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# Exploratory study of atmospheric methane enhancements derived from natural gas use in the Houston urban area

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A B S T R A C T

The extensive use of natural gas (NG) in urban areas for heating and cooking and as a vehicular fuel is associated with potentially significant emissions of methane ($CH_4$) to the atmosphere. Methane, a potent greenhouse gas that influences the chemistry of the atmosphere, can be emitted from different sources including leakage from NG infrastructure, transportation activities, end-use uncombusted NG, landfills and livestock. Although significant $CH_4$ leakage associated with aging local NG distribution systems in the U.S. has been reported, further investigation is required to study the role of this infrastructure component and other NG-related sources in atmospheric $CH_4$ enhancements in urban centers. In this study, neighborhood-scale mobile-based monitoring of potential $CH_4$ emissions associated with NG in the Greater Houston area (GHA) is reported. A novel dual-gas 3.337 μm interband cascade laser-based sensor system was developed and mobile-mode deployed for simultaneous $CH_4$ and ethane ($C_2H_6$) monitoring during a period of over 14 days, corresponding to ~ 90 h of effective data collection during summer 2016. The sampling campaign covered ~250 exclusive road miles and was primarily concentrated on eight residential zones with distinct infrastructure age and NG usage levels. A moderate number of elevated $CH_4$ concentration events (37 episodes) with mixing ratios not exceeding 3.60 ppmv and associated with atmospheric background enhancements below 1.21 ppmv were observed during the field campaign. Source discrimination analyses based on the covariance between $CH_4$ and $C_2H_6$ levels indicated the predominance of thermogenic sources (e.g., NG) in the elevated $CH_4$ concentration episodes. The volumetric fraction of $C_2H_6$ in the sources associated with the thermogenic $CH_4$ spikes varied between 2.7 and 5.9%, concurring with the $C_2H_6$ content in NG distributed in the GHA. Isolated $CH_4$ peak events with significantly higher $C_2H_6$ enhancements (~11%) were observed at industrial areas and locations with high density of petroleum and gas pipelines in the GHA, indicating potential variability in Houston's thermogenic $CH_4$ sources.

## 1. Introduction

Methane ($CH_4$), a potent greenhouse gas (GHG) that also contributes to background ozone levels, is emitted from multiple sources including natural gas (NG) and petroleum systems, mobile and stationary combustion, and microbial degradation in landfills and wastewater treatment plants (EPA, 2017; Fiore et al., 2008). Natural gas systems, including production, processing, and transmission and distribution, constitute the second largest known source of $CH_4$ emissions to the atmosphere, with estimated 6.5 million metric tons $CH_4$ emitted in 2015 (24.8% of total $CH_4$ emissions in the U.S) (EPA, 2017). Ethane ($C_2H_6$), which also contributes to surface ozone formation and impacts the oxidative capacity of the atmosphere, is co-emitted with $CH_4$ derived from NG systems but not from non-fossil sources (Brandt et al., 2016; Helmig et al., 2016; Schoell, 1980; Simpson et al., 2012; Xiao et al., 2008). Considering the impact of $CH_4$ and $C_2H_6$ in the atmosphere, fugitive emissions from NG systems may potentially outweigh the benefits associated with increased NG usage derived from replacement of coal and oil (Brandt et al., 2016).

Despite multiple studies investigating NG leakage occurring in production and processing stages (Allen et al., 2015; Brantley et al., 2014b; Mitchell et al., 2015; Subramanian et al., 2015; Zavala-Araiza et al., 2015), particular uncertainty remains on the extent of $CH_4$ emissions associated with NG distribution systems (NGDS), which

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deliver this fuel to final residential and commercial consumers in urban areas (Hendrick et al., 2016; Jackson et al., 2014). This uncertainty is reflected by differing estimates by the 1990–2010 U.S. GHG inventory (EPA, 2012) and a recent study by Lamb et al. (2015), which based on measurements in thirteen U.S urban distribution systems reported 36–70% lower $CH_4$ emissions from NGDS. Furthermore, the most recent U.S. GHG inventory (EPA, 2017) estimates $CH_4$ emissions from NGDS ~65% lower than the 1990–2013 U.S. GHG inventory for the same period of time (e.g., 2011–2013) (EPA, 2015b, 2017). NGDS have been identified as relevant $CH_4$ emission sources in different U.S. urban areas with reported NG loss rates from local NGDS varying between ~2 and 6%, and nationwide estimates between 0.1 and 0.22% (Cambaliza et al., 2015; Lamb et al., 2015, 2016; McKain et al., 2015; Wennberg et al., 2012).

In the past 60 years, the NGDS infrastructure in the U.S. has evolved from being mainly constituted by leak-prone materials such as unprotected steel (bare steel, BS) and cast iron (CI) to being dominated by plastic pipelines (DOE, 2017; PHMSA, 2016b). Pipeline replacement programs have followed distinct dynamics in different U.S. states, leading to local NGDS with marked differences in pipeline composition and infrastructure age (DOE, 2017; Gallagher et al., 2015). As such, it is expected that leaks from the NGDS are highly spatially dependent.

Recent initiatives such as those of the Environmental Defense Fund and Google Earth Outreach (von Fischer et al., 2017) have conducted $CH_4$ leak surveys in several U.S. urban areas, following previous studies mostly conducted in Northeast and Midwest cities (Chamberlain et al., 2016; Gallagher et al., 2015; Hendrick et al., 2016; Jackson et al., 2014; Lamb et al., 2016; McKain et al., 2015; Phillips et al., 2013). The incidence of $CH_4$ leaks associated with NGDS has been reported as significant for urban centers with aging NG infrastructure including Washington D.C., Boston, MA and New York City, and more moderate for cities such as Durham, NC, Cincinnati, OH and Ithaca, NY (leak densities ranging between 0.22 and 4.3 leaks/road mile) (Chamberlain et al., 2016; Gallagher et al., 2015; Jackson et al., 2014; Phillips et al., 2013). In addition to emissions from local NGDS and end-use uncombusted NG, emissions from compressed NG (CNG) fueled vehicles have been reported as relevant urban sources of atmospheric $CH_4$ (Curran et al., 2014; Hesterberg et al., 2008; Lamb et al., 2016; von Fischer et al., 2017).

The reported variability in NG leakage across the U.S. and the potential occurrence of $CH_4$ emissions from distinct in-use NG sources in urban centers highlight a need for area-specific investigations of enhancements in atmospheric $CH_4$ levels associated with NG distribution and usage. Although the Greater Houston area (GHA) is the fifth-largest metropolitan area in the U.S. and Houston is the most populated center in Texas (which in turn is the largest consumer of NG and has the second largest CNG vehicle fleet in the U.S. (EIA, 2015)), no studies on the occurrence of $CH_4$ emissions associated with the use of NG in this urban center have been reported in the scientific literature to date.

This paper describes an initial study on the incidence of NG-related $CH_4$ emissions in selected zones of the GHA during August and September 2016. Daytime mobile-mode monitoring of $CH_4$ and $C_2H_6$ concentrations was conducted primarily in eight selected residential zones with high, medium and low expected probability of $CH_4$ emissions, according to selected proxies for NGDS infrastructure age and NG usage. Multi-day sampling was performed in zones with higher expected probability of $CH_4$ emissions, while single-day monitoring was conducted in zones with lower potential of $CH_4$ leakage. More limited $CH_4$ and $C_2H_6$ sampling was completed at three GHA neighborhoods with recent reports of NGDS-related incidents associated with pipelines dating back to 1945 (PHMSA, 2016a). Additionally, monitoring of $CH_4$ and $C_2H_6$ levels was conducted continuously while en route to the selected sampling areas. Total monitoring comprised ~90 h of $CH_4$ and $C_2H_6$ concentration data and encompassed approximately 250 exclusive road miles.

$CH_4$ and $C_2H_6$ mixing ratios were measured employing a novel infrared laser-based sensor system developed for simultaneous detection of these gas species based on a single 3.337-μm light source. The compactness of this sensor system, derived mainly from the use of a single laser source and reduced-size electronics, enables its use in mobile-mode environmental monitoring allowing $C_2H_6/CH_4$ ratio-based $CH_4$ source discrimination analyses. While $CH_4$ source profiling based on off-line analysis of $(C_2H_6 + \text{propane})/CH_4$ ratios in limited subsets of samples and using the $C_2H_6/CH_4$ ratio employing separate $CH_4$ and $C_2H_6$ instruments has been previously demonstrated (Jackson et al., 2014; Yacovitch et al., 2014), this study reports, for the first time, the application of a single dual-gas instrument enabling continuous $CH_4$ source identification.

## 2. Methods

### 2.1. Selection of sampling zones

Eight residential zones in the GHA with distinct expected probability of NG leakage were selected for monitoring of $CH_4$ and $C_2H_6$ levels. The median housing age (MHA) and the NG heating units density (HUD), as proxies for the NGDS infrastructure age and NG consumption, respectively, were used to define the expected probability of $CH_4$ leakage in the block groups in the GHA (United States Census Bureau, 2014). Four categories of expected $CH_4$ leak occurrence (low, high, medium A and medium B) were defined based on the intersection between MHA and HUD levels as depicted in Fig. 1.

The transition between old and new infrastructure was established based on the predominant pipeline materials used in NG distribution systems over the past 60 years and the tendency of these materials to crack and/or leak (Fig. S1, Supplementary Information, SI). According to the timeline in Fig. S1, pre-1980 and post-1990 block groups in the GHA were classified with higher and lower expected probability of $CH_4$ leakage, respectively (high and medium A, and low and medium B categories in Fig. 1, respectively). This timeline coincides with the approximate transition between metal and plastic pipelines in the Houston area according to non-official information provided by the local NG distribution company (CenterPoint Energy Entex).

Census data from the American Community Survey (United States Census Bureau, 2014) were used to identify neighborhoods in the GHA associated with high density of pre-1980 and post-1990 housing units (above the $90^{th}$ percentile of the housing unit density in each category for the Houston area). The statistical distribution of the HUD in the preselected zones was examined, and the 10th and $90^{th}$ percentiles of this

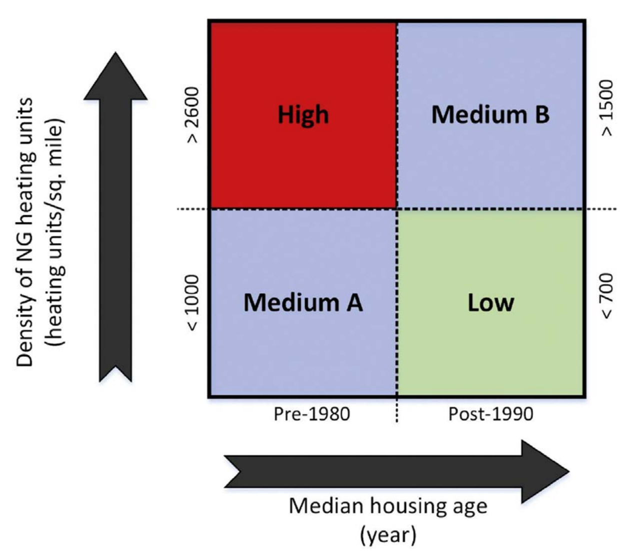


**Fig. 1.** Expected probability of NG leakage based on median housing age and density of NG heating units as proxies for infrastructure age and NG consumption, respectively.