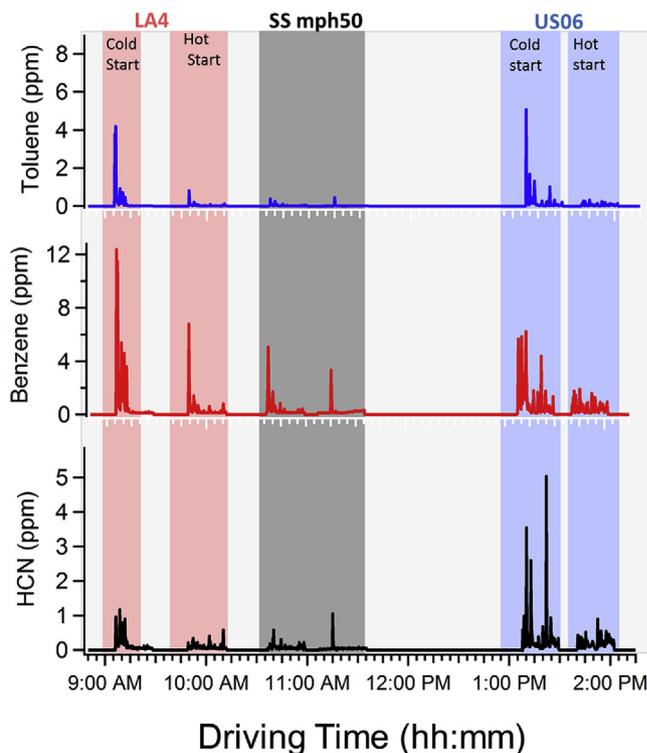


Fig. 1. Transient exhaust levels of Toluene, benzene and HCN from a GDI vehicle not equipped with a GPF as a function of different driving modes and test cycles. The PTR-ToF-MS data were collected as 60 s data and the concentration in the exhaust were corrected for CVS dilution.

the same vehicle not equipped with a GPF is ~4.4 mg/km. Although no idle mode measurements for HCN from gasoline vehicles were made in this study, the transient driving mode EFs suggest that HCN emissions from non-idle driving modes are significant compared to idle mode values in other studies (Baum et al., 2007; Harvey et al., 1983).

Despite the limited number of vehicles here, the effect of engine and/or catalyst temperature on HCN emissions is consistent with the literature. Baum et al. (2007) reported HCN emissions from 14 idling vehicles and they similarly showed that HCN emissions were higher during cold engine starts compared to vehicles operating under temperature stabilized conditions regardless of the make, year and model of the vehicle used (Baum et al., 2007). The increase in HCN emissions during cold engine starts is also consistent with studies reporting the effect of catalyst (and engine) temperature on the emissions of black carbon, THC, NO<sub>x</sub> and particulate matter (PM) from GDI and PFI engines (Chan et al., 2013, 2014, 2012).

A comparison of the calculated fuel-based emission factors for HCN from the GDI and the PFI engines used in this study is shown in Fig. 2A. The emissions of HCN from the GDI engine ranged from 2 to 100 fold larger than those of the PFI engine, depending on the driving mode. An increase in the emissions for the aromatic hydrocarbons was also observed in this study (Table 1). An increase in PM emissions from GDI vehicles relative to PFI vehicles has been reported in other studies (Chan et al., 2013, 2014, 2012). To the best of our knowledge no studies have reported VOC emissions from GDI vehicles relative to PFI vehicles. While a very large increase in HCN and VOCs emissions from the GDI vehicle compared to the PFI was observed here, it is clear that further emission studies with a larger sampling of vehicles are required to confirm this result.

The effect of a gasoline particulate filter (GPF) on the emissions of HCN from gasoline vehicles was investigated on the GDI engine.

**Table 1**

Averages of the fuel-based emissions factors (<sup>a</sup>EFs) for benzene, toluene, xylenes, acetonitrile and HCN from gasoline (PFI + GDI) vehicles for different transient cycles at different engine temperatures at the startup.

Vehicle type	Fuel injection	Exhaust treatment	Driving Mode	Engine temperature	CO (g/km)	CO <sub>2</sub> (g/km)	Emission factor (mg/kg of fuel)					HCN (mg/km)
							Benzene	Toluene	<sup>b</sup> xylenes	CH <sub>3</sub> CN	HCN	
Sonata	GDI	GPF	LA4	Cold	0.4	233.9	3 × 3.3	527.6	177.7	7.4	5.5	0.6
Sonata	GDI	GPF	LA4	Hot	0.2	212.8	19.7	143.2	17.1	5.1	4.8	0.3
Sonata	GDI	OPF	SS mph50	Warm	0.1	106.0	77.3	262.8	42.3	6.0	5.8	0.2
Sonata	GDI	GPF	US06	Cold	0.8	179.0	314.9	5966	150.6	104	149	0.8
Sonata	GDI	GPF	US06	Hot	0.8	179.0	184.8	296.4	66.0	5.4	9.2	0.5
Volvo	PFI	No GPF	LA4	Cold	0.2	259.5	395.7	795.3	319.6	23.4	7.9	0.6
Volvo	PFI	So GPF	LA4	Hot	0.2	234.0	622	204.4	28.4	6.5	0.3	0.0
Volvo	GDI	No GPF	SS mph50	Warm	0.1	133.1	73.9	151.0	33.4	90	4.7	0.2
Volvo	GDI	No GPF	US06	Cold	0.3	217.2	91.2	217.6	63.2	5.3	16.0	1.0
Volvo	GDI	No GPF	US06	Hot	0.4	217.2	52.9	141.1	26.9	2.1	6.0	0.4
Sonata	GDI	No GPF	LAI	Cold	0.8	244.2	406.7	705.2	213.6	1.8	76.0	5.6
Sonata	GDI	No GPF	LAI	Hot	0.4	217.7	103.7	321.3	48.2	1.3	46.4	3.1
Sonata	OD3	No GPF	SS mph50	Warm	0.1	103.6	57.1	134.9	15.0	06	10.7	0.4
Sonata	GDI	No GPF	LS06	Cold	1.6	205.7	291.1	410.3	122.3	1.3	77.4	4.8
Sonata	GDI	No GPF	US06	Hot	1.6	205.7	117.6	191.3	41.5	1.3	39.7	2.5
silverado	PFI	No OPF	LA4	cold	3.0	341.6	691.0	643.7	726.5	27.7	15.9	1.8
silverado	PFI	No GPF	LA4	hot	3.0	381.6	165.7	382.9	370.2	15.2	6.9	0.8

<sup>a</sup> Average of 22 min transient driving cycle.

<sup>b</sup> Sum of o,m,p-xylene and ethyl benzene.

**Table 2**

Comparison of literature HCN emission factors (mg/km) from the exhaust of different light duty vehicles (LDVs).<sup>a</sup>

	Min	Max	Average ± (1 s)	Number of vehicles	Model year
Keirns and Holt, 1978	0.8	11.8	4.5 ± 3.2	1	1977
Bradow and Stump, 1977	0.1	75.6	20.0 ± 24.8	49	1976
Karlsson, 2004	0.0	11.7	2.2 ± 4.2	5.0	1994–1998
Harvey et al., 1983	1.0	12.1	3.8 ± 4.2	206	NA
Urban and Garbe, 1979	1.0	7.0	4.1 ± 2.6	51	1978–1979
Cadle et al., 1979	0.6	8.1	4.7 ± 3.4	26	1967–1978
This study	0.0	5.6	1.4 ± 1.7	3	2008–2011

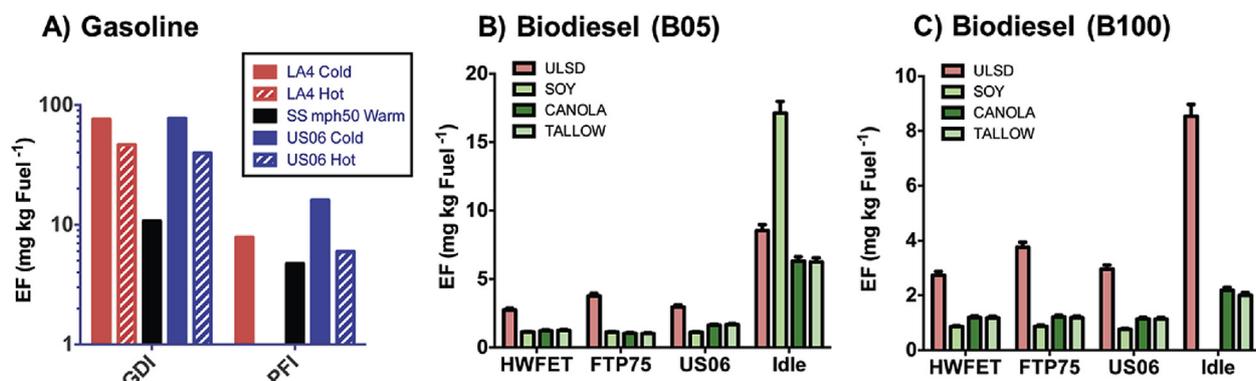
<sup>a</sup> The table does not contain emission factors for idle mode.

Fig. 2A shows fuel-based EFs of HCN from the GDI engine with/without a GPF. The presence of the GPF decreased HCN emission by a factor of 10, which may be due to the adsorption of HCN/cyanide on the metal filter surface. The GPF used in this study was made from cordierite (magnesium iron aluminum cyclosilicate) material. Yi et al. have shown that HCN, acetonitrile and benzene decrease significantly on such metal surfaces (Yi et al., 2004). Additionally, a number of studies have shown that CN<sup>-</sup> can bind efficiently to metal sites as an intermediate in the reduction of NO<sub>x</sub> on different

metal catalysts (Ni et al., 2011; Thibault-Starzyk et al., 2009; Yu et al., 2010, 2013; Zhang et al., 2007).

### 3.2. Diesel and biodiesel emission studies

A summary of the calculated fuel based EFs for HCN from ULSD, and pure biodiesel from (B100) tallow/waste fry oil, soy and canola for various steady states is shown in Fig. 2, and represents the first known report of such values. The average HCN fuel based EFs for



**Fig. 2.** Fuel-based emission factors (EFs) for HCN from: A) GDI vehicle (in the presence and absence of a gasoline particulate filter (GPF)) and a PFI vehicle under different driving modes. B) Different operation modes utilizing ULSD and B05 biodiesel blends and C) pure biodiesels B100 (Tallow, Canola, Soy). All EFs calculations accounted for dilution in the CV.

the four steady state driving modes (HWFET, FTP75, US06 and idle) from ULSD were  $3.0 \pm 0.4$ ,  $3.9 \pm 0.5$ ,  $3.4 \pm 0.4$  and  $10.3 \pm 2.8$  mg kg Fuel<sup>-1</sup>, respectively. The fuel based EFs for HCN from ULSD were ~10 times lower than those obtained from the PFI and GDI gasoline vehicles during US06 driving mode. However, it is important to note that integrating a transient drive cycle is typically not equivalent to the steady state tests, because emissions are expected to increase with the aggressiveness and transient nature of the driving conditions. A further and significant reduction in HCN emissions from the engine was achieved (relative to ULSD) when operating on the biodiesel fuels (Fig. 2B, C). The reduction ranged from 20 to 80% depending on the operating mode, where the largest reduction in HCN emissions (~80%) for all the biofuels was achieved in the idle mode. Intriguingly, the same reduction in HCN emission from pure biodiesels (B100) was achieved using B05, B20 and B50 blends (Fig. 2 and Fig. S2). This may be related to the mechanism by which HCN (an intermediate product) is converted to NO<sub>x</sub> during combustion. Further studies are needed to determine the exact formation mechanism for HCN which is beyond the scope of this study. The reduction in HCN EFs with biodiesel fuel use is also concurrent with a reduction in aromatic hydrocarbon emissions as shown in Table 3, and consistent with hydrocarbon emission reductions reported with biofuel use in a number of studies (Di et al., 2009b; Peng et al., 2008; Karavalakis et al., 2010; Corrêa and Arbilla, 2006; Lopes et al., 2014; Peng et al., 2012).

### 3.3. Ambient measurements and modelling

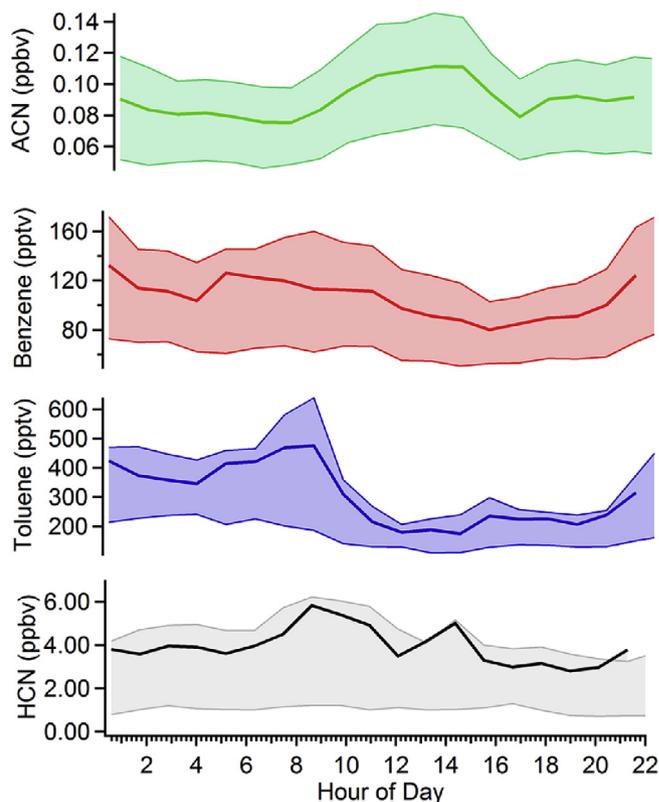
To further demonstrate the contribution of HCN vehicle emissions to air quality, near-road ambient measurements were performed in Toronto, Canada. The diurnal profiles of HCN, acetonitrile (ACN), toluene and benzene concentrations in ambient air during 2013 are shown in Fig. 3. An increase in the HCN concentration was observed during the morning rush hour period (~6:00–8:00 a.m.), which coincided with the increase in other traffic markers such as benzene and toluene, but not with acetonitrile. A positive correlation observed between HCN and benzene during ambient measurements (Fig. S3), strongly suggests that ambient HCN is, at least in large part, associated with vehicle emissions (Wentzell et al., 2013; Marshall et al., 2003). The diurnal profile of ambient HCN is consistent with the air quality model predictions in the region (Fig. 4) which shows that HCN emissions are higher during morning

periods (7:00–10:00 a.m.) relative to midday and evening. Conversely, there was a poor correlation between CH<sub>3</sub>CN and HCN during the sampling period despite both species having been used as biomass burning markers and measured in vehicle exhaust (Tables 1 and 3), suggesting different sources for both species (Crouse et al., 2009). Such an observation may be expected since the fuel-based emission factor for CH<sub>3</sub>CN from gasoline and diesel emissions were minimal compared to HCN (Tables 1 and 3). This is also consistent with a report that vehicle emissions are a minor source of atmospheric CH<sub>3</sub>CN (Holzinger et al., 2001), and with measurements over Central Mexico, where an increase in ACN levels was observed without an accompanying enhancement in HCN (Crouse et al., 2009). The HCN PTR measurements during 2013 are supported by parallel measurements conducted by the CIMS for the same period. A similar HCN profile was obtained using the CIMS (Fig. S4).

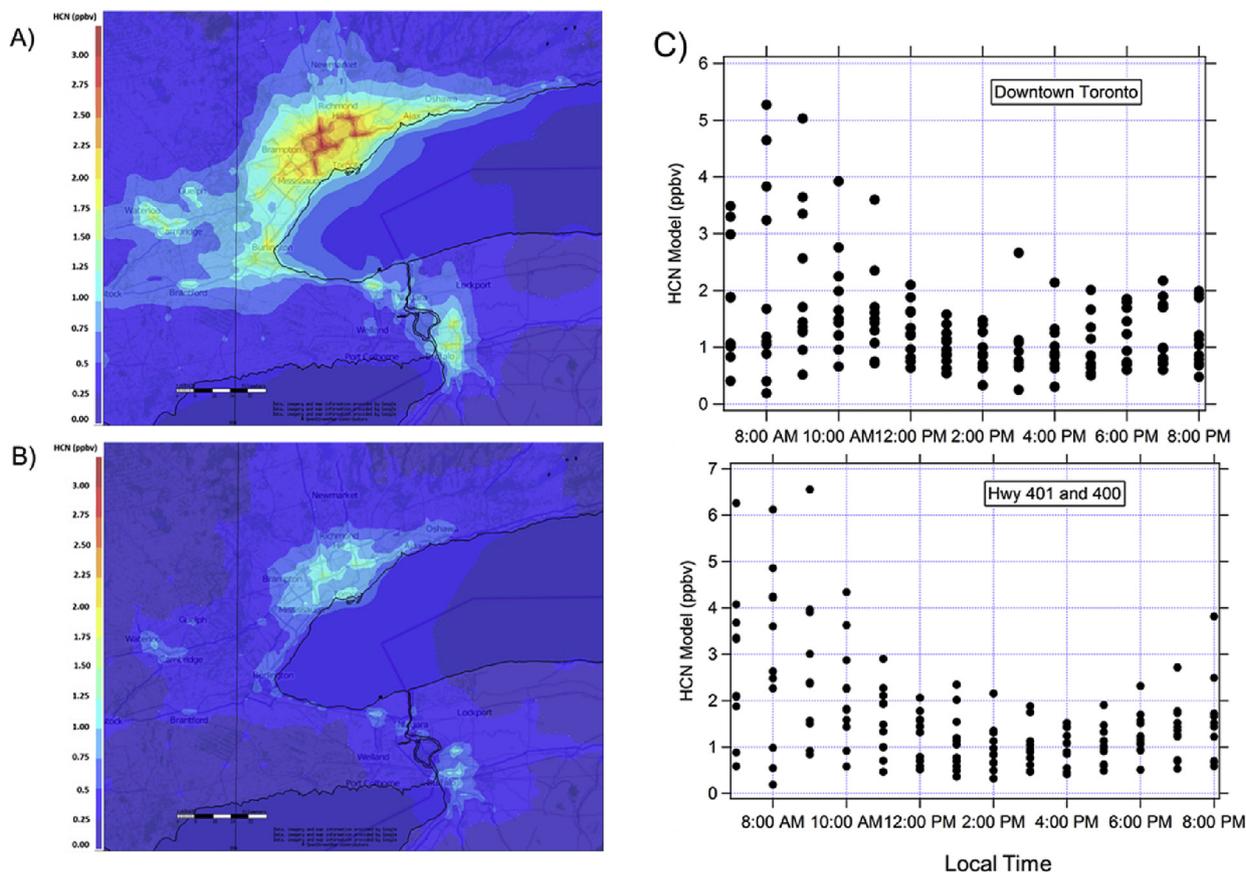
During the 2013 sampling period, HCN levels ranged from ~0.2 ppbv to 20.0 ppbv with a mean value of  $3.45 \pm 3.43$  ppbv ( $1\sigma$ ), and a median of 2.17 ppbv, respectively. To investigate the spatial extent and distribution of HCN in an urban region affected by significant vehicle emissions, a second sampling period was conducted in September 2014 coinciding with the output of an air quality model. HCN levels during this study, which was able to examine a greater number of locations due to use of a mobile lab, ranged from ~0.1 ppbv to 3.8 ppbv with a mean value of  $1.57 \pm 0.33$  ppbv ( $1\sigma$ ) (Fig. S5). A direct comparison between the two sampling periods is not straight forward since continuous sampling was conducted for 2 weeks in 2013 at one location compared to intermittent measurements (3–4 h per day) in different locations around the city during the mobile measurements in 2014. The HCN levels (Fig. S5)

**Table 3**  
Summary of HCN, benzene, toluene, and acetonitrile EFs from ULSD and pure biodiesels (B100) at different driving modes.

Fuel type	Driving Mode	Emission factor (mg/kg of fuel)				
		HCN	Benzene	Toluene	Xylene	CH <sub>3</sub> CN
ULSD	Idle	10.3	40.8	85.1	80.5	2.1
ULSD	HWFET	3.0	1.2	2.8	2.6	0.9
ULSD	FTP75	3.9	1.3	3.3	2.7	0.7
ULSD	US06	3.4	0.8	1.9	1.6	0.3
Canola	Idle	2.2	14.7	6.5	3.9	0.1
Canola	HWFET	1.2	0.5	1.2	0.7	0.3
Canola	FTP75	1.2	1.3	4.0	3.0	0.4
Canola	US06	1.1	0.5	2.3	0.8	0.3
Soy	HWFET	0.9	0.9	3.2	1.7	0.2
Soy	FTP75	0.9	1.2	2.7	1.6	0.3
Soy	US06	0.8	0.9	2.2	1.2	0.2
Tallow	Idle	2.0	29.5	8.7	4.1	1.3
Tallow	HWFET	1.2	0.8	2.8	1.3	0.3
Tallow	FTP75	1.1	1.1	4.1	2.0	0.2
Tallow	US06	1.2	0.6	2.1	1.0	0.3



**Fig. 3.** Diurnal profiles for acetonitrile (ACN, green), benzene (red), toluene (blue) and HCN (black) from ambient measurements in Toronto, Canada. Solid lines are means and shaded regions (upper and lower bounds) indicate the 75th and 25th percentiles, respectively.



**Fig. 4.** GEM-MACH Air quality model predictions for HCN over Toronto for: A) the morning period (7:00–10:00), B) evening period (16:00–20:00) and C) diurnal profile predictions for HCN in downtown Toronto and major highway from September 7 to September 17, 2014.

from 2014 are in agreement with the GEM-MACH midday and evening predictions (Fig. 4) during the same period, suggesting that HCN emissions from vehicles are likely the major source of HCN in this region, since the only source of HCN in the model was from vehicle emissions. HCN levels during the September 2013 measurement period were generally higher than during the mobile study, with a regional background of ~2 ppb. This may reflect an influence from regional biomass burning episodes during the 2013 measurement period. There were episodes of biomass burning in parts of the province of Quebec during the sampling period; however, backward wind trajectories calculated using NOAA-Hybrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT) indicated that the biomass burning plume did not impact the near-road location.

Measurements of HCN during both sampling periods were significantly higher than the mean HCN mixing ratios of  $\sim 0.2$  ppb and  $0.36 \pm 0.16$  ppb reported by Knighton et al. (2009) and Ambrose et al. (2012), respectively. Such differences may be attributed to differences in the sampling locations. Specifically, during 2013, the measurements were made about 100 m from a heavily commuted street in Toronto whereas the study of Ambrose et al. (2012) was conducted near a hardwood/pine forest. Additionally, the strong correlation between HCN and  $\text{CH}_3\text{CN}$  in Ambrose et al. (2012) was more consistent with a large scale, aged biomass burning influence rather than vehicle emissions (Ambrose et al., 2012). Knighton et al. (2009), sampled at a suburban site in Boston; however, their HCN measurements were likely influenced by interferences from  $\text{C}_2\text{H}_4^+$  in the quadrupole PTR-MS signal which could not be resolved from HCN at  $m/z$  28 (Knighton et al., 2009), whereas both ions were

resolvable in the current study with the HR-TOF mass spectrometer. In the PTR-TOF the signal from  $\text{HCN}\cdot\text{H}^+$  and  $\text{C}_2\text{H}_4^+$  are detected at  $m/z$  28.01818 and  $m/z$  28.0308, respectively. However in the PTR-quadrupole MS, both signals will be observed at nominal  $m/z$  28. Attempts at subtracting the contribution of  $\text{C}_2\text{H}_4^+$  from the signal at  $m/z$  28 in that study will increase the uncertainty in the derived HCN. The aforementioned studies represent the most relevant comparisons for HCN in the urban ambient air, since most of the other studies have been performed in the middle to upper troposphere to provide HCN estimates for large scale biomass burning episodes (Singh et al., 2003; Rinsland et al., 2007; Zhao et al., 2002).

### 3.4. HCN emissions estimates for Canada

The strong correlation between HCN and aromatic compounds (Fig. S3) during ambient measurements and the fuel-based EFs of HCN from the gasoline and diesel engine laboratory studies clearly suggest that vehicle emissions can be a source of HCN in urban areas. Despite the caveats discussed in section 3.1, and to put our results in perspective, we assumed that the on-road vehicle fleet has HCN EFs similar to the values reported in this study. In that case, the annual emissions of HCN for Ontario and Canada can be estimated using the fuel based emission factors obtained from the current laboratory study and from the annual sales of gasoline (~99%) and diesel (1%) for LDV reported by Statistics Canada (Statistics Canada). A summary of total annual HCN emissions estimates for Ontario and Canada is provided in Table 4. Approximately  $40 \times 10^6$  thousand liters of gasoline were sold in Canada nationwide in 2012, of which 38.5% were sold in the province of

Ontario (Table 4). Using an average fuel-based emission factor for HCN (21.0 mg/kg of gasoline, Table 1) and 0.77 kg/L as the density of gasoline, we estimate that 654 tonnes of HCN were emitted in 2012 from LDV in Canada, including ~252 tonnes in Ontario. The same approach can be used to estimate HCN emissions from LDVS operating on ULSD which results in 14 and 49 tonnes of HCN emitted in 2012 from vehicles for Ontario and Canada, respectively (Table 4). The average emission factor from the current diesel study is 3.2 mg/kg of ULSD (Table 3, excluding idle mode) and the density of diesel used was ~0.87 kg/L.

On a national scale, we estimate that 703 tonnes of HCN are emitted annually from the combined gasoline and diesel LDV fleets. However, this likely represents an underestimate of the total HCN emissions as it does not account for the contribution of heavy duty diesel vehicles (HDDV), and is based upon a sampling of three vehicles only, and does not account for the variability in HCN EFs. The 703 tonnes is further considered an underestimate since there are several studies which suggest that poor maintenance of vehicles and malfunctioning catalysts enhances HCN emissions (as discussed in more details in section 3.1) (Urban and Garbe, 1979, 1980) whereas the vehicles in the current study were relatively new and well maintained.

To place vehicle emissions of HCN in the context of the total Canadian HCN budget (which includes biomass burning emissions of HCN) the emission ratio (ER) of HCN/CO for forest fires is used to estimate the contribution of HCN from biomass burning nationwide. These estimates are also summarized in Table 4 and described in detail in SI. The estimates in Table 2 indicate that despite the large uncertainties and the number of assumptions involved in biomass burning estimates for HCN, national emissions from biomass burning are 3–321 times higher than HCN emissions from vehicles. It is estimated that 70–85% of the global HCN budget is due to biomass burning emissions (O'Shea et al., 2013; Li et al., 2003), therefore HCN vehicle emissions (703 tonnes) may be considered small but non-negligible. However, this likely represents an important source of population exposure to HCN in urban areas particularly since forest fire plumes are episodic in nature while vehicle emissions of HCN are persistent and concentrated near the ground in close proximity to population. Clearly, more emission studies of HCN from a bigger sampling of vehicles are required.

#### 4. Conclusions and implications

The results of the present combined laboratory exhaust emissions, modelling and ambient sampling study reports HCN emissions from different types of vehicles and fuels under a range of standard driving modes. The results indicate that gasoline vehicle emissions under transient driving conditions are likely the

dominant source of ambient HCN in urban areas. This is important since a large fraction of urban population is continuously exposed to vehicle emissions, either by being inside a vehicle or by living and working in the vicinity of traffic, including major roadways (HEI Panel, 2010; Jerrett et al., 2009; McKeown, 2007).

The shift from PFI to GDI vehicles is occurring rapidly due to the promise of increased fuel efficiency and reduced CO<sub>2</sub> emissions. It is expected that by 2025, GDI vehicles will dominate the market (~93%), replacing less efficient PFI vehicles (Karavalakis et al., 2014). Our results demonstrate that, moving fully towards GDI vehicles, will not only increase HCN emissions but it will also increase the emissions of other toxic VOCs such as benzene and xylene. This is intriguing and calls for more emission studies that include a bigger and more representative sampling of on-road PFI and GDI vehicles to investigate the consequences of shifting from PFI to GDI vehicles on air quality. While GPF may provide future GDI vehicles a means to reduce ultrafine particle emissions (Wang et al., 2000; Tani et al., 2003; White et al., 2009), our data suggest that there may also be an unexpected co-benefit of lower HCN emissions with the use of a GPF. However, additional work will be required to confirm not only this reduction but also that it is maintained as the GPF ages.

The current data also indicates that HCN emissions are significantly reduced when using biodiesel blends relative to ULSD. Note that the gasoline HCN emissions were obtained from transient driving conditions while diesel HCN emissions were measured during steady state. Consequently a direct comparison between gasoline and diesel EFs is not quantitatively possible. However, considering that 99% of the diesel fuel sold in Canada is used by heavy duty vehicles (HDVs; not LDDVs), in a relative sense, the total HCN emissions contributed by all light-duty gasoline vehicles are likely much higher than all HCN emissions from light-duty diesel vehicles. Additional data is required to assess effect of biodiesel on the emissions of HCN from heavy-duty vehicles.

From the human health perspective, there is increased evidence that traffic related air pollution (TRAP) is linked to cardiovascular and respiratory diseases, cancer, and increased mortality and morbidity rates (Jerrett et al., 2009). While the acute effects for exposure to high levels of HCN are known, the acute and chronic effects of low exposures (i.e., at the ambient levels reported here) are poorly understood.

There is no federal air quality standard for HCN in Canada; however, based upon the inhalation reference concentration (RfC) reported in an occupational study by El Ghawabi et al. (1975), the province of Ontario has established an air quality standard (AAQC) for HCN. The 24 h average and half hour point impingement AAQC for HCN in Ontario are 8 µg/m<sup>3</sup> (~7 ppb) and 24 µg/m<sup>3</sup> (~20 ppb), respectively (Standards Development Branch, 2005). During the ambient measurements of this study in Toronto, Canada's largest city and the third largest in North America, the average HCN

**Table 4**  
Annual HCN emissions from the transportation sector and biomass burning for Ontario and Canada.

	Gasoline LDV (tonnes)	Diesel LDV (tonnes)	Total on-road vehicles (tonnes)	Biomass burning (tonnes)
Ontario	252 <sup>a</sup>	14 <sup>a</sup>	266 <sup>b</sup>	N/A
Canada	654 <sup>a</sup>	49 <sup>a</sup>	703 <sup>c</sup>	2,101 <sup>d</sup> –10,419 <sup>e</sup> 45,496 <sup>f</sup> –225,600 <sup>g</sup>

<sup>a</sup> Estimates of annual emissions of HCN for Ontario and Canada-wide using the fuel based emission factors obtained from the current laboratory study and from the 2012 annual sales for gasoline and diesel for LDV reported by Statistics Canada (Statistics Canada). 17,435,813 and 5,043,892 thousand liters of diesel were sold in Canada and Ontario, respectively. On the other hand, 40,444,101 and 17,435,813 thousand liters of gasoline were sold in Canada and Ontario, respectively (Statistics Canada).

<sup>b</sup> Derived by adding HCN emissions from gasoline and Diesel LDV for Ontario.

<sup>c</sup> Derived by adding HCN emissions from gasoline and Diesel vehicles for Canada.

<sup>d</sup> Value derived from using 0.00242 as HCN/CO ER (Rinsland et al., 2007) and CO data from NPRI (National Pollution Release, 2012).

<sup>e</sup> Value derived from using 0.012 as HCN/CO ER (Akagi et al., 2011) and CO data from NPRI (National Pollution Release, 2012).

<sup>f</sup> Value derived from using 0.00242 as HCN/CO ER (Rinsland et al., 2007) and CO data from GFED (Global Fire Emission Data).

<sup>g</sup> Value derived from using 0.012 as HCN/CO ER (Akagi et al., 2011) and CO data from GFED (Global Fire Emission Data).

concentration in the 2013 ambient data was 3.34 ppb. During the 19 day sampling period in 2013, the 24 h average exceeded the Ontario AAQC and the EPA RFC value (0.003 mg/m<sup>3</sup> or ~3 ppb) (U.S. EPA, 2010) on 3 and 5 days, respectively (Fig. S6). Model predictions (Fig. 4C) also demonstrate that HCN levels (derived from vehicle emissions) can reach ~ 5 ppb during the morning rush hour in downtown Toronto and on major highways.

This study suggests that there is a need for more emission studies and new health/exposure data characterizing the effect of prolonged exposure to ambient levels of HCN, particularly in light of the development of new vehicle technologies and after-treatment devices, which have the potential to increase HCN emissions and other traffic related pollutants.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2016.01.050>.

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