**COMMONWEALTH OF MASSACHUSETTS**
**DEPARTMENT OF PUBLIC UTILITIES**

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| Petition of Liberty Utilities (New England Natural Gas Company) Corp. d/b/a Liberty for Approval of an Agreement to Purchase Renewable Natural Gas from Fall River RNG LLC and of the Liberty RNG Program | D.P.U. 22-32 |

# DIRECT TESTIMONY OF MICHAEL J. WALSH AND JONATHAN KRONES

## Exhibit CLF-MJW-JK-01 (July 15, 2022)

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## I. INTRODUCTION AND QUALIFICATIONS

***Michael J. Walsh***

**Q. Please provide your name and business address.**

A. My name is Michael J. Walsh. I am the president of the sole proprietorship Michael Jay Walsh LLC. My business address is 42 Hudson St. Apt. 1 Somerville, Massachusetts 02143.

**Q. On whose behalf are you offering testimony?**

A. I am offering testimony on behalf of Conservation Law Foundation ("CLF").

**Q. Please provide your educational background and work history.**

A. I hold a B.A. in Chemistry from Colby College (2005) and a Ph.D. in Environmental Engineering from Cornell University (2013). From 2013-2017 I was employed as a Sustainable Energy Technology Fellow at the Bentley University Center for Science and Industry, where I researched the development and commercialization of Bioenergy Technologies. From 2017-2019 I was a Senior Research Scientist at the Boston University Institute for Sustainable Energy and a Research Assistant Professor in the Boston University Department of Earth and Environment. In this role, I oversaw the technical analysis for the Carbon Free Boston study. From 2019-2020 I was a Senior

Associate with the Cadmus Group and was responsible for overseeing state and local decarbonization projects, including the Massachusetts 2050 Decarbonization Roadmap. Since 2021 I have been an independent consultant working on projects relating to gas transition planning, waste-to-energy pathways, and assessing Boston's climate progress.

**Q. Please list any publications, specialties, and matters in which you provided expert testimony regarding issues related to the present docket.**

A. I was a lead author on the Massachusetts 2050 Decarbonization Roadmap Study, a co-author on the Roadmap study's Economic Impact, Buildings, and Transportation sector reports, and as project director was the lead editor of all volumes associated with that project. I was also a co-author on all volumes of the Carbon Free Boston Report. In addition to these Massachusetts-focused studies, I have authored or co-authored climate policy and energy efficiency reports for other states.

I have published scholarly articles on GHG Accounting in Waste Management, techno-economic analysis of biorefineries, bioenergy technology policy, and evaluation of the impacts of bioenergy and bioproducts on global decarbonization pathways.

***Jonathan Krones***

**Q. Please provide your name and business address.**

A. My name is Jonathan S. Krones. I am an assistant professor of the practice of engineering at Boston College as well as an independent consultant. My business address is 10 Newburg St., Unit 1, Roslindale, MA 02131.

**Q. On whose behalf are you offering testimony?**

A. I am offering testimony on behalf of Conservation Law Foundation ("CLF").

**Q. Please provide your educational background and work history.**

A. I received a PhD in Engineering Systems from MIT in Cambridge, MA in 2016, a Masters in Earth Resources Engineering from Columbia University in New York, NY in 2011, and a Bachelor of Science in Materials Science and Engineering from MIT in 2007. I was a postdoctoral associate at the Yale University Center for Industrial Ecology in New Haven, CT from 2016-2018. I have been on the Boston College faculty for four years. In parallel with my academic career, I have maintained a consulting practice for ten years in which I apply my expertise mainly to public policy challenges in the domains of energy, environment, solid waste, and sustainability.

**Q. Please list any publications or other materials you have authored regarding issues that do or may arise in the present docket.**

A. I was the lead author of the non-energy sector report for the Massachusetts 2050 Decarbonization Roadmap Study, which included analysis of emissions from solid waste

disposal facilities and the natural gas transmission and distribution system. My academic expertise is in the field of industrial ecology, a systems approach to thinking about the environmental impacts of materials and technology selection. I have published scholarly articles on various issues of solid waste generation and management, focusing mainly on non-hazardous industrial waste systems and municipal organics collection and processing.

## II. TESTIMONY OVERVIEW

**Q. What is the purpose of your testimony?**

A. This testimony is being filed in Massachusetts Department of Public Utilities ("MA DPU") Docket No. 22-32, *Petition of Liberty Utilities (New England Natural Gas Company) Corp. d/b/a Liberty for Approval of an Agreement to Purchase Renewable Natural Gas from Fall River RNG LLC and of the Liberty RNG Program* for the purpose of identifying areas in Liberty Utilities' ("Liberty" or "the Company") petition which require additional review or clarification.

**Q. What is your understanding of what is being considered in this docket?**

A. In MA DPU Docket No. 22-32, the Company is seeking Department approval of a petition to enter into an agreement to purchase biomethane (sometimes called "renewable natural gas") from Fall River RNG LLC, a subsidiary of Fortistar Methane Group for a

contract term of twenty years. The Company also seeks to establish a customer participation program called "Liberty RNG", under which customers would choose to purchase biomethane representing a percentage equivalent of their natural gas usage and to establish a tariff for the Liberty RNG program.

**Q. Are you presenting any exhibits with this testimony?**

A. Yes, we are attaching the Exhibits referenced below:

| | |
|---|---|
| Exhibit CLF-MJW-JK-02 | CV of Michael J. Walsh |
| Exhibit CLF-MJW-JK-03 | CV of Jonathan Krones |
| Exhibit CLF-MJW-JK-04 | Peer Reviewed Study Referenced in Testimony |
| Exhibit CLF-MJW-JK-05 | Peer Reviewed Study Referenced in Testimony |

## III. COMPANY PETITION – PUBLIC POLICY ENVIRONMENTAL CONSIDERATIONS

**Q. The Company asserts that biomethane (also known as "renewable natural gas") will play a significant role in Massachusetts' energy future and that incorporation of biomethane into Massachusetts' fuel mix will help Massachusetts to achieve its mandate under the Roadmap Law. Do you agree with this assertion? Why or why not?**

A. The ability of biomethane to contribute meaningfully to the deep decarbonization goals of the Commonwealth depends very much upon how the resource is used. In my opinion, pipeline injection of biomethane to replace fossil methane for the end uses of heating buildings, light industrial applications, and production of electricity, which are the end uses for which the Company proposes use of biomethane, is unlikely to play a significant role in Massachusetts's decarbonization plans for several interrelated reasons.

First, there is simply not enough feedstock for biomethane production for significant substitution of fossil methane. In their 2018 Deep Decarbonization study, the California Energy Commission concluded that "assuming California could access up to its population-weighted share of the U.S. supply of sustainable waste-product biomass, excluding purpose-grown biomass crops, there appears to be insufficient biomethane to displace the necessary amount of building and industry fossil natural gas consumption to meet the state's long-term climate goals."[1] The shortfall is significant: a factor of two, even excluding natural gas demand in electricity production, and there is no reason to expect the situation in Massachusetts to differ meaningfully.

[1] California Energy Commission, *Deep Decarbonization in a High Renewables Future: Updated Results from the California PATHWAYS Model*, June 2018, available at: https://www.ethree.com/wp-content/uploads/2018/06/Deep_Decarbonization_in_a_High_Renewables_Future_CEC-500-2018-012-1.pdf (accessed July 14, 2022).

The 2018 ICF International study sponsored by the American Gas Foundation, "Renewable Sources of Natural Gas: Supply and Emissions Reduction Assessment,"[2] referenced in the Company's initial filing, is slightly disingenuous in its presentation of its results. In that study, the authors found that the 2040 biomethane potential is between 34-77% of *residential natural gas consumption*, a figure that falls to 8-19% of all building and industry needs and just 5-11% when total natural gas demand (including for electricity generation) is considered.

Second, the "Massachusetts 2050 Decarbonization Roadmap" outlines the development of a net-zero emissions energy system, which demands the strategic use deployment of all available resources available. Different end-use sectors have different energy needs and are difficult to decarbonize in various ways. Building heating and light industry are excellent candidates for electrification through heat pumps and other technologies. The pipeline injection of biomethane for these end uses diverts limited bioenergy feedstocks and derived fuels from the end-use sectors that are much more challenging to electrify, like aviation, heavy industry, shipping, and chemical feedstocks.

Converting bioenergy resources into biomethane is also an inefficient use of energy. The purification and upgrading of landfill gas and biogas from anaerobic digestion (~50% methane) to pipeline-injectable quality (nearly 100% methane) is quite energy-intensive.

[2] https://gasfoundation.org/wp-content/uploads/2019/12/AGF-2019-RNG-Study-Full-Report-FINAL-12-18-19.pdf (accessed July 14, 2022).

Since gas consumption is largely fungible between the heating and electric generation sectors, and the fact that raw biogas (~50% methane) can be used to generate electricity directly, the production of biomethane is inefficient.

Third, the development of biomethane for pipeline injection, particularly in these early years of decarbonization, creates an incentive to defer electrification of eligible gas-served end uses in part by providing the opportunity for renewable attribute procurers to make individual "net-zero" claims. Small steps towards decarbonization are important, but only inasmuch as they can accumulate to achieve the deep decarbonization aims. To this end, it is much more difficult to envision fully decarbonizing pipeline gas transmission and distribution through biomethane and synthetic fuels than it is achieving the same ends through electrification over the next three decades.

Fourth, when considering the life-cycle emissions of biomethane, it is far from clear that it is a zero emissions fuel as claimed. Methane is a much more powerful greenhouse gas than carbon dioxide, so even small leaks of methane are consequential. All gas infrastructure leaks, so continued use of digesters, compressors, transmission and distribution mains, service lines, valves, meters, and end-use equipment—even with biomethane—will have a significant GHG emissions footprint. Despite efforts to accelerate replacement of the aging gas distribution infrastructure in Massachusetts (e.g., 310 CMR 7.73), recent research shows no change in atmospheric methane concentrations

in Boston over a study period of eight years, suggesting leaks from the gas system and end-use equipment like heaters, boilers, and stoves may be much more significant than previously thought.[3]

In conclusion, we do not see a significant role for pipeline-injected biomethane in achieving the deep decarbonization goals of the Commonwealth of Massachusetts by 2050. On the contrary, investment in this resource today could have the countervailing effect of hindering or delaying achievement of net-zero GHG emissions through the strategic usage of all our energy resources.

**Q. The Company asserts that this project is consistent with the public interest because it will contribute to the reduction of GHG emissions. Do you agree with this assertion? Why or why not?**

A. Assessing the emissions effect is not as simple as assuming a one-to-one replacement of a fossil fuel with a renewable fuel. The landfill gas (LFG) that Fortistar is intending to convert to biomethane is currently being used to generate electricity. To determine whether this project is environmentally preferable, we must know what will happen to the electrical capacity that will be taken offline.

[3] Sargent, M. R., et al., *Majority of US urban natural gas emissions unaccounted for in inventories*, PNAS, 118(44) e2105804118. doi: 10.1073/pnas.2105804118. 2021 (attached as Exhibit CLF-MJW-JK-04).

In the Company's initial filing, there is an attempt to head off this counterfactual. In Exhibit LU-DG/KJ-1, p.34, the Company asserts that "Fortistar maintains that the electric generating facility will soon be approaching a point where it is no longer economically viable to operate, and that without approval of the RNG Contract, Fortistar would shut down the existing electric generation facility and flare the remaining gas into the atmosphere." Without more information it is difficult to evaluate this claim. According to the EPA's Landfill Methane Outreach Program (LMOP) Landfill and Project Database, a gas turbine generator has been operational at Fall River Landfill since July 2000, providing 3.39 MW of electricity (out of a rated capacity of 5.244 MW).[4] This electricity is considered low-carbon, as it is produced by burning LFG, converting the constituent methane into biogenic CO2. There are some net GHG emissions, such as the formation of N2O during combustion and fugitive emissions of LFG, but they are minor. LFG is also considered a renewable fuel both by the US EPA and the Massachusetts Renewable Energy Portfolio Standard. If the facility were to be taken offline, the customers of that electricity would turn to the grid to satisfy their demand. As Massachusetts's electric grid is primarily powered by natural gas, switching suppliers will result in a net increase in GHG emissions, and because new electric load is satisfied by the marginal power plant on the dispatch curve (often more carbon-intensive than the average baseload plant in this

[4] U.S. Env. Prot. Agency, *LMOP Landfill and Project Database*, available at: https://www.epa.gov/lmop/lmop-landfill-and-project-database (accessed July 14, 2022).

part of the country), those new MW are likely to be considerably more emissions intensive than the average.

So, if this project results in the LFG resource being redirected from electricity production to biomethane production, any emissions benefits arising from avoided fossil methane consumption must be compared with the increased emissions associated with A) electricity generated (to offset the LFG generator); B) the energy consumed to upgrade the LFG to pipeline-quality biomethane; and C) leakage of biomethane from the transmission, distribution, and end-use infrastructure.

Fortistar's claim that continued operation of its LFG electric generator is becoming economically unviable requires further investigation. If the generation equipment is failing, then how do the replacement costs compare with the $12-20 million proposed for the biomethane facility? If, on the other hand, the LFG production volumes are dropping too rapidly as to undermine the economics of the generator, how could they be sufficient to satisfy the 20-year term of this proposed project?

**Q. Do you agree with the Company's assertion in Exhibit LU-DG/KJ-1, page 35, about landfill gas "flaring"?**

A. No. We believe that this text is misleading. When LFG is flared, it is burned, which converts the methane to carbon dioxide (and other combustion products). Because LFG is renewable and biogenic, this $CO_2$ is not considered to be a net increase in emissions. So,

when the Company states "flaring the gas…results in unnecessarily increased GHG and CO2 emissions" (LU-DG/KJ-1, p.35), this belies the fact that flared LFG does not result in a net increase in GHG emissions. Even more so, flared LFG is quite different from "purely vented landfill gas," as the Company's initial filing states. Flaring is a controlled destruction of LFG, whereas venting refers to direct release of the gas to the atmosphere, which would have a tremendously negative environmental consequence, due to the uncontrolled release of methane, sulfides, and other constituent parts of the LFG.

**Q. The Company asserts that that this project "compares favorably to reasonably available alternatives based on price and non-price factors," citing specifically its ability to mitigate costs associated with peak loads. Do you agree with this assertion? Why or why not?**

A. The Company's analysis of the effects that biomethane might have on mitigating peak day costs seems reasonable. However, the Company did not consider all reasonably available alternatives to address these peak demands, specifically: energy efficiency. In the initial filing, the Company acknowledges its efficiency plan, but makes no connection between it and its peak day needs. To suggest that the only reasonable way to meet peak demand is by increasing supply goes against all energy efficiency logic and experience. We are not claiming that efficiency measures (including temporally resolved ones like

peak shaving) are necessarily more cost effective; rather, the analysis is needed to determine biomethane's favorability.

Electrification of building heating and light industrial energy needs are also potential strategies for peak day cost mitigation. Electric heat pumps have a coefficient of performance (COP) between 2-3 even on some of the coldest days in Massachusetts winter. This COP is high enough to offset conversion losses from natural gas to electricity in a power plant, decreasing overall gas demand.

## IV. COMPANY PETITION – ECONOMIC CONSIDERATIONS

**Q. The Company asserts that biomethane will provide economic benefits, such as increased jobs. In your expert opinion and based on the record, what economic impacts can Fall River and the surrounding communities expect to see if this project moves forward? Is the Company's characterization of these impacts accurate? Please provide quantifiable detail such as number of jobs, time frame, etc., to the best of your ability.**

A. The Company has not conducted an economic impact assessment on the proposed project and instead relies on a separate study that evaluates typical landfill gas projects.[5] The job

[5]The Coalition for Renewable Natural Gas, *Economic Analysis of the US Renewable Natural Gas Industry*, Dec. 2021, available

estimates of this report – cited by the Company – appear to be reported as FTE job years and include activity associated with developing landfill gas collection.

An assessment of a typical RNG project simulated in the EPA's LFG-cost-Web Model (Version 3.5) indicates that job impacts are limited, with only eight construction jobs and two annual jobs being created directly tied to the facility. For comparison, an electric engine project would create 2.5 FTE construction jobs and 0.5 FTE annual operating jobs.

Fig. 1

| **FTE** | **EPA LFG-Cost-Web Estimate** | | | **RNG Economic Impacts Study (Includes collection)** |
|---|---|---|---|---|
| | *Construction Phase* | *Operating Phase (Annual)* | *Total Job-Years* | |
| *Direct* | 7.8 | 2 | 47.8 | 115 |
| ***Total*** | 24.9 | 4.6 | 116.9 | 343 |

at:https://static1.squarespace.com/static/53a09c47e4b050b5ad5bf4f5/t/61ba25c889b4fb7566404e6c/1639589328432/RNG+Jobs+S tudy.pdf (accessed July 14, 2022).

The direct jobs impacts are modest. The LFG-cost-Web Model and the RNG Economic Impacts Study use input-output cost accounting, which does not factor in the opportunity cost of the investment from potential spending in other areas. For example, the Company claims that the investment will reduce costs associated with trucking LNG which will result in a commensurate loss of jobs in that area of economic activity. Thus, any job impacts are modest and will be dwarfed by jobs created by the offshore wind industry in the region.

The Massachusetts 2050 Decarbonization Roadmap's Economic Impacts Report found that continued reliance on pipeline gas results in lower employment per dollar spent than strategies that invest in deep electrification.[6] It is reasonable to assume that other decarbonization efforts such as efficiency and electrification in Liberty's area will have far greater economic impacts than this project will be able to deliver.

## V. COMPANY PETITION – PUBLIC HEALTH CONSIDERATIONS

**Q. What concerns do you have, if any, regarding health and safety issues for gas customers which may arise from incorporation of biomethane into a Local Distribution Company's fuel mix?**

[6] Cadmus Group and Evolved Energy Research, *Economic and Health Impacts Report*, Dec. 2020, available at: https://www.mass.gov/doc/economics-and-health-impacts-report/download (accessed July 14, 2022).

A. In the abstract, because the chemical makeup of biomethane is indistinguishable from conventionally-sourced natural gas, the addition of biomethane to pipeline gas would not add additional health and safety risk to the current gas system in Massachusetts if. In reality, however, not all sources of methane and biomethane should be considered as equivalent. This project aims to source biomethane produced from landfill gas (LFG), which is mainly composed of methane and carbon dioxide, but also includes nitrogen gas, oxygen gas, hydrogen sulfide, hydrogen gas, ammonia, and a variety of hydrocarbons and other non-methane organic compounds (NMOCs), many of which are hazardous to human and environmental health and others which can damage gas distribution infrastructure. According to the US EPA, "Nearly 30 organic hazardous air pollutants have been identified in uncontrolled LFG, including benzene, toluene, ethyl benzene, and vinyl chloride."[7]

In the Company's signed contract with the gas provider Fortistar, there are provisions for impurities and contaminants: extensive gas quality requirements, facility design specifications that include gas removal and filtration, quality sensors and automatic cutoff valves, and the right to reject any "Non-Conforming RNG" (Exhibit LU-WC/TW-2, p. 15). Even with these precautions, the existence of NMOCs in the input LFG means that this project poses a nonzero exposure risk to the Company's service territory. It should

[7] U.S. Env. Prot. Agency, *Frequent Questions about Landfill Gas – Landfill Methane Outreach Program (LMOP),* 2022, available at: https://www.epa.gov/lmop/frequent-questions-about-landfill-gas (accessed July 14, 2022).

also be noted that while the "RNG Pipeline Gas Quality Specifications" included in the Company's initial filing as part of the Request for Proposal includes restrictions on volatile organic compounds and halocarbons (Exhibit LU-DG/KJ-2, pp.10-11), the same document included with the signed contract with Fortistar does not include those specifications (Exhibit LU-WC/TW-2, pp. 39-41).

The materials provided in the Company's initial filing also do not clarify the fate of the biomethane that fails quality testing. There is a reference to "costs…incurred to store or transfer" the non-conforming gas, but no assurance that all such gas would be prevented from entering the Company's gas distribution system. LFG is continuously generated and the proposed upgrading facility would similarly operate continuously, and it is unclear the physical capacity for storing and/or returning large volumes of off-spec gas to the provider. A possible alternate scenario is that off-spec gas is rejected in a financial sense (as in, the Company does not pay for that volume of gas), but it gets injected into the pipeline nonetheless—particularly if the quality issues are transient. In this not-unreasonable scenario, NMOCs and other hazards would find their way into the homes of the Company's customers. Recent research from the Harvard T.H. Chan School of Public Health confirms the presence of benzene and other volatile organic compounds in indoor

environments from natural gas leaks,[8] a risk which would be exacerbated if other hazardous organic compounds were to be injected into the pipeline alongside biomethane.

**Q. Do you note any other risk factors for gas company customers from the profile of this specific landfill?**

A. Yes. Considering the risk profile over the 20-year lifetime of this project, two factors stand out. First, while the multi-layer safety system outlined by the Company's initial filing appears to be in line with industry standard practice, systems that rely on sensors and automated valves can degrade in quality over time, requiring a commitment by all parties to a culture of maintenance and upkeep. It is unclear if that culture and capability are in place. Second, NMOCs originate from chemicals, paints, and similar wastes discarded in the landfill over its history, which are mobilized by a variety of mechanisms and decay at different rates from the organic matter which is digested anaerobically to methane. As a result, NMOC concentrations in the LFG may increase over time.

The Fall River Landfill accepted waste from 1940 to 2014. The age of the landfill (and the industrial history of the region) means that there is likely a wide assortment of

[8] Michanowicz, D.R., et al., *Home is Where the Pipeline Ends: Characterization of Volatile Organic Compounds Present in Natural Gas at the Point of the Residential End User*, Environmental Science & Technology, in press. Doi: 10.1021/acs.est.1c08298 (attached as Exhibit CLF-MJW-JK-05).

organic chemicals that are evolving NMOCs. Empirical measurements are required to confirm NMOC characteristics and concentrations.

**Q. Do you have any additional public policy concerns about the impacts of the project that would result from the Company's contract with respect to the host community for the project?**

A. Yes. The proposed project poses a risk to the local community. At present, LFG is being collected, treated, and combusted in a gas turbine generator to produce electricity. Converting this gas to biomethane for pipeline injection involves more intensive treatment, processing, and, notably, compression. All of these activities come with risks. The conversion of LFG to biomethane requires the removal of upwards of the out-of-spec constituent gases. Some of these can be directly vented (e.g., carbon dioxide), while others must be destroyed or disposed as hazardous waste. The resulting gas is then compressed up to pipeline pressures, no higher than 55 psig, as stated in the Company's filing document. While this is much lower than the pressures involved in natural gas transmission, the pressurized biomethane nonetheless presents an increased risk to the landfill and its neighborhood.

The risks and hazards associated with this proposed project must finally be considered in their appropriate geographic and historical context. Fall River, the site of the Fall River Landfill and many of the potential customers for the biomethane, has more than 75% of

its population classified by the Massachusetts Executive Office of Energy and Environmental Affairs as "Environmental Justice Populations."[9] This is one of the highest proportions of any city or town in the Commonwealth, and the historical injustices done to these populations mean that they should not also shoulder the additional environmental and health risk associated with this project.

**Q. Does that conclude your testimony?**

A. Yes.

[9] Massachusetts Executive Office of Energy and Environmental Affairs, *Massachusetts Cities & Towns with Environmental Justice Populations*, 2021, available at: https://www.mass.gov/doc/massachusetts-cities-towns-with-environmental-justice-populations (accessed July 14, 2022).

# Michael Jay Walsh, Ph.D.

Independent Decarbonization Consultant
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*Climate change and energy consultant with experience in integrated multi-sector greenhouse gas forecasting, modeling, and policy analysis from the local to global scales.*

## PROFESSIONAL EXPERIENCE

*Independent Consultant, January 2021 – Present*

- Founded an independent practice focused on decarbonization strategy and analysis
- Launched a study evaluating costs, tradeoffs, and equity implications for thermal transition strategies at the municipal scale
- Supporting the Dukakis Center at Northeastern on the Boston Climate Progress Report for the Green Ribbon Commission and The Boston Foundation
- Supporting a three-year (~$1M) study for Pacific Northwest National Laboratory by developing stakeholder-informed indicators and analyzing tradeoffs for waste-to-energy pathways in metropolitan areas
- Assessed waste sector emissions for a university based on its zero-waste strategy
- Drafted policy position paper for City-focused climate convening organization
- Provided policy and technical support to several climate advocacy organizations to comment on gas transition regulatory proceedings

*Senior Associate, The Cadmus Group, September 2019 - December 2020*

- Project Director for the Massachusetts Decarbonization Study, an ambitious $2.25M multi-sector pathways analysis to inform state climate policy; oversaw a large internal project team and five sector-focused subcontractors
- Oversaw Rhode Island Carbon Pricing Study, evaluating impacts associated with a carbon tax across various sectors
- Served as project director for several other state and local decarbonization, efficiency program, and policy studies
- Developed approach for natural carbon stock accounting for a Boston-based conservation cultural institution
- Managed three direct reports; supported quantitative work across practice area

*Senior Research Scientist, Boston University, September 2017 - September 2019*

- Technical lead for the Carbon Free Boston project, a $1.2M comprehensive city-level, equity-focused decarbonization analysis. Managed an internal project team of four and two sector-focused subcontractors
- Managed the development of competitive state, federal, and foundation-focused grant proposals in advanced fuels, sustainable urban systems, and electrification

*Energy & Sustainable Technologies Fellow, Bentley University, June 2013 - July 2017*

- Conducted innovation-focused research on emerging clean and pharmaceutical technologies
- Evaluated economic, financial, and environmental trade-offs of algal food and fuel products using advanced modeling techniques
- Collaborated on a successful grant application for $5.2M from the U.S. Department of Energy to explore pathways to algae food & energy production
- Developed methods for assessing technology maturity using publication data
- Designed and taught an award-winning course on climate and energy modeling for business students

## EDUCATION

*Ph.D. Environmental Engineering*, Cornell University, 2013

- Dissertation: The Influence of Thiols on Copper Bioavailability to Marine Algae
- Advisor: Professor Beth A. Ahner
- Minor Fields of Study: Analytical Chemistry, Biogeochemistry

*B.A. with Honors, Chemistry, Colby College,* 2005

- Honors Thesis: An Analysis of the Effect of CO2 on the Decay Rates of Superoxide

## PUBLICATIONS

Google Scholar Listing

## SERVICE, HONORS & ACCOMPLISHMENTS

| | |
|---|---|
| 2021- | Browning the Greenspace. Communities Committee |
| 2019 | Livable Streets GoBoston 2030 Accountability Report Advisory Committee |
| 2018 | MA GWSA Implementation Advisory Committee Data Focus Group |
| 2015 | Innovation in Teaching Award, Bentley University |
| 2011 | Emerging Public Policy Leadership Honorable Mention, AIBS |
| 2009 | N.G. Kaul Award, New York Water Environment Association |
| 2008 | Student-Elected Trustee, Cornell University |
| 2006 | Distinguished Student Volunteer Award, Cornell University |

## TECHNICAL SKILLS

Projects Completed:
- Python, R, Excel, MATLAB, Tableau
- GCAM, IMPLAN, COBRA
- Cross-model Integration
- System Dynamics (Stella)
- Techno-economic Analysis
- Life Cycle Analysis
- Various Energy Tools & Datasets

Subject Matter Expertise:
- Thermal Electrification Planning
- Local & Regional Decarbonization
- Integrated Systems Modeling
- Food-Energy-Climate Nexus
- Advanced Fuels, Waste, Bioenergy
- Clean Technology Innovation
- Scenario & Pathway Analysis

Coached or Collaborated:
- GIS (ArcGIS, QGIS, census data)
- Capacity Expansion
- Building Energy Modeling
- Transportation Planning
- Visualization & Design
- Economic Impact Analysis

# Jonathan S. Krones

Independent Sustainability Consultant
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## EDUCATION

| | |
|---|---|
| Ph.D., Engineering Systems, MIT | 2011–2016 |
| M.S., Earth and Environmental Engineering, Columbia University | 2009–2011 |
| S.B., Materials Science and Engineering, MIT | 2003–2007 |

## ACADEMIC APPOINTMENTS

| | |
|---|---|
| Assistant Professor of the Practice, Department of Engineering, Boston College | 2021–pres. |
| Core Fellow/Visiting Assistant Professor of Environmental Studies, Boston College | 2018–2021 |
| Postdoctoral associate, Center for Industrial Ecology, Yale School of the Environment | 2016–2018 |

## RESEARCH AFFILIATIONS

| | |
|---|---|
| Olivetti Group, Department of Materials Science and Engineering, MIT | 2015–2021 |
| Centre for Industrial Sustainability, Institute for Manufacturing, University of Cambridge | 2014 |
| Urban Metabolism Group, Singapore-MIT International Design Center, MIT | 2011–2015 |
| Singapore University of Technology and Design | 2010–2011 |
| Center for Life Cycle Assessment, Department of Earth and Environmental Engineering, Columbia University | 2009–2010 |

## RELEVANT PROFESSIONAL EXPERIENCE

| | |
|---|---|
| Technical Consultant & Non-Energy Sector Modeling Lead, Massachusetts 2050 Decarbonization Roadmap, Massachusetts Executive Office of Energy and Environmental Affairs (Cadmus Group) | 2019–2020 |
| External Reviewer, Life Cycle Assessment, Ernst & Young Canada | 2019 |
| Sustainability Consultant, Hamel Environmental Consultants (Boston, MA) | 2012–2014 |
| Intern, Office of the Federal Environmental Executive, White House Council on Environmental Quality (Washington, DC) | 2010 |
| Intern, New York State Public Service Commission (New York, NY) | 2009 |

## SELECTED PUBLICATIONS

9. **Krones, J. S.** (2020). *Non-Energy Sector Report: A Technical Report of the Massachusetts 2050 Decarbonization Roadmap Study*. Prepared for the Commonwealth of Massachusetts. https://www.mass.gov/doc/non-energy-sector-technical-report
8. **Krones, J. S.**, M. R. Chertow & X. Li. (2020). *Making up for Lost Time (and Space): Quantifying Non-hazardous Industrial Waste Generation in the U.S.* Prepared for the Environmental Research and Education Foundation (EREF). https://erefdn.org/making-lost-time-space-quantifying-non-hazardous-industrial-waste-output-beneficial-use-opportunities-us/
7. **Krones, J. S.** (2020). The emergence of a food-waste-based commodity frontier in the United States. *Capitalism, Nature, Socialism, 13*(4). doi:10.1080/10455752.2019.1686531

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**RECENT TALKS and PRESENTATIONS**

8. "Deep Decarbonization of Non-energy-related Emissions in Massachusetts," Environmental Business Council of New England Webinar, November 2021.
7. "Avoiding the Unintended Consequences of Fluorinated Gas Emissions from Residential Heat Pumps," 350 Mass Webinar, November 2021.
6. "Addressing plastic waste: Scientists engaging locally for sustainability," Online panel presentation & discussion, Engineers & Scientists Acting Locally (ESAL), April 2021.
5. "Food Waste: Can We Reach Zero?" Fireside Chat (with Amy Perlmutter and Caroline Howe), MIT Enterprise Forum, Cambridge, MA, January 2020.
4. "Yes, you (probably) CAN fix that! How to cultivate a culture of repair and a circular economy in the 21st century," Boston Public Library, Boston, MA, USA, December 2019.
3. "Garbage Numbers: Accounting for Solid Waste in the United States and Pathways to Sustainability," Colloquium Series at Weston Observatory, Weston, MA, USA, April 2019.
2. "Uncovering the Structure & Dynamics of the Sharing Economy: Evidence from a Food Sharing Platform," MIT Waste Alliance Lecture Series, Cambridge, MA, USA, February 2019.
1. "Updating National Estimates of Non-Hazardous Industrial Waste (NHIW) Generation and Beneficial Use Opportunities," Environmental Research and Education Foundation (EREF) Webinar, June 2018.

**RELEVANT SERVICE ACTIVITIES**

| | |
|---|---|
| Boston Zero Waste Advisory Committee | 2018 |
| Boston-area Fixit Clinic Organizer | 2017–pres. |
| Yale University Pay-As-You-Throw (PAYT) Task Force | 2017–2018 |
| Somerville, MA Curbside Composting Task Force | 2014–2015 |

**TOOLS & SKILLS**

Life cycle assessment (LCA); carbon footprinting; waste system modeling; material flow accounting (MFA); social and complex networks analysis; data visualization

# Majority of US urban natural gas emissions unaccounted for in inventories

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**Across many cities, estimates of methane emissions from natural gas (NG) distribution and end use based on atmospheric measurements have generally been more than double bottom-up estimates. We present a top-down study of NG methane emissions from the Boston urban region spanning 8 y (2012 to 2020) to assess total emissions, their seasonality, and trends. We used methane and ethane observations from five sites in and around Boston, combined with a high-resolution transport model, to calculate methane emissions of 198 ± 47 Gg/yr, with 127 ± 24 Gg/yr attributed to NG losses. We found no significant trend in the NG loss rate over 8 y, despite efforts from the city and state to increase the rate of repairing NG pipeline leaks. We estimate that 2.5 ± 0.5% of the gas entering the urban region is lost, approximately three times higher than bottom-up estimates. We saw a strong correlation between top-down NG emissions and NG consumed on a seasonal basis. This suggests that consumption-driven losses, such as in transmission or end-use, may be a large component of emissions that is missing from inventories, and require future policy action. We also compared top-down NG emission estimates from six US cities, all of which indicate significant missing sources in bottom-up inventories. Across these cities, we estimate NG losses from distribution and end use amount to 20 to 36% of all losses from the US NG supply chain, with a total loss rate of 3.3 to 4.7% of NG from well pad to urban consumer, notably larger than the current Environmental Protection Agency estimate of 1.4% [R. A. Alvarez *et al.*, *Science* 361, 186–188 (2018)].**

urban | methane | natural gas | greenhouse gas emissions

Atmospheric methane ($CH_4$) is the second-most important greenhouse gas (GHG) after carbon dioxide ($CO_2$); the Intergovernmental Panel on Climate Change (IPCC) estimates that it was responsible for ∼20% of global anthropogenic direct radiative forcing from 2000 to 2010 (1). Oil and natural gas (NG) systems are estimated to account for 31% of US anthropogenic methane emissions (2). NG emissions have increased over the last decade, as it has become an increasingly important energy source in the United States due to advances in extraction technology, reduction in cost, and its promotion as having lower $CO_2$-equivalent emissions relative to other fossil fuels.

Densely populated urban areas are well positioned to effect change in GHG emissions, as they have concentrated population, infrastructure, and emissions along with, in many cases, political will to implement emission reductions policies (3). Pipelines, transmission infrastructure, household and commercial appliances, meters, stationary combustion, and service leaks are thought to be the most significant source types for urban NG emissions (2). Bottom-up inventories estimate that distribution and end use contribute 6% of US emissions from the NG supply chain (2), but that estimate is highly uncertain. Urban NG emissions have been reported for several cities including Boston, Indianapolis, Washington, DC, Los Angeles, New York City, and Philadelphia using top-down methods based on tower, aircraft, and remote sensing measurements (e.g., refs. 4–8). Top-down studies consistently estimate distribution and end use NG emissions to be significantly (two to 10 times) larger than the bottom-up estimates. The large gap between bottom-up and top-down analyses indicates that there are likely large missing sources in inventories, and it is unclear from which sector those emissions originate. In order to implement effective GHG mitigation policies, it is necessary to understand the dominant sources of $CH_4$ emissions from NG distribution and end use.

We present an 8-y top-down study of NG emissions from the Boston urban region to assess the NG loss rate over time and investigate the potential missing sources of NG emissions in inventories. We also assess the impact of the COVID-19 shutdown on $CH_4$ emissions during April 2020. This is one of only a few long-term, top-down studies of urban $CH_4$ emissions and is in an east-coast city with older, leak-prone infrastructure. Previous studies in other cities have not found any statistically significant trend in emissions over time (7, 9–11). Boston has set a target of becoming carbon neutral by 2050 (12), and Massachusetts has been working to reduce NG leaks, with several laws and regulations implemented between 2014 and 2019 requiring timelines for utilities to report and repair large leaks

## Significance

**Methane emissions from distribution and end use of natural gas (NG) are not well known. We analyzed atmospheric methane measurements to quantify NG emissions in the Boston area over ∼8 y, finding NG emissions approximately three times larger than calculated by usage-based inventories. We observed no change in emissions over 8 y despite efforts from the state to address NG pipeline leaks. Seasonal emissions are directly related to consumption of NG, implying that sources other than pipelines, such as transmission and appliances, are important and may require future policy action. We estimate total supply chain losses of 3.3 to 4.7% for NG consumed in urban areas, which significantly increases the climate impacts of NG compared to Environmental Protection Agency estimates.**

Author contributions: M.R.S., L.R.H., J.R., and S.C.W. designed research; M.R.S., C.F., J.B., and L.R.H. performed research; M.R.S. and K.M. contributed new reagents/analytic tools; M.R.S. and E.W.G. analyzed data; and M.R.S. wrote the paper.

The authors declare no competing interest.

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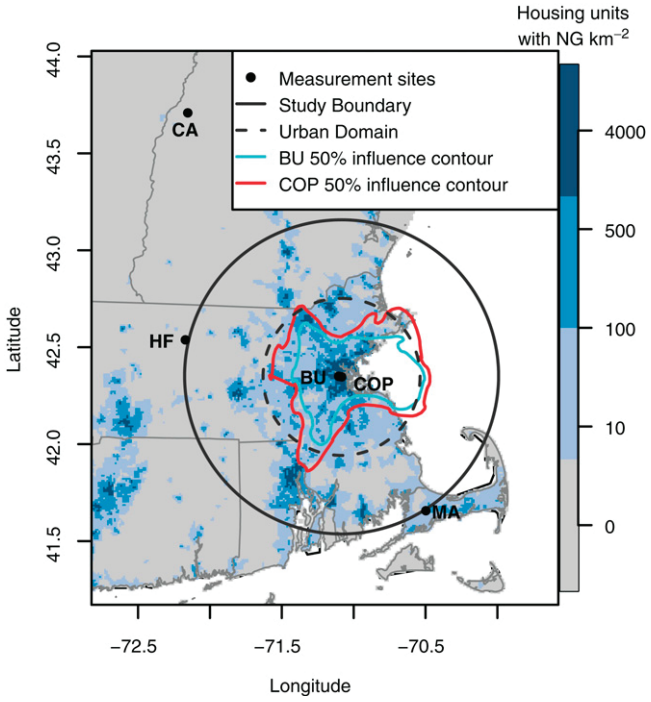


**Fig. 1.** Map of measurement stations in the Boston network. Study Boundary (black line) bounds the 90-km radius circle in which emissions were optimized. Urban Domain (dashed line) bounds the area for which optimized emissions were reported. The blue shading represents the number of housing units with NG per square kilometer (4). The red (blue) contour encloses 50% of the average footprint (sensitivity area) initiated at the COP (BU) site.

based on their size (13, 14); our study will assess whether these efforts have produced a measurable change in NG emissions.

To put this study in context with other cities and evaluate current knowledge of $CH_4$ emissions from NG distribution and end use, we then compare top-down NG emission estimates from four US cities with new studies estimating bottom-up emissions from pipeline leaks and in-house losses. By updating top-down versus bottom-up comparisons with the latest available data, we assess the current understanding of the total carbon footprint of NG, the state of the NG budget, and how well we can constrain urban end-use emissions.

## Methods

Atmospheric $CH_4$ concentrations were measured continuously using Picarro cavity ring down spectrometers at two sites in Boston near the urban center, Boston University (BU) and Copley Square (COP), and three locations 90 to 175 km outside of Boston at Harvard Forest in Petersham, MA (HF), Canaan, NH (CA), and Mashpee, MA (MA) (Fig. 1 and *SI Appendix*, Table S1) from September 2012 to May 2020. BU, COP, and HF are operated by Harvard while CA and MA are operated by Earth Networks Inc. and the National Institute of Standards and Technology. The urban sites at BU and COP are 1.7 km apart and sample at 29 m and 215 m above ground level, respectively, providing a direct observation of the surface-layer vertical gradient.

The model-measurement approach used in our inverse analysis has been described by McKain et al. (4) who analyzed $CH_4$ observations from 2012 to 2013 and Sargent et al. (15) who analyzed $CO_2$ observations from 2013 to 2014. Briefly, we modeled changes in the $CH_4$ concentration as air traveled from the boundary of our study region, a 90-km radius circle centered on Boston, to our urban measurement sites at BU or COP. The modeled $CH_4$ enhancement ($\Delta CH_4$) above the concentration at the region boundary was determined using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (16) run in the recently upgraded "Stochastic Time-Inverted Lagrangian Transport (STILT) mode" coupled with a spatially resolved bottom-up inventory of $CH_4$ emissions (4).

The HYSPLIT model released an ensemble of 500 particles at each hour at the urban measurement sites (receptors) and followed their trajectories backward in time based on wind fields and turbulence. We used two meteorological drivers, the North American Mesoscale Forecast System (NAM) at 12-km resolution and the High-Resolution Rapid Refresh (HRRR) at 3-km resolution (available 2017 through 2020). HYSPLIT generates an influence function ("footprint" units: parts per million $CH_4$ per unit flux in $\mu mole*meter^{-2}*second^{-1}$), which quantitatively links upwind surface fluxes to changes in $CH_4$ concentration at the receptor. In the near-field, the mixing layer height in HYSPLIT was adjusted based on the particle heights as described in ref. 15 to better account for the particles' interaction with the surface before they are fully mixed through the planetary boundary layer.

The footprints were convolved with a 1-km resolution prior model of anthropogenic and biogenic $CH_4$ emissions previously described by McKain et al. (4), which was augmented with updated landfill and NG point source fluxes (17–19), residential (20–22) and commercial (23) building losses, and seasonally varying wetland emissions (24) (*SI Appendix*, section S2). The inventory also included newly reported pipeline losses from Weller et al. (25), who assessed pipeline leaks with methane analyzers driven through four cities, covering ~10,000 km of pipelines. The convolution of the HYSPLIT footprint within our study region and gridded prior emissions enabled us to compute $\Delta CH_4$, the expected increase in $CH_4$ concentration between our study boundary and urban measurement site based on the bottom-up emissions estimate.

Ethane ($C_2H_6$) measurements from the two urban sites as well as aircraft measurements were used to quantify the fraction of the observed $\Delta CH_4$ that was due to NG emissions. Ethane is a significant component of NG, whereas microbial $CH_4$ sources, such as landfills, sewage, and wetlands, produce little or no ethane (26). Because Boston has no geologic $CH_4$ seeps, no oil and gas production or refining, and low rates of biomass burning, there are no known significant sources of ethane in the region other than NG. Ethane concentrations were measured using a laser spectrometer (26) at BU for 3 mo in the fall and winter of 2012 to 13 and 1 mo in the late spring of 2014 (5); they were measured via aircraft in August/September 2017 and March 2018 (27); they were also measured at COP for 5 mo in the fall and winter of 2019 to 2020. Following the method of McKain et al. (4), the atmospheric $C_2H_6$:$CH_4$ ratio was determined from the slopes of colocated $C_2H_6$ versus $CH_4$ measurements and compared to the $C_2H_6$:$CH_4$ ratio of NG flowing into the region during the measurement period (*SI Appendix*, section S3 and Fig. S1). The percentages of observed $CH_4$ due to NG from these three studies are shown in Table 1, with average values of 91% NG in the dormant season and 76% in the growing season. The aircraft study shows a much smaller change in NG fraction with season than the tower study, likely because the aircraft sampled a smaller, more urban domain with less biogenic emissions. Due to large uncertainties in prior NG emissions estimates, the NG emissions layer in our prior inventory was scaled to be consistent with the attribution results from ethane data. Without adjusting the biogenic component of prior $CH_4$ emissions, the prior NG emissions were scaled such that they contributed on average 91%, 84%, and 76% of the footprint-weighted $\Delta CH_4$ at the urban sites in the dormant, transitional, and growing seasons, respectively. Unscaled priors were also tested, along with NG fractions spanning the range of observed values and a range of wetland emissions from different inventories.

The $CH_4$ concentrations at the boundary of the study region were calculated as the lower 20th percentile, 48-h running average of $CH_4$ measurements from the HF, CA, or MA sites, with the upstream site chosen based on the average azimuth at which the HYSPLIT particles exited the 90-km radius circle around Boston. The model selected the MA site for exit angles from 120 to 180°, the HF site for 180 to 300°, and the CA site for 300 to 360°.

Observations corresponding to easterly wind directions (0 to 120° exit azimuth) were discarded due to lack of a suitable boundary site and uncertainty in modeling sea breezes that account for a significant fraction of the easterly inflow conditions. As westerly winds are the most common, this criterion excluded 25% of days in the spring and fall and 11% of days in the winter. During sea breeze conditions, air can recirculate over the city, picking up large amounts of pollution. This is very difficult for the HYSPLIT model to capture accurately using regional scale meteorology (28); we therefore excluded these angles.

The observed $\Delta CH_4$ was calculated as the difference between the observed $CH_4$ at each urban site and the background concentration, with a time delay between the upwind and downwind sites equal to the average travel time from the receptor to the study region boundary. Hourly average $\Delta CH_4$ values were aggregated into daily afternoon averages (11 to 16 h EST) to focus on periods when the atmosphere is well-mixed.

Optimized $CH_4$ emissions were calculated for groups of 2mo with similar NG consumption (January/February, December/March, November/April, May/October, June/September, and July/August) in each year from September 2012

**Table 1. Fraction of atmospheric $CH_4$ attributed to NG sources based on three measurement campaigns**

| | Time period | Location | Dormant | Growing |
|---|---|---|---|---|
| Ref. 4 | 2012 through 2013 | BU | 98% | 67% |
| Ref. 27 | 2017 through 2018 | Aircraft | 87% | 85% |
| This work | 2019 through 2020 | COP | 88% | |

to May 2020 (or for single months for which a corresponding month was not available). For each 2-mo group, a single scaling factor (SF) was determined by dividing the mean observed $CH_4$ enhancement by the mean modeled $CH_4$ enhancement:

$$SF = \text{mean}(\Delta CH_4\text{obs})/\text{mean}(\Delta CH_4\text{model}).$$

Optimized $\Delta CH_4$ and $\Delta NG$ emissions were calculated as the product of the prior emissions and the SF for each period:

$$CH_4\text{optimized} = CH_4\text{boundary} + SF * \Delta CH_4\text{model}.$$

We compared optimized emissions from the portion of MA within our 90-km circle to state-level monthly NG consumption (29) multiplied by 0.88, the fraction of state NG use estimated to be within our study area based on the spatially resolved map of NG consumption from McKain et al. (4). We did not include the emissions or consumption from other states because the vast majority of the HYSPLIT footprint falls within MA. Fractional loss rates to the atmosphere were obtained by dividing optimized NG emissions by total NG consumption in MA and within the study region. Uncertainties in optimized emissions were calculated through a bootstrap analysis that accounted for variations of hourly and daily observed and model enhancements and boundary $CH_4$, as well as uncertainties in prior emissions and atmospheric transport.

## Results

We quantified average methane emissions within a 45-km radius of Boston to be 37.5 ± 9 $g \cdot m^{-2} \cdot y^{-1}$ (95% CI) from 9/2012 to 5/2020, with 24.1 ± 4.6 $g \cdot m^{-2} \cdot y^{-1}$ of that total originating from NG, corresponding to total emission of 127 Gg/yr of NG methane from this region. Average NG emissions in the 90-km radius study domain were 14.0 ± 2.7 $g \cdot m^{-2} \cdot y^{-1}$, which is comparable to the value of 15.3 ± 3.5 $g \cdot m^{-2} \cdot y^{-1}$ calculated by McKain et al. for the same domain (4). The 45-km radius study area corresponds to ∼50% of the HYSPLIT footprint influence (Fig. 1) and approximates the Boston urban area defined by the US Census Bureau Topologically Integrated Geographic Encoding and Referencing (TIGER) database (30).

We found an average NG loss rate of 2.5 ± 0.5% from 2012 to 2020 by comparing NG emissions to consumption in our study area. There was no statistically significant trend in loss rate over our 8-y study period (Fig. 2), despite new regulations in Massachusetts requiring utilities to repair large leaks (14). We also saw no trend in $\Delta CH_4$ between our Boston and background sites over that time period (*SI Appendix*, Fig. S3). Our calculated loss rate is three times higher than the 0.8% loss rate indicated by our prior inventory for Boston and six times higher than the Massachusetts Department of Environmental Protection (MassDEP) estimate and the Gridded Environmental Protection Agency (EPA) inventory (31), neither of which include end-use emissions. The variability among the three inventories shown in Fig. 2 is mainly due to using pipeline emission factors based on different studies.

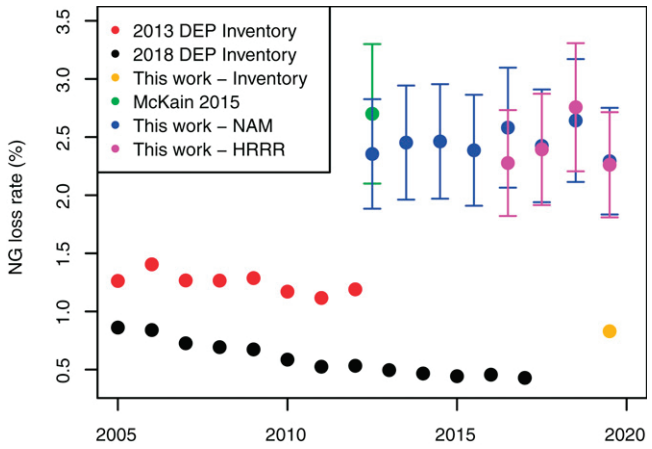


**Fig. 2.** Yearly NG loss rates based on inventories released by MassDEP in 2013 (red) and 2018 (black), calculated with a top-down method by McKain et al. (4) (green), by this work from the inventory (orange), and top-down analysis using NAM12 (blue) or HRRR (purple) meteorology. Error bars were calculated using a bootstrap method and represent 95% CI.

From 2017 to 2020, we calculated a loss rate of 2.4 ± 0.5% using the HYSPLIT model; the loss rates calculated using the NAM 12-km resolution and HRRR 3-km resolution meteorologies were indistinguishable. These rates and the 2.5 ± 0.5% loss rate based on NAM for 2012 to 2020 are comparable to the 2.7 ± 0.6% loss rate calculated by McKain et al. (4) from 2012 to 2013 using the Weather Research and Forcasting (WRF) model meteorology and the STILT model. The excellent agreement among models using three different meteorology products and two transport models provides confidence that wind errors are not the cause of discrepancies between top-down and bottom-up studies. There was also excellent agreement in annual average emissions between analyses based on the COP and BU sites (Fig. 3), providing confidence in the total emissions and temporal trends.

As a check, we also calculated methane emissions for December 2013 through February 2014 using the observed atmospheric $CO_2$:$CH_4$ ratio and optimized $CO_2$ emissions calculated by Sargent et al. (15) and calculated a loss rate of 1.7%, slightly lower than our CI. The ratio method uses the Anthropogenic Carbon Emissions System (ACES) $CO_2$ inventory, which is entirely independent from the methane inventory. This method implicitly assumes that methane emissions are colocated with $CO_2$ emissions and focused on winter when biological emissions are low and emissions of both species are dominated by anthropogenic sources. This assumption is imperfect given that $CO_2$ emissions from traffic and $CH_4$ emissions from landfills and wastewater may not be colocated with the other species, but the method is useful as an independent order of magnitude check. This estimate also gives a loss rate more than double that of bottom-up methods.

Our model reproduced daily and weekly variability in atmospheric $CH_4$ well (Fig. 4). Both the observed methane concentrations and the enhancement between the urban and background sites were highest in the winter and lowest in the summer (*SI Appendix*, Figs. S3 and S4). Fig. 3 shows a strong seasonal cycle in optimized NG emissions, with a larger amplitude at the COP site than at the BU site. There is no strong seasonal variability in optimized total $CH_4$ emissions (*SI Appendix*, Fig. S7). The seasonal variability in NG emissions is larger than the variability in the observed $\Delta CH_4$, because the $C_2H_6$:$CH_4$ ratio indicates a larger fraction of $CH_4$ from NG in the winter than in the summer, while wetland $CH_4$ emissions peak in the summer.

Summer NG emissions at COP and BU were 58% and 28% lower, respectively, than winter emissions. The difference in seasonal amplitude between the two sites is likely due to different emitters in the footprints of each site, with a larger fraction of NG emissions in the footprint of the BU site that are independent of season, such as restaurants and pipeline leaks. We expect the much taller COP site, which samples at 215 m, to be more representative of regional emissions, while the 29 m BU site is more sensitive to local emissions. Though the amplitude of the seasonal cycles differs at the two sites, the average

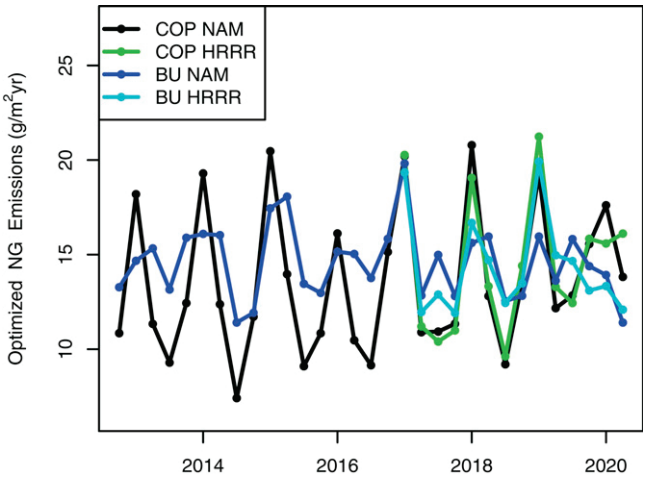


**Fig. 3.** Seasonal average optimized NG emissions (grams/meter$^2$year) based on observations at the COP and BU sites using NAM12 or HRRR meteorology.

annual emissions and temporal trends calculated from the two sites are in excellent agreement (Fig. 3).

We find that NG emissions and consumption are highly correlated. This is surprising, because distribution pipelines, thought to be a dominant source of NG losses, are at fairly constant pressure year-round, and thus, their emissions are not expected to vary with consumption. Posterior NG emissions from measurements at the COP site were compared with Massachusetts monthly NG consumption in the study area from the residential, commercial, and industrial sectors from the US Energy Information Administration (EIA) (29) (Fig. 5). As the COP site has a larger footprint than the BU site, we expect state-level consumption values to be more representative of consumption in its footprint than in the BU footprint (city-level NG consumption was not available) (*SI Appendix*, Fig. S5). Fig. 5 shows a weighted, linear least-squares fit between emissions and consumption. The intercept of this line implies a seasonally invariant loss of 6.4 g/m$^2$/yr which is ~3 times higher than the pipeline emissions estimated by Weller et al. (25). The slope of this line (0.025) implies an additional loss of 2.5% of consumed NG, which is in good agreement with the 2.5% loss rate calculated by comparing total yearly emissions to consumption. The correlation also holds for total methane emissions during the dormant season (Fig. 5, *Right*, blue points). Note that NG emissions and consumption are fully independent datasets, as NG consumption was not used in the prior inventory.

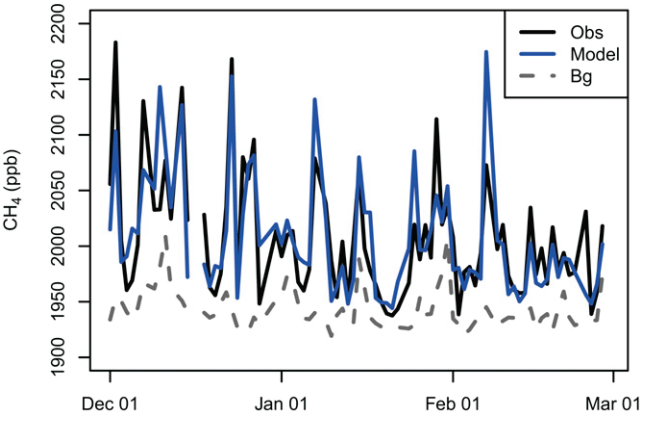


**Fig. 4.** Observed (Obs), scaled model (Model), and background (Bg) $CH_4$ at COP. Daily afternoon average (11 to 16 h EST) concentrations for December, January, and February 2014 to 2015.

In bottom-up studies of residential and commercial buildings, appliances and furnaces were reported to have loss rates of 0.1 to 0.3% of consumed gas (20, 21, 23); transmission (compressor stations, etc.) is estimated to have a loss rate of 0.2% (4). Though we expect the slope of 2.5% at COP (215-m sampling height) to be more representative of regional emissions than the slope of 1% at BU (which, sampling at 29 m, compares fairly local emissions to state-level consumption), even taking a loss of 1% of consumption as a lower bound is significantly higher than is expected from bottom-up inventories. Thus, while there is some uncertainty in the regional seasonality of NG losses based on the difference between our two urban sites, both sites indicate consumption-driven losses that are significantly higher than bottom-up estimates.

To test whether the correlation between emissions and consumption was an artifact of the seasonality of the prior inventory, we performed sensitivity studies with a range of NG fractions and wetland emissions as well as a seasonally invariant prior. These sensitivity studies produced NG emissions within ±20% of the main configuration and maintained the strong relationship between emissions and consumption (*SI Appendix*, section S5). We also ran a test which included angles of 0 to 120°, using MA as a background; it produced NG and $CH_4$ emissions which agreed with the main configuration to within 2%. Additionally, we compared results with and without MA exit angles, as they can sometimes be difficult to model due to sea breezes. We found no difference in results when MA angles were excluded. We found that the wetland methane source in our prior inventory is not significantly different for east versus west winds, so wind direction could not be used to separate out the wetland methane source.

Total methane emissions do not follow NG consumption in the summer when the ethane:methane ratios indicate that biological sources such as wetlands and landfills are a larger portion of the total methane enhancement in the city. Because they tend to be located farther from our urban sites than the NG emissions, wetland and landfill emissions lead to relatively small changes in concentrations at the receptor. Therefore, our network cannot strongly constrain emissions from biological sources, leading to larger uncertainty in total methane emissions, particularly in the summer, than in NG emissions (*SI Appendix*, Fig. S7). We have confidence in the NG component of methane emissions throughout the year, as these emissions are concentrated near the receptors and strongly influence observations. The optimized emissions of NG are not significantly influenced by adjusting wetland emissions in the prior by up to a factor of 6.

Seasonal changes in urban methane emissions have previously been found by Huang et al. (32) in Washington, DC (summer $CH_4$ emissions were 41% lower than winter emissions) and He et al. (10), Wong et al. (10), and Yadav et al. (33) in Los Angeles (summer emissions were 26%, 22%, and 40% lower than winter emissions, respectively). However, the fraction of NG was not determined in these studies, which assessed total methane emissions only. The associated consumption in the measurement footprint and relationship to consumption was calculated by He et al., who found a slope of 0.014 between $CH_4$ emissions and residential and commercial consumption, which is notably lower than the slope of 0.025 (versus NG) or 0.021 (versus $CH_4$ in dormant season) that we found in Boston. He et al. used a remote mapping spectrometer to measure the $CO_2$:$CH_4$ ratio, combined with a prior $CO_2$ inventory to calculate top-down $CH_4$ emissions. The difference in slopes could be influenced by the different ages of infrastructure, the types of emitters, and the NG heating demand due to different climates in the two cities.

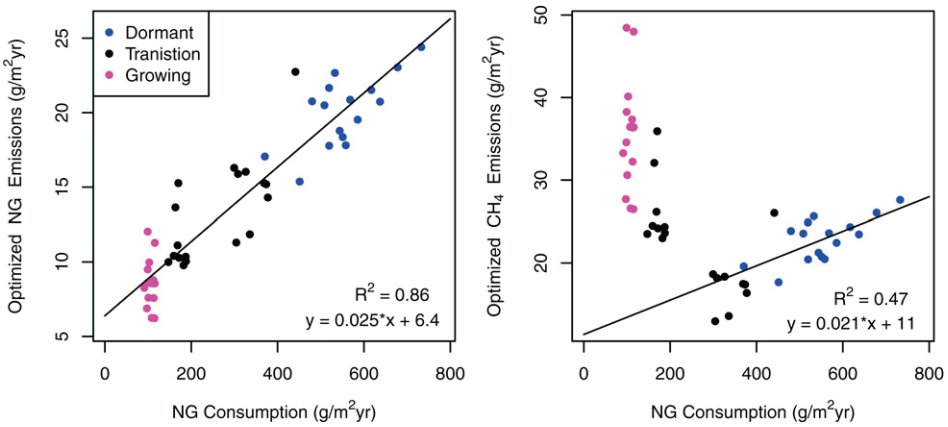


**Fig. 5.** Optimized NG emissions (*Left*) and total methane emissions (*Right*) compared to residential and commercial NG consumption in MA based on measurements at the COP site. The linear fit to all data (*Left*) and dormant season data (December through March) (*Right*) is shown. Each point represents a 2-mo average.

We were also able to investigate the impact of the 2020 Covid-19 shutdown on methane and NG emissions in Boston. April 2020 emissions of both methane and NG determined by inverse analysis at the BU site were 42% lower than the average of previous April emissions and 22% lower than the lowest April emissions from our study period in 2017. In contrast, April 2020 emissions based on inverse analysis at the COP site were approximately equal to the average of April emissions from 2013 to 2019. Fig. 6 shows that 2020 was the only year in which the average April methane concentration at the 215-m COP site was higher than that at the 29-m BU site (which is only 1.7 km away), demonstrating an inversion of the typical atmospheric concentration gradient.

Massachusetts' total NG consumption during April 2020 showed no change in the residential or industrial sectors compared to previous years, while the electrical sector showed a 35% decrease in consumption compared to 2018 and 2019, and there was a small decrease in commercial consumption (29) (*SI Appendix*, Fig. S8). However, state-level data are not necessarily representative of changes that could have happened locally near BU, as evidenced by the weaker correlation between emissions calculated from the BU site and state-level consumption compared to the correlation at the COP site. The marked decrease in methane emissions at BU could be due to reduced appliance use in office buildings, restaurants, and/or the BU campus surrounding the BU site. There is no evidence that BU buildings changed their heat consumption, though they did stop cooking and serving food. Like the strong correlation between NG emissions and consumption over the 8-y period, the significant change in methane emissions at BU during the Covid-19 shutdown indicates that changes in local consumption are driving methane enhancements and retrieved emissions at this station, reflecting the low sampling altitude (29 m agl). The significant decrease in $CH_4$ emissions locally around BU during April 2020, when residential NG consumption and pipeline losses were constant, points to the importance of other sources such as beyond-the-meter losses and the necessity of further studies to quantify these sources.

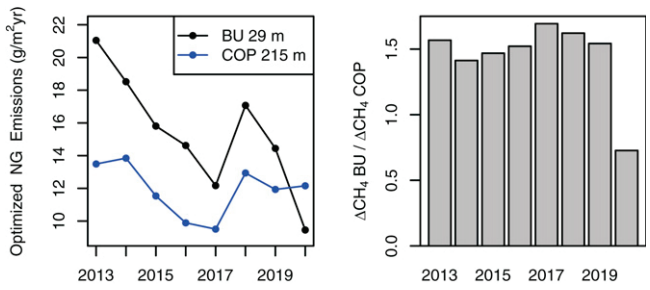


**Fig. 6.** (*Left*) Mean April optimized emissions from inverse model based on observations from BU or COP site. (*Right*) Ratio of mean April $\Delta CH_4$ BU versus $\Delta CH_4$ COP, in which $\Delta CH_4$ is the enhancement between the urban and background $CH_4$.

Fig. 7 compares this study's top-down and bottom-up per capita NG emissions for Boston with other cities that have been studied across the United States. We compared seven top-down studies that explicitly calculate NG emissions. In order to compare NG emissions from as many studies as possible, we also calculated the NG component of methane emissions for top-down studies which estimated total methane emissions only by multiplying methane emissions by the fraction of methane from NG determined by other studies of the same city (*SI Appendix*, section S8).

Across the six cities, we find remarkably similar levels of NG emissions when adjusted for population. The emissions per capita are significantly higher than bottom-up estimates in every study, irrespective of the infrastructure age, notwithstanding many differences among study designs. Tower-based, top-down estimates for Boston, Indianapolis, Washington, DC, and Los Angeles were three, six, 10, and two times greater, respectively, than bottom-up estimates. We find that while the updating the Boston inventory with the latest pipeline, appliance, and building losses increased estimated emissions and reduced the gap between top-down and bottom-up studies, large, unexplained gaps remain (Fig. 7*B*). Among these studies, loss rates from NG infrastructure were calculated in different ways; for comparison, we recalculated loss rates for some studies according to our method (*SI Appendix*, Table S3). These studies produce loss rates of 1.1 to 2.1% for Washington, DC (8, 32) and 2 to 2.3% for Los Angeles (9, 35), comparable to the 2.5% shown here for Boston.

## Conclusions

Top-down studies which estimate methane emissions from atmospheric concentration measurements are a powerful tool that can be used to quantify the scale of NG emissions and assess how the total carbon footprint of NG compares to that of other fuels. We analyzed nearly 8 y of methane observations from five sites in and around Boston in an inverse model framework and found that NG emissions are three times higher than our bottom-up inventory estimates and six times higher than

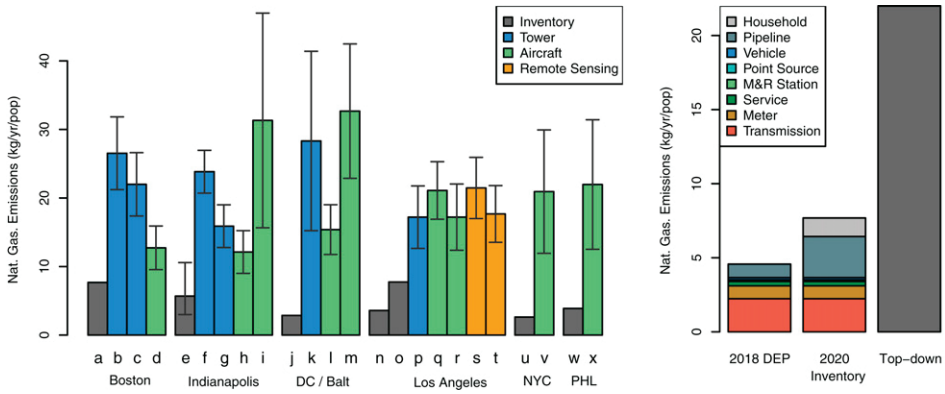


**Fig. 7.** (*Left*) Per capita NG emissions from top-down studies in six US cities. Boston: (a) This work, (b) McKain (4), (c) This work, (d) Plant (5), Indianapolis: (e) Lamb (6), (f) Lamb (6), (g) Balashov (11), (h) Lamb (6), (i) Cambaliza (34), DC/Baltimore: (j) EPA (8), (k) Huang (32), (l) Ren (8), (m) Plant (5), Los Angeles: (n) CARB (35), (o) EPA (33), (p) Yadav (33), (q) Cui (36), (r) Peischl (35), (s) Wunch (7), (t) Wong (10), New York City: (u) EPA (5), (v) Plant (5), Philadelphia: (w) EPA (5), and (x) Plant (5). (*Right*) Boston bottom-up inventory NG emissions by sector compared to top-down emissions. "2018 DEP": vehicle, point source emissions as described in *Methods*, no household emissions, and all other sources from 2018 DEP (37); "2020 inventory": same as "2018 DEP" except pipeline emissions from Weller et al. (25), household and building emissions from Fischer et al. (20), Lebel et al. (22), and California Energy Commission (23); "Top-down": emissions from this study.

the most recent MassDEP estimate, which does not include end use. Comparing NG emissions to consumption in the region, we find an average loss rate of 2.5 ± 0.5% from urban infrastructure or about 49 Gg/yr of NG methane for the metro area.

The city of Boston has set a goal of becoming carbon neutral by 2050 (12), and Massachusetts implemented new laws and regulations between 2014 and 2019 requiring utilities to report and repair large leaks based on their size (13, 14). A 2019 study by the Home Energy Efficiency Team (HEET) predicted that the 2018 law requiring the repair of leaks deemed "significant environmental impact" could reduce pipeline emissions by half, based on a finding that 7% of leaks emit half of all gas by volume (38). Our analysis finds that these efforts have not yet resulted in a measurable change in methane emissions, as we find no statistically significant trend over the last 8 y (Fig. 2; changes larger than 19% should be detectable given the model uncertainty).

Pipeline emissions account for 42% of total NG emissions in the bottom-up inventory; if they account for the same fraction of unknown emissions, a reduction of 50% due to policy action would be detectable by our model. All gas companies in Massachusetts have released the number of known leaks and repairs on their systems each year since 2014 (39). Notably, there has been no significant change in the number of grade 1 or 2 leaks on the pipeline system and only a slight reduction in the number of grade 3 leaks, with no sign of change after the 2018 law (*SI Appendix*, Fig. S9). Hence, from both a bottom-up leak count and our top-down analysis, it seems that new leaks are appearing in the aging Boston pipeline system as fast as old ones are being fixed. In contrast, the MassDEP bottom-up estimate indicated a 15% decrease in transmission and distribution emissions from 2012 to 2018, which was mainly due to changes in emission factors (estimated leaks per mile of pipeline, based on studies performed in other cities).

We found a strong, unexpected correlation between NG emissions and consumption in Boston (Fig. 5), a relationship which has also been demonstrated in Washington, DC (32) and Los Angeles (9, 10, 33). During the COVID-19 shutdown in April 2020, we calculated a 42% decrease in methane emissions retrieved at our lower sampling height compared to the average from April of previous years. As NG usage changed significantly in some sectors during this period, this is further evidence that NG emissions are significantly driven by consumption. This correlation between emissions and consumption is surprising because distribution pipelines, thought to be a dominant source of NG losses, are at fairly constant pressure year-round, and thus, their emissions are not expected to vary very much with consumption. Our results therefore indicate that either pipeline emissions do vary with throughput, and/or a large fraction of emissions are from other sources in which emissions are directly linked to consumption, such as space heating and other appliances in residential, industrial, and commercial buildings, transmission intersection points, flow meters, boosting compressors, or step-down and regulation. Current efforts to reduce NG emissions often target pipeline leaks; however, if a significant portion of NG emissions are not from pipelines but from consumption-driven processes, it could require changing the scope of future policy. The results also imply that policies aimed at reducing NG consumption such as shifting away from NG use in buildings could substantially reduce GHG emissions if NG is replaced with green alternatives.

To put this research in context with other cities across the United States, we compared top-down methane emissions from 12 studies across six cities with bottom-up emissions estimates based on the latest studies of pipeline, appliance, home, and commercial building losses (Fig. 7). The longest of these studies were 4 y (10) and 9 y (7); both used tracer-tracer ratios with a $CO_2$ or CO prior inventory. Of the studies using a $CH_4$ prior, the longest was 3 y (11). Across the cities, we found top-down emissions to be two to 10 times greater than bottom-up emissions estimates. The cities studied, Boston, Indianapolis, Washington, DC, Los Angeles, New York City, and Philadelphia, represent cities with both older and newer infrastructure, warmer and colder climates, and a wide range of populations. We therefore expect the range of emissions from those cities to be fairly representative of the variability across US cities. Somewhat surprisingly, though the cities with newer infrastructure, Indianapolis and Los Angeles, had slightly lower estimated emissions per capita than the cities with older infrastructure, the difference was small and within the uncertainty of the studies. This result might also point to an important role of consumption-associated emissions.

In these cities, NG emissions were estimated to account for 43 to 88% of total methane emissions. Indianapolis was an outlier at only 43% of methane from NG, because the city has a large landfill within the urban area that accounts for a large fraction of the city's emissions. These studies include tower and

aircraft-based sampling as well as ground-based remote sensing methods and span cities with very different topography, wind patterns, and infrastructure. They employ model frameworks based on a variety of meteorological datasets and with methane emissions inventories, tracer–tracer methods based on $CO_2$ or CO emissions inventories combined with the observed $CO_2$:$CH_4$ or CO:$CH_4$ ratios, and aircraft mass balance. Each model may have bias due to wind speed errors, background calculations, or atmospheric mixing parameterizations, but given the diversity of approaches to the problem, it seems unlikely that such errors could account for the consistently larger emissions from top-down compared to bottom-up estimates across this heterogeneous group of urban studies. We conclude therefore that it is very likely that there are large missing sources of emissions in bottom-up methane inventories related to NG distribution and, in particular, end use.

The rate of urban NG emissions calculated by top-down studies also has important implications for the carbon footprint of NG as a fuel. An estimated 2.2% (40) of NG is lost to the atmosphere from production and transmission of the fuel before it arrives in the city. Adding to that loss rates of 1.1 to 2.5% from distribution and end use across the studies summarized here yields total loss rates of 3.3 to 4.7% associated with the full NG value chain supplying urban areas. Therefore, 30 to 50% of value chain losses for NG consumed in urban areas are from distribution and end use. For Boston, a city with older infrastructure, we calculate a total loss rate from the entire NG supply chain of 4.7%.

If the top-down emissions from these cities are representative of emissions across the country, we estimate that NG losses from distribution and end use amount to 20 to 36% of all losses from the US NG supply chain (including all end uses, not only urban; based on supply chain losses from ref. 2) and 6 to 11% of all anthropogenic methane emissions (including agriculture) (*SI Appendix*, section S8). These top-down studies thus indicate that the climate footprint of NG is larger than generally supposed, implying the need to identify and mitigate urban sources. Because methane has 86 to 125 times the global warming potential of $CO_2$ over 20 y and 25 to 36 times over 100 y, if 3 to 6% of consumed NG is lost directly to the atmosphere as $CH_4$, the greenhouse impact of NG is equivalent to that of coal (2). We note, however, that reductions in criteria pollutants emissions continues to be a benefit of NG use compared to coal or oil.

Determining the processes and source types responsible for NG emissions unaccounted for in bottom-up inventories remains a significant challenge. In Boston, the largest NG emitters from our bottom-up estimate are pipelines, transmission, and buildings, which account for 14%, 8%, and 6%, respectively, of our estimated top-down emissions; 67% of top-down emissions are unaccounted for in the bottom-up inventory. Appliance and building emissions including furnaces and boilers, which are expected to follow NG consumption consistent with this study, warrant further study to understand whether they could be a significant source of missing emissions; in particular, few studies have assessed commercial and industrial building emissions. However, as current bottom-up estimates for building losses are 0.1 to 0.3% of consumed gas (20, 21, 23), accounting for only 6% of top-down emissions in Boston (Fig. 7), these estimates would need to be increased by fivefold or more to account for a significant fraction of missing emissions.

Transmission emissions have been fairly extensively studied at a facility level, with thousands of stations assessed (e.g., refs. 41 and 42) and an estimated loss rate of 0.2% (4). The most important unaccounted-for transmission losses are likely due to "super-emitters" representing operating anomalies or failed systems; facility-level studies have shown them to be very important, and they are difficult to statistically sample using bottom-up methodology. "Super-emitters" could also play a role in missing emissions across other sectors such as losses from appliances and NG pipes within buildings. Combining building and transmission emissions, which should both correlate with consumption, bottom-up estimates are approximately sixfold lower than the 2.5% of consumed gas that is indicated by the relationship between our top-down emissions and consumption.

Weller et al. (25) assessed pipeline leaks with methane analyzers driven through four cities, covering ~10,000 km of pipelines; their extensive coverage of roadways makes it unlikely that they missed a significant fraction of street-level emissions. One potential unaccounted-for source of emissions is pipeline gas that escapes away from streets, such as through sewage pipes or stacked vents in buildings. When we compare top-down emissions from this study to gas consumed, the intercept of the regression line implies a seasonally invariant loss of 6.4 g/m$^2$/yr, which is approximately three times higher than the pipeline emissions estimated by Weller et al. The seasonally invariant emissions in excess of those expected from Weller et al. could be due to a combination of additional pipeline emissions and appliances used year-round such as stoves and water heaters.

Our Boston top-down analysis as well as a review of studies in other cities indicate that a majority of NG emissions in urban areas are not accounted for in bottom-up inventories. Bottom-up studies have assessed each portion of the NG supply chain, and none of these studies can account for the NG emissions that we observe from top-down methods. Therefore, bottom-up studies must be missing significant emissions. Fixing fugitive NG pipeline emissions in the streets is a policy priority in many cities; however, if beyond-the-meter, transmission station, or pipeline losses away from streets make up a significant fraction of the unknown emissions, they could necessitate greater focus in policy action. Targeted, neighborhood level studies from both top-down and bottom-up perspectives will be essential to identify the emissions not accounted for in bottom-up inventories so that stakeholders can effectively focus on mitigating the largest methane emissions sources.

**Data Availability.** Data have been deposited in Oak Ridge National Laboratory Distributed Active Archive Center (https://doi.org/10.3334/ORNLDAAC/1982).

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Article

# 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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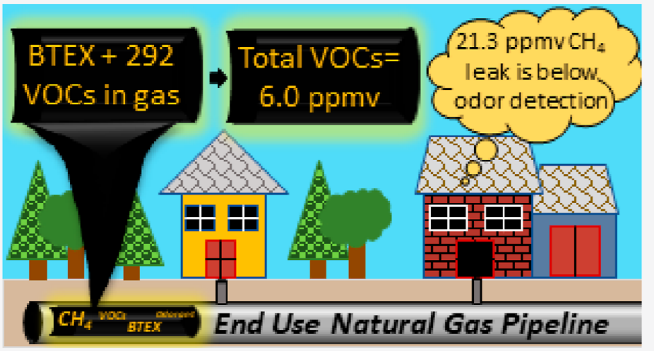
**ABSTRACT:** The presence of volatile organic compounds (VOCs) in unprocessed natural gas (NG) is well documented; however, the degree to which VOCs are present in NG at the point of end use is largely uncharacterized. We collected 234 whole NG samples across 69 unique residential locations across the 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

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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 $C_4$+ 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 $CH_4$ and $C_2H_6$ 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



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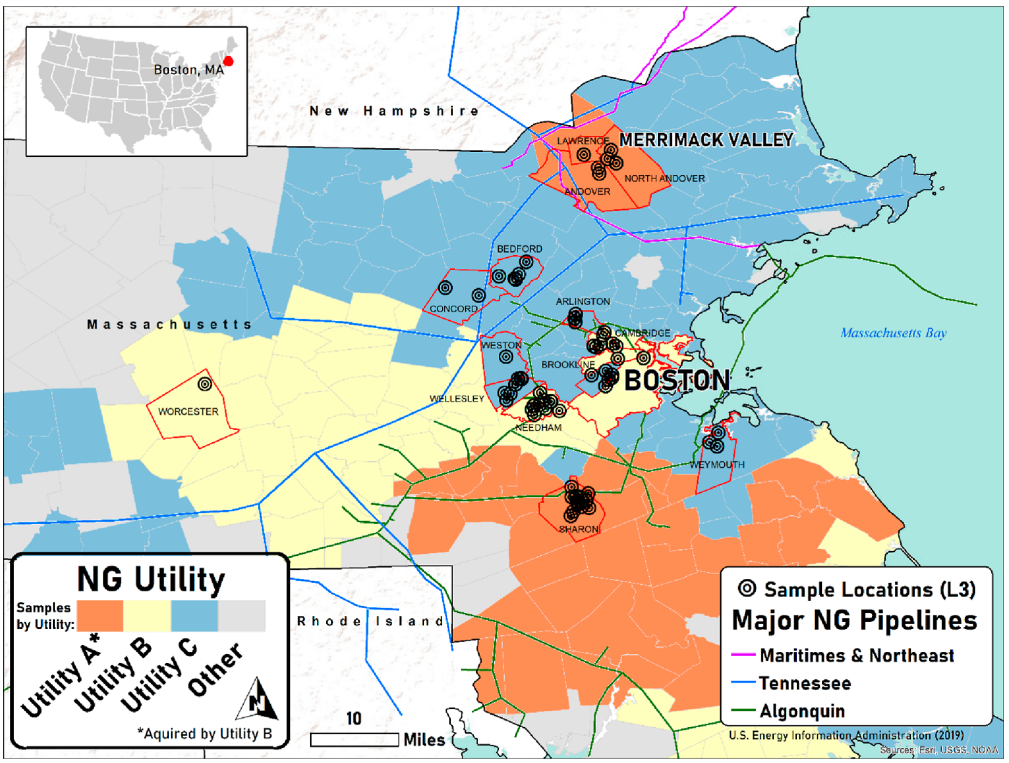


**Figure 1.** Unique sample locations (black markers) by municipality (red outline) across the three major Greater Boston NG utility providers. Note, some locations were sampled multiple times. *Utility A was acquired by Utility B on October 13, 2020.

**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) | *n* (% 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 |
| *m,p*-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 |
| *o*-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-sichloroethane [107-06-2] (ppbv) | 24 (10) | 0.0652 | 0.039 | 0.0129 | 0.159 |

[a]VOCs 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 %. [b]Methane and ethane tested according to the EPA method 3C/modified 3C via aliquot from the original sample canister. [c]Methane 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. [d]At 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



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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: ±9.7%; toluene: ±12%; ethylbenzene: ±14%; xylenes: ±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.

$$\begin{aligned}&\text{BTEX emissions (kg yr}^{-1}\text{)}\\&\quad = \text{CH}_4\text{ flux (kg yr}^{-1}\text{)} \times \text{MW BTEX (g mol}^{-1}\text{)/MW}\\&\qquad \text{CH}_4\text{ (g mol}^{-1}\text{)} \times [\text{BTEX}]/[\text{CH}_4] \qquad (1)\end{aligned}$$

## 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 $iC_5$/



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$nC_5$ 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 $\mu g/m^3$) 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 $PM_{2.5}$. 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 review[21] 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 ∼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 $6.26 \times 10^{-3}$ 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 $6.26 \times 10^{-3}$ 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 0.08[39] or 0.029 ppbv.[40] Relatedly, after scaling $CH_4$ content to 100% minus $C_2H_6$% 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



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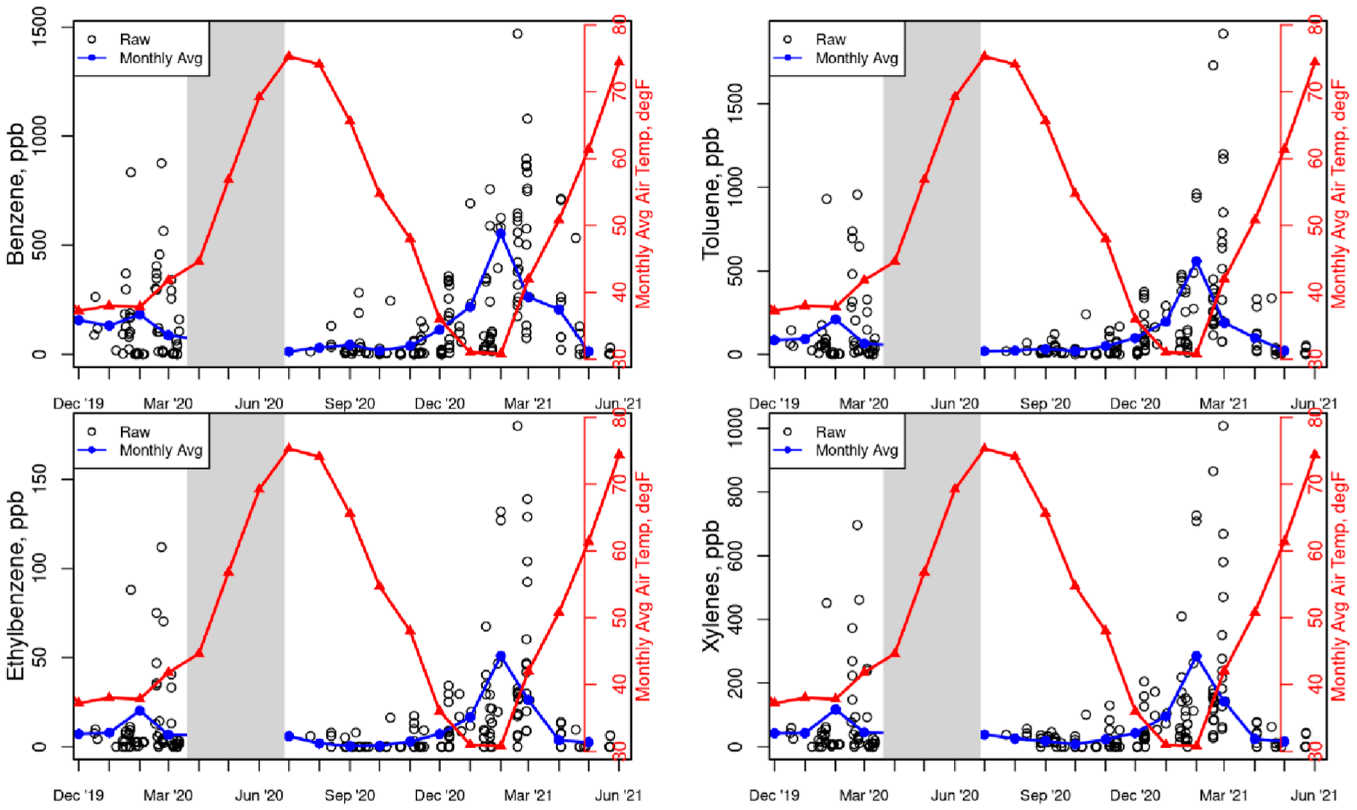


**Figure 2.** BTEX content of NG in raw (markers) and monthly averages (blue). Monthly averaged regional air temperature (°F) from the National Oceanic and Atmospheric Administration (NOAA) is displayed in red. The COVID-related sampling pause from mid-March 2020 through mid-July 2020 is highlighted 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 $6.26 \times 10^{-3}$ 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 $6.26 \times 10^{-3}$ 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 anosmia[41] 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 ± 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



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Table 2. BTEX by Local Distribution Company Territory[a]

| | mean (95% CI) for BTEX constituents by LDC, ppbv | | | |
|---|---|---|---|---|
| | benzene | toluene | ethylbenzene | xylenes |
| 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***) |

[a]All 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 $CH_4$ 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 ($\sigma_{sp}^2$) versus time ($\sigma_t^2$). $\sigma_t^2$ was calculated by pooling variances from each unique location having two or more samples across multiple dates. Similarly, $\sigma_{sp}^2$ 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, $CH_4$ varied approximately 3 times as much spatially versus temporally. However, while the $CH_4$ 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 $CH_4$ variation across samples. See the Supporting



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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[1] hydrocarbon sources via transmission pipeline,[2] natural reservoir variability,[3] NG processing steps and time in transit, and[4] 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 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.

**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 |

[a]Ratio and 95% CI calculated from RMA regression of BTEX data at end user points. [b]Burger et al.,[3] ratios estimated through published chromatographs of distribution-level NG samples; therefore, no uncertainty estimates are available. [c]Gulf 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. [d]DiGiulio and Jackson,[52] ratio and 95% CI calculated from RMA regression of BTEX data scraped from a pdf table of Bradenhead well-head data. [e]Goetz 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.

**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 $CH_4$ 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 $CH_4$ 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 $CH_4$ leakage throughout Greater Boston. For context, 216 kg/yr (476 lbs/yr) of benzene emitted annually (estimated via NG methane emissions from[17] 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 $CH_4$ 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.



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Table 4. Annual BTEX Emissions for the Entire 18,000 km$^2$ Area in McKain et al.[17] and the Approximately Similar Boston Bounds Used by Plant et al.[20] and Sargent et al[22]

| | Boston region NG $CH_4$ leaks (Tg/yr) | BTEX (kg/yr)* based on the Boston region NG leak estimates | | | |
|---|---|---|---|---|---|
| reference | $CH_4$ (95%CI) | benzene (95% CI) | toluene (95% CI) | ethylbenzene (95% CI) | xylenes (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) |

[a]18,000 km$^2$. [b]12,351 km$^2$.

## 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/XGNGEO (PDF)

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### Notes

The authors declare no competing financial interest.

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