

Home is Where the Pipeline Ends: Characterization of Volatile Organic Compounds Present in Natural Gas at the Point of the Residential End User

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Cite This: <https://doi.org/10.1021/acs.est.1c08298>



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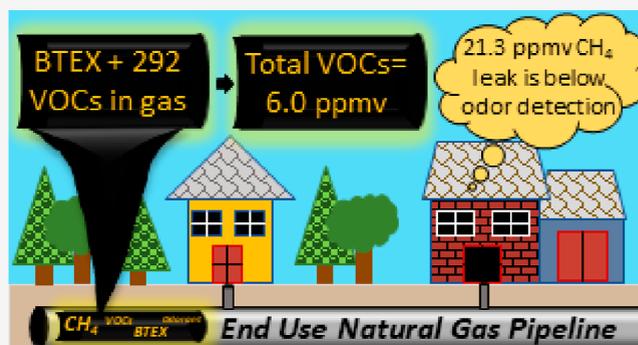
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Supporting Information

ABSTRACT: The presence of volatile organic compounds (VOCs) in unprocessed natural gas (NG) is well documented; however, the degree to which VOCs are present in NG at the point of end use is largely uncharacterized. We collected 234 whole NG samples across 69 unique residential locations across the Greater Boston metropolitan area, Massachusetts. NG samples were measured for methane (CH_4), ethane (C_2H_6), and nonmethane VOC (NMVOC) content (including tentatively identified compounds) using commercially available USEPA analytical methods. Results revealed 296 unique NMVOC constituents in end use NG, of which 21 (or approximately 7%) were designated as hazardous air pollutants. Benzene (bootstrapped mean = 164 ppbv; SD = 16; 95% CI: 134–196) was detected in 95% of samples along with hexane (98% detection), toluene (94%), heptane (94%), and cyclohexane (89%), contributing to a mean total concentration of NMVOCs in distribution-grade NG of 6.0 ppmv (95% CI: 5.5–6.6). While total VOCs exhibited significant spatial variability, over twice as much temporal variability was observed, with a wintertime NG benzene concentration nearly eight-fold greater than summertime. By using previous NG leakage data, we estimated that 120–356 kg/yr of annual NG benzene emissions throughout Greater Boston are not currently accounted for in emissions inventories, along with an unaccounted-for indoor portion. NG-odorant content (*tert*-butyl mercaptan and isopropyl mercaptan) was used to estimate that a mean NG- CH_4 concentration of 21.3 ppmv (95% CI: 16.7–25.9) could persist undetected in ambient air given known odor detection thresholds. This implies that indoor NG leakage may be an underappreciated source of both CH_4 and associated VOCs.

KEYWORDS: fossil fuels, natural gas leak, odorants, cooking, hazardous air pollutants, hazard identification, BTEX



INTRODUCTION

U.S. oil and natural gas (O&NG) production has grown substantially since 1990 and now makes up over 69% of the total U.S. energy consumption. Natural gas (NG) has become the dominant energy source for nearly all-consuming sectors in the U.S., including industrial (41%), commercial (38%), residential (42%), and electrical power generation (33%).¹ Unprocessed NG can vary in the methane (CH_4) fraction (typically 60–90%),² with the remaining fraction consisting of impurities including a suite of nonmethane volatile organic compounds (NMVOCs; e.g., alkanes, cycloalkanes, and aromatics) and nonorganic compounds (e.g., hydrogen sulfide, carbon dioxide, water vapor, nitrogen, and helium).^{2,3} An estimated 2.49 million tons of VOCs are emitted annually from upstream oil and NG production processes alone, making it the largest anthropogenic source of VOCs in the U.S.⁴ The presence of certain NMVOCs in NG, including the aromatic

compounds benzene, toluene, ethylbenzene, and *ortho*-, *meta*- and *para*-xylenes (collectively BTEX), are particularly relevant given their toxicity, carcinogenicity, and/or atmospheric reactivity as precursors to both ozone and secondary organic aerosol (SOA) formation.⁵ While the presence of BTEX in unprocessed NG is well documented,^{5–7} the degree to which BTEX is present in distribution-grade NG when delivered to end users is largely uncharacterized due to lack of direct measurements; for example, a 1994 study noted the presence of benzene in end-use NG, but this was inferred through

Received: December 10, 2021

Revised: June 8, 2022

Accepted: June 13, 2022

ambient air measurements rather than directly from the end use gas stream.⁸ A more definitive characterization of NMVOCs in the end use NG stream is, therefore, warranted, as several NMVOCs could produce air quality impacts and human health risks at any point where NG is leaked or incompletely combusted.

U.S. pipeline operators and local gas distribution companies employ standardized gas chromatography (GC) compositional analytical procedures (i.e., ASTM D1945 or ASTM D7833) on processed NG to determine the heating value and to satisfy tariff gas quality specifications consistent with the North American Energy Standards Board (NAESB) standards. These methods, however, typically focus only on the 16 most abundant constituents (e.g., Supporting Information Table S3); in addition, they generally do not differentiate C6+ organic compounds except for hexane where available. NG utilities do perform more extensive trace gas analyses on occasion; however, these data are typically not publicly available.³ In 1992, the Gas Research Institute (now the Gas Technology Institute) conducted a large-scale NG characterization campaign collecting 6800 samples in 26 major U.S. cities to better determine fuel efficiency related to NG-powered vehicles. While the study found substantial spatial and temporal variability of C1–C3 and inert gases among and within cities, constituent analyses were not differentiated for C4+ hydrocarbons (i.e., “butanes plus”); however, a national mean C₄+ concentration of 0.4 (mol %) was observed with a maximum of 2.1 (10th–90th percentile: 0.1–0.6) indicating the widespread presence of heavier hydrocarbons.⁹ More recently, a study by the National Institute of Standards and Technology identified BTEX and other NMVOCs in distribution-grade NG; however, only two samples were analyzed from the laboratory gas valve supplied by the local NG distribution system in Colorado.³ Two other NG compositional analyses found that underground storage and transmission pipeline NG consisted of approximately 93% methane and ~1% VOC;⁷ however, it is undetermined whether the NG composition in these midstream systems is fully representative of downstream systems.

As federal vehicle emissions requirements continue to regulate NMVOC emissions, nontransportation sources of NMVOCs have become increasingly important and have garnered significant attention in recent years.^{10,11} Given the limited characterization of trace gas-phase compounds in local NG distribution systems, the widespread use of NG, and the numerous studies that have now confirmed NG distribution systems as the largest source of urban methane,^{12–23} we performed a 16 month hazard identification sampling campaign in the Greater Boston region to characterize NMVOC constituents and odorant content in distribution-grade NG. As sampling from distribution-NG infrastructure (e.g., pipelines or gas processing plants) is not possible without operator coordination, we instead accessed the many endpoints of the distribution system via residential NG stoves and building risers. The methods provide a safe and reliable approach for sampling whole NG at the point of end users using commercially available the United States Environmental Protection Agency (USEPA) methods. The results demonstrate methane, ethane, mercaptan odorant, and NMVOC whole NG characterization throughout Greater Boston, MA, with implications for air quality at any point where NG is leaked or incompletely combusted.

METHODS

Sample Collection and Processing. All sampling procedures and safety protocols were IRB approved with an additional approval from Harvard’s chief research compliance officer. This project received IRB approval on October 29, 2019, from the Harvard T.H. Chan School of Public Health, ref: IRB19-1587 titled “Contaminants in the Kitchen.”

Whole NG samples were collected from indoor NG-fired stovetop appliances and outdoor gas appliance lines across three local NG distribution territories. VOCs were analyzed by GC/mass spectrometry via grab samples of whole NG collected in evacuated 1.4L Entech Silonite-lined canisters prepared by a commercial environmental testing lab (Phoenix Environmental Laboratories, Manchester, CT) according to the USEPA Method TO-15. To verify sufficient sample capture, a subset of samples was tested for CH₄ and C₂H₆ using the USEPA Method 3C performed by New England Testing Laboratory, West Warwick, RI (managed internally by Phoenix Environmental Laboratories). Analytical methods for ASTM D1945, ASTM D1946, and EPA 3C are identical, though differ by QC criteria and compounds specified for each method. Tentatively identified compounds (TICs) were also reported for nontarget compounds including thiol-group compounds, such as common NG odorants (e.g., *tert*-butyl mercaptan [TBM; CAS no. 75-66-1], and isopropyl mercaptan [IPM; CAS no. 75-33-2]). TIC identification and estimation generally followed USEPA’s National Functional Guidelines for Superfund Organic Methods Data Review.²⁴ As per this guidance, a compound must meet a set of 10 analytical criteria and 9 QA/QC evaluation checks to be considered a TIC. Most notably, the spectral peak for a TIC must have an area or height >10% of the area or height of the nearest internal standard and must receive a spectral library search match of 80% or higher to meet the definition of a “probable match.” The concentration of a TIC can then be calculated normally by using total ion areas for both the TIC peak and the internal standard with the closest chromatographic retention time. Therefore, tentatively identified sulfur compounds herein are considered “NJ” flagged in that results are qualitatively identified and reported as estimated concentrations based upon the nearest internal standard.²⁴ While ASTM D5504—the standard test method for determining sulfur compounds in NG was not employed—fused-silica lined canisters (i.e., silonite) have been well validated for their suitability for volatile sulfur compound collection.²⁵

Stovetop sample collection entailed a direct in-line connection between the stove’s NG outlet and the sample canister via flexible Teflon-lined tubing (Figure S1). For all stoves sampled, the tubing diameter fully encompassed the gas outlet orifice. The in-line connection effectively bypassed the stovetop ignition source (where present) and ensured that the sample was not diluted by ambient air and that very minimal unburned NG was released. Building NG appliance line sampling was identical to stovetop sampling, except samples were collected from building risers that were typically used to connect to outdoor NG grills or firepits. Canisters were sampled within 5 days of arrival and returned within 3 days of sample collection. All lab analyses were completed within 3 weeks of sampling, and chain of custody forms were maintained for all samples. Samples were donated by homeowners since they were collected after NG was paid for and delivered to the home (i.e., after or “behind” the

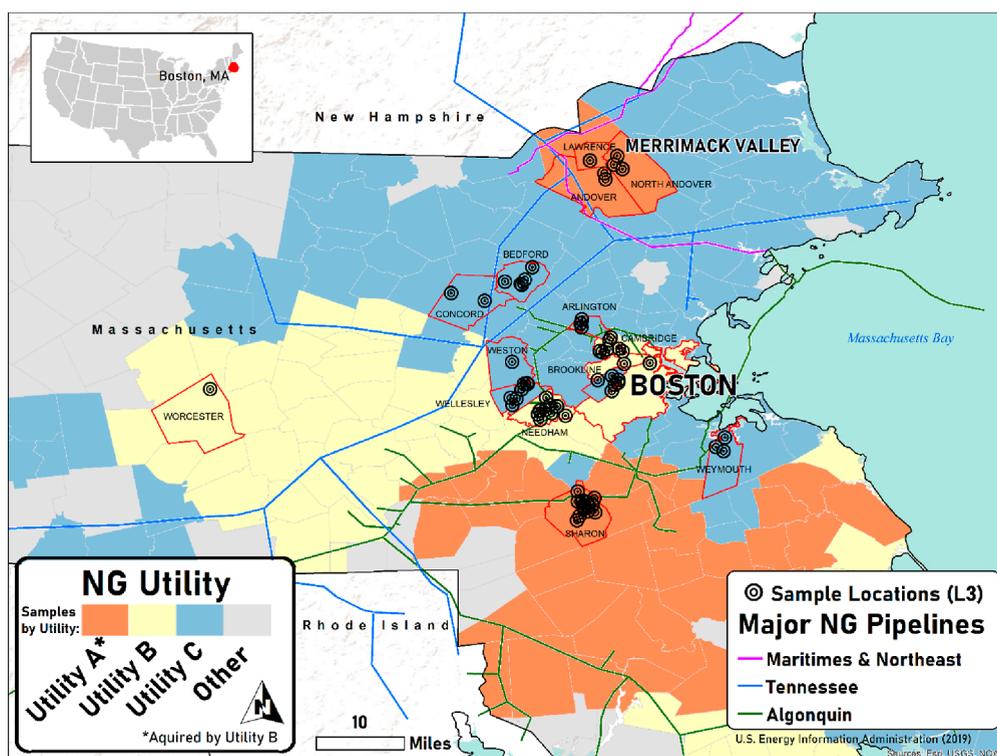


Figure 1. Unique sample locations (black markers) by municipality (red outline) across the three major Greater Boston NG utility providers. Note, some locations were sampled multiple times. *Utility A was acquired by Utility B on October 13, 2020.

Table 1. Top 15 VOCs (Standard TO-15 Suite) with Statistical Measures and Confidence Intervals Derived from a 1000-Sample Bootstrap of Data from 234 Total Whole NG Samples^a

VOC [CAS] (units)	<i>n</i> (% detect)	Mean	SD	95% LCI	95% UCI
methane [74-82-8] (%) ^{b,d}	184 (79) ^c	101	1.0	99.2	103
ethane [74-04-0] (%) ^b	184 (79) ^c	2.07	0.05	1.98	2.17
hexane [110-54-3] (ppbv)	229 (98)	567	61	460	696
benzene [71-43-2] (ppbv)	223 (95)	165	16	136	195
toluene [108-88-3] (ppbv)	220 (94)	151	17	119	197
heptane [142-82-5] (ppbv)	219 (94)	267	26	220	324
cyclohexane [110-82-7] (ppbv)	208 (89)	215	20	176	254
<i>m,p</i> -xylene [108-38-3; 106-42-3] (ppbv)	175 (75)	58	7.2	44.9	73
ethanol [64-17-5] (ppbv)	153 (65)	126	18	92.4	164
<i>o</i> -Xylene [95-47-6] (ppbv)	148 (63)	17.5	2.4	13.1	22.4
ethylbenzene [100-41-4] (ppbv)	131 (56)	12.8	1.7	9.64	16.2
1,2,4-trimethylbenzene [95-63-6] (ppbv)	108 (46)	7.86	1.2	5.62	10.3
4-ethyltoluene [622-96-8] (ppbv)	95 (41)	6.02	0.88	4.35	7.68
1,3,5-trimethylbenzene [108-67-8] (ppbv)	66 (28)	3.04	0.51	2.08	4.06
acetone [67-64-1] (ppbv)	37 (16)	10.3	5.4	2.71	22.1
isopropylbenzene [98-82-8] (ppbv)	31 (13)	0.764	0.2	0.386	1.17
1,2-dichloroethane [107-06-2] (ppbv)	24 (10)	0.0652	0.039	0.0129	0.159

^aVOCs reported as parts per billion by volume (ppbv). A subset of samples was analyzed for methane and ethane using the EPA Method 3C and are reported as vol/vol %. The sample size and frequency of detection are noted by *n* and the associated %. ^bMethane and ethane tested according to the EPA method 3C/modified 3C via aliquot from the original sample canister. ^cMethane and ethane were only regularly tested in samples after the COVID sampling pause. 77% detection reflects the lack of testing rather than implying sampling nondetects. ^dAt high concentrations, reported Methane results can slightly exceed 100% but are within the margin of error for the EPA method 3C. The noise associated with translating GC peak areas to concentrations based on a calibration response curve (area/ppmv) can lead to calculated concentrations that are >100% when sample concentrations are close to 100%.

residential gas meter). See the [Supporting Information](#) Section 1.1 for details on sample collection methodology, including additional sampling safety precautions.

Sampling Design. A spatially-stratified sample design was employed to represent the three major local distribution

companies (Columbia Gas, Eversource, and National Grid—see [Figure 1](#)) that operate across the Greater Boston region. The sampling campaign was originally designed to capture 90 unique sampling locations—sampled twice in each of the cooling and heating seasons—in addition to 10 unique

locations (100 total sampling sites) sampled approximately monthly (“monthly”) for 12 months to resolve temporal variability; however, the COVID-19 pandemic required an alteration to this sample design. Sampling was suspended on March 12, 2020, in response to the COVID-19 pandemic. By that time, our research team had collected 109 samples from 81 unique locations across our six sampling areas and approximately 4 months of sampling at the 10 “monthly” locations. Abbreviated sampling activities were reinstated on June 26, 2020; however, our original sampling plan was altered as follows. First, additional sampling was limited to “monthly” stovetop sampling for pre-existing and willing participants that were repeated monthly for 11 months. We also recruited 20 new participants within our target areas who had an accessible outdoor NG service line typically connected to an outdoor NG-fired grill (i.e., not propane). In addition, two stove participants switched to sampling from their outdoor NG grill. Each of these NG grill locations were sampled at least twice.

Data Filtering Methodology. The final analysis-ready data set (L3) contained 234 individual samples collected from 69 unique residential NG grills and NG stoves. The original raw data set (L1) contained 312 samples and underwent two iterations of quality control and filtering to ensure that all final data were representative of end use whole NG. While all post-COVID pause samples included methane and ethane analyses, only the last 19 of the 109 pre-COVID pause samples were tested for ethane and methane. Therefore, in the absence of methane and ethane measurements, we combined the pre- and post-COVID pause samples in an analytical framework to maximize our confidence in sample capture sufficiency without unnecessarily rejecting valid samples lacking methane content measurements. Correlation matrices indicated NG capture was highly positively correlated with the extent to which an evacuated sample canister was filled and highly negatively correlated with the length of time to fill a canister (See the Supporting Information Figures S4 and S5). See the Supporting Information Section 1.2 for additional details on the data filtering results and methodology.

Sample Collection QA/QC. A total of four sampling blanks were collected (two field blanks, two sample tubing blanks); all blanks were returned clean (i.e., criteria compounds were nondetects) and were removed from the main analysis data set. In addition, seven sample duplicates were collected (four from stoves, three from grills) and were retained as additional samples in the main analysis. Using BTEX as a replicate precision indicator, the median percent error aggregated across each set of sample duplicates was 1.7, 2.6, 5.8, and 8.1 for each of the four BTEX constituents, respectively. As per USEPA method guidance, these precisions indicate acceptable repeatability and are also within one standard deviation of the BTEX means from the full data set (benzene: $\pm 9.7\%$; toluene: $\pm 12\%$; ethylbenzene: $\pm 14\%$; xylenes: $\pm 13\%$; see Table 1).

Ethane: Methane Ratio. Ethane (C_2H_6) is typically used as a thermogenic CH_4 tracer for attributing CH_4 measurements to NG sources in the absence of other appreciable sources of thermogenic methane (McKain et al., 2015). We obtained C_2H_6/CH_4 ratios for 184 samples as an additional indicator for sufficient NG sample collection.

VOC Emissions from NG in Great Boston Region. To estimate emissions of VOCs from NG systems throughout the Greater Boston region, we bootstrapped mean ratios of VOCs to whole NG- CH_4 from our data set in combination with

previous regional CH_4 emissions apportioned to NG systems over the approximately 90 km Greater Boston radius.^{17,20,22} Following similar methods to Marrero, Townsend-Small,²⁶ and Deighton, Townsend-Small,²⁷ emission rates ($kg\ yr^{-1}$) of BTEX associated with CH_4 from NG leaks were calculated according to eq 1, where the CH_4 flux ($kg\ yr^{-1}$) is directly taken from each of McKain, Down,¹⁷ Plant, Kort,²⁰ and Sargent, Floerchinger;²² MW is the molecular mass of CH_4 and each BTEX constituent in $g\ mol^{-1}$; and $[BTEX]/[CH_4]$ is the bootstrapped mean ratios of each BTEX constituent (ppbv) to CH_4 (ppbv) across our field sample data set. See the Supporting Information Section 2.9 for additional details on this calculation.

$$\begin{aligned} \text{BTEX emissions (kg yr}^{-1}\text{)} \\ &= CH_4 \text{ flux (kg yr}^{-1}\text{)} \times MW \text{ BTEX (g mol}^{-1}\text{)}/MW \\ &\quad CH_4 \text{ (g mol}^{-1}\text{)} \times [BTEX]/[CH_4] \end{aligned} \quad (1)$$

RESULTS AND DISCUSSION

Overview of Final Analysis Data Set. We initially collected 312 NG samples from 99 unique households throughout the Greater Boston region. After removal of flagged samples and blanks, along with two layers of quality control, 234 whole NG samples across 69 locations were retained, reflecting a 77% sample retention (see the Supporting Information Section 1.2 for details on QC data processing). Unique sample locations were spatially representative across the three major local distribution companies (utility A, $n = 20$; utility B, $n = 20$; utility C, $n = 29$; see Figure 1). Two separate winter (heating) seasons were sampled, spanning December 2019 to May 2021. In addition, locations were sampled throughout the December 2019 to May 2021 period to produce an 18 month time series (barring a 4 month sampling pause from April to July 2020 due to restrictions during the COVID-19 pandemic).

Verifying Sample Representation of the NG Stream. Whole NG sample collection was verified using multiple analytical markers. Of the 234 L3 samples, 184 were analyzed for CH_4 and C_2H_6 . 92% of the samples measured for CH_4 and C_2H_6 exhibited a sample CH_4 concentration of 90% or greater. The bootstrapped mean CH_4 concentration of the L3 data set was 101% (95% CI: 99.2–103%). Note that at concentrations that approach 100% CH_4 , reported CH_4 results can slightly exceed 100% due to measurement and calculation noise; however, these concentrations are within the margin of error for the EPA method 3C (see explanation in Table 1). Importantly, unlike many of the accompanying NMVOC compounds that exhibited a high skew, the raw C_2H_6/CH_4 ratios approach a normal distribution with a median ratio of 1.89 (median absolute deviation: 0.34%), indicating that regardless of the individual sample CH_4 content, the CH_4 itself was NG in origin (Figure S7). Our C_2H_6 and CH_4 results agree with posted pipeline hourly data and previous research showing Boston NG pipeline C_2H_6/CH_4 ratios of 2.04% (2.01, 2.07%) with a corresponding NG percentage of 110 (68,170).²⁰ Additionally, two of the primary NG odorant compounds were frequently detected: TBM was detected in 97% of samples, and IPM was detected in 81% of samples (see below). Finally, the iso-pentane to *n*-pentane (iC_5/nC_5) ratio has been utilized elsewhere as a source signature of O&NG.²⁸ Using reduced major axis (RMA) regression, we found an $iC_5/$

nC_5 ratio of 1.48 (95% CI: 1.44–1.52; $R^2 = 0.95$) that approximates enhancement ratios of raw NG downwind of O&NG operations (0.82–1.10) and is distinctly different than the iC_5/nC_5 ratio of 2.96 consistently reported for sources related to fresh gasoline.²⁹ Collectively, these analytical markers indicate a high fidelity of whole NG sample capture of the L3 data set with minimal ambient air intrusion and residential NG as the source of NMVOCs.

NMVOC Profile of End Use NG Samples and Implications for Exposure to Hazardous Air Pollutants.

From the L3 data set, 296 unique constituents were detected in end use NG, of which 21 (or approximately 7%) are designated as hazardous air pollutants (HAPs) (see accompanying analytical results). The top 15 VOCs and TICs by abundance are shown in Table 1 and Supporting Information Table S2, respectively. Given the long-tailed distribution, statistics were derived from bootstrapping (1000 resamplings). We found that benzene and toluene are persistent in distribution-grade NG at the point of the end user (Table 1). Benzene (mean = 165 ppbv; SD = 16; 95% CI 136–195) and toluene (mean = 151 ppbv; SD = 17; 95% CI 119–197) were detected in 95 and 94% of samples, respectively. Hexane, heptane, and cyclohexane were also commonly detected at 98, 94, and 89%, respectively (Table 1). Overall, the mean total NMVOCs in distribution-grade NG throughout the study area was ~ 6.0 ppmv (95% CI 5.5–6.6; max 21.4 ppmv); the NMVOC total for each sample is the sum of all TO-15 and TICS NMVOCs, excluding ethane. While the concentrations of BTEX observed in NG herein are likely lower compared to other source types, the proximity of these emissions to populations—and the widespread use of NG indoors warrants further exposure assessment. Moreover, given benzene's genotoxicity, no safe level of benzene exposure can be recommended, which is often reflected in its relatively low reference exposure levels. For example, the Commonwealth of Massachusetts has a threshold effect exposure level of 0.2 ppbv (24 h average) and an annual average allowable ambient level of 0.03 ppbv ($0.1 \mu\text{g}/\text{m}^3$) for benzene.³⁰ Therefore, addressing NG-methane leakage for climate reasons may produce additional health co-benefits through this inhalation risk pathway.

Recently, there has been an acknowledgment of the increasing contribution of indoor emissions of certain VOCs from volatile chemical products impacting air quality^{11,31} both as direct human health toxicants and indirectly as ozone precursors and precursors of SOA that make up a fraction of $\text{PM}_{2.5}$. Sourcing indoor emissions of VOCs largely to household chemical products (e.g., pesticides, coatings, adhesives, cleaning agents, and personal care products), McDonald et al.¹¹ notably did not consider indoor sources of VOCs coemitted with NG, noting that “NG is a clean-burning fuel, so combustion emissions of VOCs located at the point of use are small and negligible.” This assumption likely misclassified any VOC emissions associated with both fugitive emissions and combustion-related emissions from NG-fired appliances such as cook-top burners, ovens, and ventless heaters that are not automatically vented to the outdoors. To date, three studies^{12,18,23} and one critical review²¹ have quantified unburned NG emissions (CH_4) indoors, indicating that cooking appliances (stovetops and ovens) exhibit the highest emissions rates per unit fuel consumption compared to other appliances.¹⁸ Steady-state-off emissions from cooking appliances have been shown to contribute disproportionately

to total cooking appliance-use emissions, indicating the presence of a persistent leakage source of NG and associated VOC emissions.²³ Moreover, the long-tailed distribution of steady-state-off leakage rates observed by Lebel et al.²³ carries implications for understanding the range of potential VOC exposures from leaking NG appliances, particularly from cooking appliances that are likely centrally located within the home and are generally not required to be externally ventilated. There is also evidence showing the formation of gas-phase aromatics and polycyclic aromatic hydrocarbons from CH_4 combustion itself through multiple kinetic pathways that coincidentally are not removed by coformation of soot particles due to methane's relatively clean burning nature.^{32–34}

Odorant Detection Thresholds: Implications for Chronic CH_4 Leaks and HAP Exposure. From the Supporting Information Table S2, the most abundant TIC observed was the NG odorant TBM (97% detection) ($\mu = 579$ ppbv; SD = 41; 95% CI 499–661). The other commonly detected odorant, IPM, was also detected in 81% of samples ($\mu = 22.2$ ppbv; SD = 3; 95% CI 16.8–28.3). Notably, no differences were observed between gas companies for either TBM ($X^2 = 4.9$; $p = 0.2$) or IPM ($X^2 = 2.8$; $p = 0.09$); however, both TBM and IPM exhibited substantial variability with 3 and 2 orders of magnitude, respectively, yet were highly correlated (Pearson's $r = 0.94$, $p = <0.00001$). This variability was partly explained by seasonal variability with significantly lower odorant concentrations in the winter season for both TBM ($X^2 = 20.9$; $p = 0.007$) and IPM ($X^2 = 25.2$; $p = 0.001$). This variability is also partly explained by the fact that TBM and IPM were outside the target compound list as per the USEPA Method TO-15 and, therefore, are considered “NJ” flagged results that exhibit a high degree of uncertainty in terms of compound detection and concentrations. However, given the high frequencies of detection and the suitability to identify sulfurous compounds using fused silica-lined canisters, quantitative results are reported but should be viewed with extra caution. Furthermore, odorants are reported to be added to NG at concentrations ranging from 1–4 ppmv,^{35,36} which agree with odorant data observations, particularly, after considering the likelihood of decreased odorant concentrations at the point of the end user due to some expected odor fade or other forms of degradation or removal.³⁷

According to federal regulations (49 CFR 192.625), distribution-grade NG must contain odorants at a detectable concentration in air that is one-fifth of the lower explosive limit (LEL) for NG—that is, equal to detectable odor at $\sim 1\%$ NG in air by volume. While general human odor detection thresholds can differ by up to 1000-fold for the least and most sensitive population subgroups, a recently updated odor detection threshold for the NG odorant TBM was estimated at 6.26×10^{-3} ppbv^{37,38} and is similar to the odor detection threshold for IPM.³⁹ Using these criteria, all samples that reported TBM ($n = 235$) met the 6.26×10^{-3} ppbv odor threshold (not including IPM or other thiol compounds) at one-fifth the LEL. The lowest TBM concentration at this level was 0.09 ppbv which also meets less conservative TBM odorization detection thresholds of 0.08³⁹ or 0.029 ppbv.⁴⁰ Relatedly, after scaling CH_4 content to 100% minus $\text{C}_2\text{H}_6\%$ in all samples, we found that 1% CH_4 —or approximately 1/5th the LEL—would coincide with a mean benzene concentration of 1.66 ppbv.

Using the sampled NG odorant content, we can also determine an NG leakage CH_4 concentration that coincides with the odor detection threshold—or the CH_4 level in air at

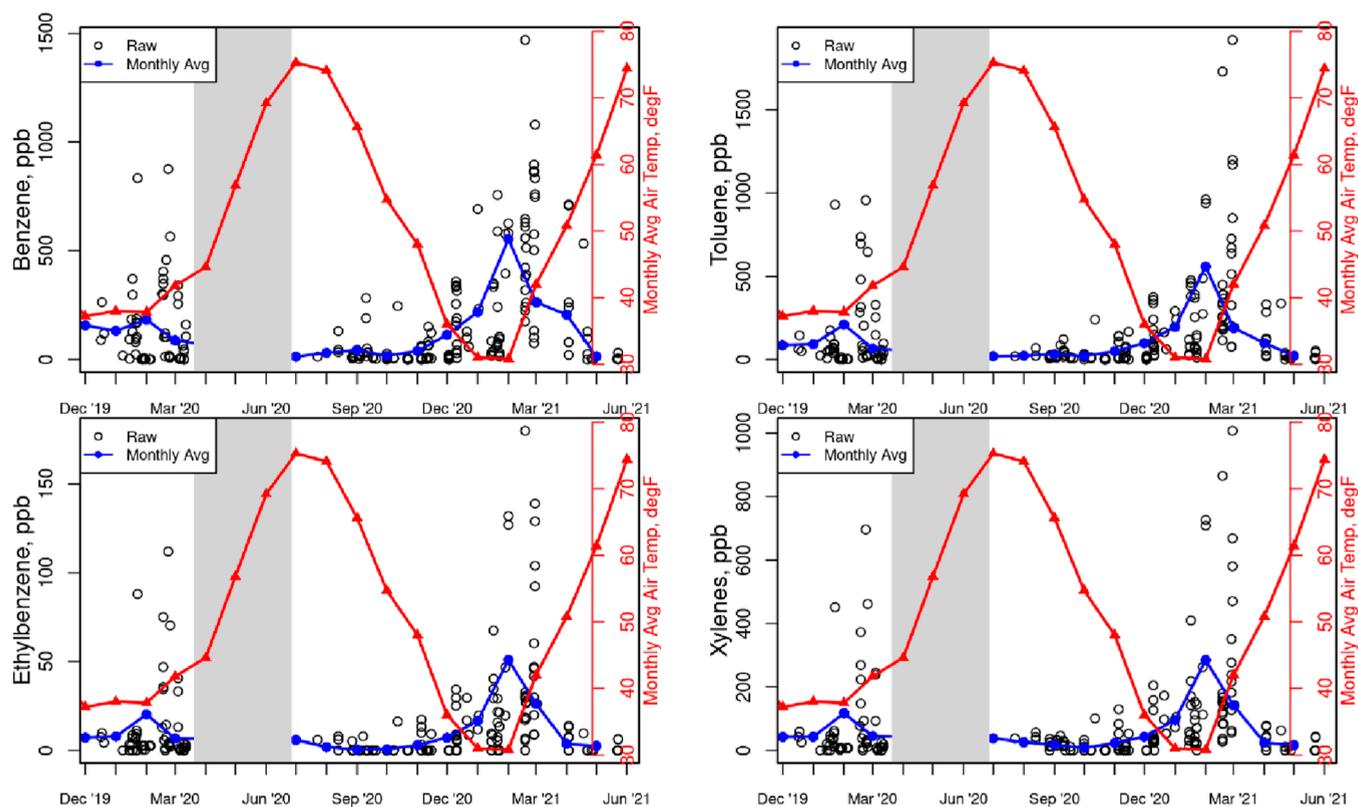


Figure 2. BTEX content of NG in raw (markers) and monthly averages (blue). Monthly averaged regional air temperature ($^{\circ}\text{F}$) from the National Oceanic and Atmospheric Administration (NOAA) is displayed in red. The COVID-related sampling pause from mid-March 2020 through mid-July 2020 is highlighted in the grey box.

which the odorant in NG cannot be detected by 50% of persons with a normal sense of smell. Given the similarity in odor detection thresholds for both TBM and IPM, we added the odorant concentrations together and used a 6.26×10^{-3} ppbv odorant detection threshold taken from the literature.^{38–40} Using the 184 NG samples that were analyzed for CH_4 , TBM, and IPM, we conserved the mean molar ratios and found that the odor detection threshold of 6.26×10^{-3} ppbv coincided with a mean concentration of 21.3 ppmv CH_4 (95% CI: 16.7–25.9) and median of 8.8 ppmv (see the [Supporting Information](#) Section 2.10 for details). This implies that a steady-state ambient NG- CH_4 concentration of approximately 21.3 ppmv could persist undetected by persons with a normal sense of smell, and perhaps greater concentrations for those with anosmia⁴¹ and those who may be unable to smell NG odorants either chronically and/or as a result of COVID-19 illness.⁴² However, this NG-associated CH_4 odor threshold requires additional verification considering the unreliability of these TIC odorant data and is likely an overestimate, assuming that sulfurous compounds in NG went undetected or were underestimated. Additionally, NG leak detection would be mediated by other factors as well, such as the location of a leak within a home, considering that the heavier sulfur-odorant compounds tend to sink versus CH_4 , which is lighter than air. Nonetheless, Sargent et al.²² recently found that an estimated $2.5 \pm 0.5\%$ of NG entering the Boston region is lost, noting that emissions are correlated with seasonal end use consumption implying that emissions may predominate from consumption-driven source types that includes beyond-the-meter leaks and residential end use appliances. The odorant content observed in end use NG in combination with known

odor detection thresholds supports this hypothesis in the sense that small NG leaks may persist undetected and, therefore, may be more prevalent and not be immediately mitigated as has been previously assumed.

The odorant-threshold CH_4 concentration of 21.3 ppmv coincides with a mean benzene concentration of 0.004 ppbv—a concentration below MA’s annual average allowable ambient level of 0.03 ppbv. Assuming a steady-state ambient concentration and ignoring any chemical transformation or other sinks, a CH_4 concentration of 21.3 ppmv would require the benzene content in NG to exceed 1162 ppbv to reach MA’s allowable ambient level of 0.03 ppbv, which was not met in any samples herein (maximum whole NG benzene = 1080 ppbv). In their annual air quality reports, the Massachusetts Department of Environmental Protection (MassDEP) provides annual averages of 24 h outdoor ambient benzene concentrations measured at two monitoring sites within the greater Boston area (Boston, MA and Lynn, MA). The average annual 24-h ambient benzene during 2010–2020 ranged from 0.11 to 0.19 ppbv (Boston) and 0.09–0.13 ppbv (Lynn). Therefore, assuming similar indoor benzene levels, benzene coemitted with the 21.3 ppmv NG- CH_4 odorant threshold represents a 3% (95% CI: 2–4) enhancement over ambient with a 20% enhancement using the maximum observed whole NG benzene concentration of 1080 ppbv. Alternatively, in scenarios where NG can be detected by odor, such as at some gas utility worksites, it’s possible that NG concentrations would be high enough to produce a benzene concentration that exceeds MA’s AAL but likely not result in scenarios where OSHA’s 8 h time-weighted average limit of 1 ppmv or the 15

Table 2. BTEX by Local Distribution Company Territory^a

	mean (95% CI) for BTEX constituents by LDC, ppbv			
	benzene	toluene	ethylbenzene	xylene
Columbia (utility A)	236 (171, 302)	249 (158, 349)	24.4 (14.8, 35.4)	146 (87.6, 213)
Eversource (utility B)	122 (78, 171)	98.5 (57.9, 147)	8.57 (5.08, 12.7)	50.3 (30.3, 74.0)
National Grid (utility C)	143 (109, 180)	123 (92.6, 157)	8.94 (6.03, 12.0)	54.3 (41.02, 69.5)
Difference (Columbia—Eversource)	114 (111, 116)	150 (147, 154)	15.8 (15.5, 16.2)	95.7 (93.8, 98.1)
Difference (Columbia—National Grid)	93.3 (90.8, 95.8)	126 (123, 129)	15.5 (15.1, 15.8)	91.7 (90.0, 94.1)
Difference (Eversource—National Grid)	-20.9 (-22.8, -19.0)	-24.1 (-25.9, -22.4)	-0.365 (-0.514, -0.215)	-4.00 (-4.76, -3.12)

^aAll statistics are derived from bootstrapped L3 data. Significant differences between LDCs are denoted by *italicized bold font*.

min short-term exposure limit of 5 ppmv for benzene is exceeded (29 CFR 1910.1028).

Characterizing Variability in NMVOC Content of NG with a Focus on BTEX Compounds. We also observed strong temporal trends in BTEX across the 18 month sampling campaign. Generally, BTEX content in NG peaked during the late winter season, with the highest overall concentrations observed spanning the 2020–2021 winter season (i.e., February to March 2021). As shown in Figure 2, the variability of BTEX in NG also increased substantially in the winter months compared to other seasons. In aggregate, winter BTEX concentrations were 3-fold greater on average compared to the spring season and nearly 8-fold greater than the summer season. The maximum BTEX concentrations were observed at nearly the same time of the year in the two successive heating seasons (late February). Notably, the wintertime BTEX peak also corresponded with regional low ambient air temperatures potentially corresponding with an increased NG demand which can alter NG source and supply practices (e.g., upstream underground storage withdraws, LNG-peak shaving).⁹

Consistent with the observation that greater CH₄ emissions coincide with NG usage during winter months, NMVOCs enhancement in NG observed during the winter months suggests that seasonality is an important effect modifier in considering potential associated health risks of leaked NG. For instance, lower indoor air exchange rates are generally more prevalent during the winter months, particularly for homes that rely on radiant heat, which could prolong exposure to any indoor NG emissions.^{43,44} In regard to ambient air, photochemical activity (i.e., OH radical availability) is generally lower in the wintertime compared to summer, effectively increasing atmospheric lifetimes of certain NMVOCs such as BTEX.⁴⁵ Additionally, lower NG odorant content in the winter season was unexpected. One explanation could be that a higher odorant content is used during the warm season to counteract increased diffusivity of thiol compounds into pipe materials with increased temperatures;⁴⁶ however, it is ultimately unclear whether the variability in odorant content was intentional or a result of physiochemical processes.

Sample collection was designed to capture NG composition by the three largest local distribution companies in MA (LDCs, i.e., distribution utilities) to create a representative stratified sample (Figure 1). NG BTEX abundances varied by LDC and were elevated in Columbia's territory (utility A in Figure 1), as indicated by bootstrapped CIs (Table 2). All BTEX constituents were each significantly elevated in samples collected from Columbia's former territory compared to Eversource (utility B in Figure 1) and National Grid (utility C in Figure 1) (note—Eversource acquired all territories previously owned by Columbia Gas on October 13, 2020). Notably, Columbia's former service territory in MA entailed

two geographically distinct territories—one in the Merrimack Valley (Lawrence, Andover, North Andover, MA—Figure 1), and the other encompassing a large swath south of Boston. Upon the finding of BTEX differences by territory, results were further differentiated by location and showed that elevated BTEX in the Merrimack Valley largely explained the elevated BTEX in Columbia's territory. For example, mean NG benzene concentrations were 439 ppbv in the Merrimack Valley compared to 102 ppbv in Sharon, MA—an area serviced within Columbia's former south Boston territory—and the differences were significant ($t = 4.08$; $p = 0.0006$). Moreover, NG NMVOCs were significantly higher in the Merrimack Valley region compared to all other contiguous municipalities that were sampled. These results suggest that the geographic location better explains trace gas variability or is a better proxy for gas source and that service territory may have only a marginal or second-order effect.

We next attempted to differentiate NG end use from its major transmission pipeline source; however, the complexity of the pipeline systems and lack of definitive pipeline flow data did not lend to clear source apportionment for individual samples. Both the Algonquin and Tennessee pipelines traverse the Greater Boston area from the west, which would coincide with estimates that, on average, 84% of the region's NG is generally sourced from the Marcellus formation.⁴⁷ A third transmission pipeline, the Maritimes & Northeast pipeline, traverses the Canadian Maritimes provinces and through Maine prior to reaching its terminus in the Merrimack Valley, which could indicate a distinct NG source into the area that could help explain the elevated NMVOCs observed in the Merrimack Valley. It is also worth noting that all sample collection in the Merrimack Valley occurred after the overpressurization event that took place on September 13, 2018. It is therefore unclear to what extent, if any, the subsequent replacement of ~77 km of underground pipelines had on results herein.

Provided that both substantial temporal and spatial variability were observed, we formally tested the differential variability of space (σ_{sp}^2) versus time (σ_t^2). σ_t^2 was calculated by pooling variances from each unique location having two or more samples across multiple dates. Similarly, σ_{sp}^2 was calculated by pooling variances from each sampling day having two or more samples across multiple locations. All BTEX constituents varied approximately twice as much across time than across space. In contrast, CH₄ varied approximately 3 times as much spatially versus temporally. However, while the CH₄ content of NG showed a higher spatial variance compared to temporal variance, this is not unexpected and is more likely an artifact of differential sample capture sufficiency rather than actual CH₄ variation across samples. See the Supporting

Information Section 2.3 and Supporting Information Table S1 for details of this analysis.

While it was beyond the present scope to formally test root causes of seasonal and locational NMVOC variability in NG, possible sources of variation are likely some combination of hydrocarbon sources via transmission pipeline,² natural reservoir variability,³ NG processing steps and time in transit, and⁴ utilization of supplemental hydrocarbon sources, such as upstream underground NG storage or LNG facilities. The observed ~1 month lag between temperature lows and peak BTEX could also signal an NG source change, whereby this latency period could represent a depletion of initial NG reserves and a switch to other NG sources (e.g., LNG-peak shaving). Increased C4+ concentrations were observed by Liss et al.,⁹ where it was noted that LNG- and propane-peak shaving practices—deployed during peak demands during the heating season—had the greatest effect on the composition of NG delivered to customers. It is unclear to what degree peak shaving was utilized during sample collection herein; however, very low NG-propane content was observed, reducing the likelihood of any propane-peak shaving ($\mu = 579$ ppbv; see Table S2).

Overall, it is difficult to infer the generalizability of data collected in the Greater Boston area to areas outside of this. However, considering that most of the Northeastern U.S. sources NG in a similar manner, data collected herein are likely representative of the major cities along the northeast. We also note that benzene and hexane were highly correlated within our data set with an $R^2 = 0.80$ ($p < 0.0001$). Considering that publicly available midstream NG postings typically report NG hexane abundance, it is noteworthy these data appear to provide a reasonable approximation of the NG benzene content. From this study, the abundance ratio of benzene/hexane was 0.28 (95% CI: 0.26–0.30, RMA regression) (see the Supporting Information Section 2.4), which could be used as a scaling factor to infer benzene concentrations from hexane concentrations, assuming these relationships are robust outside of the data collected herein.

Using BTEX concentrations from this and other NG composition studies, it is also possible to calculate source-dependent ratios of individual constituents relative to benzene. While the magnitude of individual BTEX constituents can vary significantly across individual samples, the relative abundances of toluene, ethylbenzene, and xylenes to benzene collectively across all samples were relatively consistent (Table 3). In general, NG is benzene-dominant (or on par with toluene) relative to other anthropogenic sources of BTEX, such as gasoline combustion, which tends to be toluene-dominant, exhibiting a T/B ratio > 2 .⁴⁸ While it is unclear whether whole NG NMVOCs measured in Boston are representative of other cities or upstream portions of its supply chain, NG BTEX abundance ratios in Table 3 indicate that the geologic source likely exhibits a greater NG VOC variability than the variability between midstream and downstream portions of the supply chain. For example,⁴⁹ the distinct differences found in T/B molar ratios between SW PA and NE PA drilling regions possibly indicate distinct hydrocarbon makeup in the Marcellus region, PA alone. Similarly, Marrero et al.²⁶ found clear differences in NMVOC content measured downwind of various portions of the NG supply chain in the Barnett region of Texas. Nonetheless, given the difficulty in distinguishing BTEX sources in urban areas,⁵⁰ these data provide a distribution-grade NG source signature for comparison to

Table 3. Relative Abundances of Previously Published NG-Sourced BTEX Compared to the Present Study

	T/B (95% CI)	E/B (95% CI)	X/B (95% CI)
downstream—this study ^a	1.1 (1.0,1.2)	0.11 (0.10, 0.12)	0.59 (0.53, 0.65)
downstream—distribution-grade NG ($n = 2$) ^b	1.1 (NA)	0.10 (NA)	0.60 (NA)
midstream—NG (TX) ^c	1.29 (NA)	0.136 (NA)	1.28 (NA)
upstream—NG wells (WY) ^d	0.94 (0.73, 1.2)	0.13 (0.060, 0.26)	0.51 (0.34, 0.73)
upstream—NG (SW PA) ^e	1.45 (NA)	NA	NA
upstream—NG (NE PA) ^e	0.77 (NA)	NA	NA

^aRatio and 95% CI calculated from RMA regression of BTEX data at end user points. ^bBurger et al.,³ ratios estimated through published chromatographs of distribution-level NG samples; therefore, no uncertainty estimates are available. ^cGulf South Pipeline Company LLC,⁵¹ ratios of overall median values across seven separate interconnected pipelines near Houston, TX, reporting 5-minute data from Dec 1, 2020, through July 1, 2021. ^dDiGiulio and Jackson,⁵² ratio and 95% CI calculated from RMA regression of BTEX data scraped from a pdf table of Bradenhead well-head data. ^eGoetz et al.⁴⁹ molar ratios for southwest (SW) and northeast (NE) PA via mobile monitoring in proximity of shale gas activity throughout the Marcellus, PA.

other sources of VOCs and can be used in developing emission inventory estimates for fugitive NG from distribution- and beyond-the-meter source types. Figure S9 provides BTEX RMA regressions used in calculating the relative abundances and their uncertainties from end user NG samples.

Inferred NG-Sourced BTEX Emissions for Greater Boston. Annual NG-sourced BTEX emissions were estimated for the Greater Boston area by combining our whole NG sample results with regional NG CH₄ emissions fluxes estimated by McKain et al.,¹⁷ Plant et al.,²⁰ and Sargent et al.²² (Table 4). Downstream NG system loss estimates indicate that NG-sourced BTEX emissions contribute to a modest NMVOC enhancement that is currently not accounted for in emissions inventories. Using NG CH₄ leak estimates from McKain et al.,¹⁷ Plant et al.,²⁰ and Sargent et al.,²² an estimated 338–608 kg/yr (745–1340 lbs/yr) of total BTEX is annually emitted alongside CH₄ leakage throughout Greater Boston. For context, 216 kg/yr (476 lbs/yr) of benzene emitted annually (estimated via NG methane emissions from¹⁷ equates to nearly 10% of on-road diesel light-duty vehicles for all of Massachusetts).⁴ Of the 35 benzene source sectors tracked by the USEPA's 2017 NEI, benzene emissions from NG leakage alone would rank 25th in MA. Depending on the NG CH₄ leak estimate used, our work suggests that benzene emissions from NG leaks are 11–31% of the median benzene sources tracked by the USEPA's 2017 NEI. More specifically, annual NG benzene emissions associated with NG leakage (120–327 kg/yr) are likely greater than benzene emissions in MA from NG-combustion associated with industrial (129 kg/yr), residential (121 kg/yr), and commercial/institutional sectors (119 kg/yr). While VOC emissions from leaking NG are not currently accounted for in inventories and do not appear to be a major contributing source of VOCs, it is important to note that an uncertain fraction of these emissions occurs indoors and, therefore, may be subject to a relatively high human exposure-based intake fraction.

Table 4. Annual BTEX Emissions for the Entire 18,000 km² Area in McKain et al.¹⁷ and the Approximately Similar Boston Bounds Used by Plant et al.²⁰ and Sargent et al.²²

reference	Boston region NG CH ₄ leaks (Tg/yr)	BTEX (kg/yr)* based on the Boston region NG leak estimates			
	CH ₄ (95%CI)	benzene (95% CI)	toluene (95% CI)	ethylbenzene (95% CI)	xylene (95% CI)
McKain et al. ¹⁷ 2015 ^a	0.33 (0.27, 0.4)	254 (174, 356)	272 (179, 398)	25.3 (15.8, 38.1)	153 (98.9, 223)
Plant et al. ²⁰ 2019 ^a	0.16 (0.12, 0.2)	120 (75.3, 175)	132 (81.6, 197)	12.1 (7.07, 18.9)	73.6 (43.5, 112)
Sargent et al. ²² 2021 ^b	0.17 (0.14, 0.21)	132 (90.4, 186)	141 (92.9, 204)	13.4 (8.33, 20.2)	80.0 (51.0, 119)

^a18,000 km². ^b12,351 km².

CONCLUSIONS

Overall, we conducted a first-of-its-kind trace-gas characterization of unburned NG collected directly from indoor residential kitchen stovetops and outdoor building NG service lines throughout Greater Boston, Massachusetts. Trace gas analyses found that distribution-grade NG contains numerous NMVOCs, including HAPs, such as benzene, that were enhanced during the winter months. We also observed distinct trace gas variability by location but were unable to delineate root causes. Full implications extend beyond the need for additional research in other service territories to include several actions that would improve a general understanding of potential health risks posed by NMVOCs in distribution-grade NG. First, pipeline operators and utilities have a ready access to their own product and could regularly measure and report differentiated C6+ NMVOC content in NG postings; current reporting of NG constituents varies significantly between operators, even for the two major pipelines supplying Greater Boston.^{53,54} Relatedly, NG odorization practices could be made publicly available in informational postings to better understand end use odorant content and its implications for low-level leaks behind-the-meter. Also, while more data is needed relating to behind-the-meter NG leakage, home inspectors and contractors serving in that capacity could easily perform NG-appliance leak detection surveys with measurement devices that detect in the low ppmv range, similar to radon tests done prior to the completion of a real estate transaction. Ultimately, we categorize this study as a hazard identification study within the larger health risk assessment context.

Future studies should better determine HAP source–concentration relationships from both pre- and post-combustion with considerations of microenvironments with either a high NG use (e.g., utility worksites, commercial kitchens) or built environments with poor indoor ventilation. Finally, alongside known NG leakage pathways, these data represent a source of VOCs in indoor and urban areas that is not currently accounted for in emissions inventories and provide a previously unaccounted for public health cobenefit associated with reductions of NG-methane emissions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.1c08298>.

Additional data processing details, supporting analyses, and sensitivity tests. L3 data set and associated documentation can be downloaded from <https://doi.org/10.7910/DVN/XGNNGEO> (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by grants from the Barr Foundation (grant #19-07957) and Putnam Foundation. A special thank you to all the study participants who welcomed us into their homes, particularly during uncertain times. Thank you to Jose Vallarino for help in designing the sampling protocols and hours of troubleshooting. Thank you to Megan Jones, Wendy Wang, and Sara Gillooly for the field sampling activities. Thank you to Marty Alvarez and Gary Adamkiewicz for IRB guidance. The authors thank the editor and peer reviewers for their suggestions and contributions. Finally, thank you to Regina

LaRocque, Barbara Taggart, Leanne Westfall, and Andee Krasner for their insights and early contributions.

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