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Street-level emissions of methane and nitrous oxide from the wastewater collection system in Cincinnati, Ohio

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Abstract

Recent studies have indicated that urban streets can be hotspots for emissions of methane (CH₄) from leaky natural gas lines, particularly in cities with older natural gas distribution systems. The objective of the current study was to determine whether leaking sewer pipes could also be a source of street-level CH₄ as well as nitrous oxide (N₂O) in Cincinnati, Ohio, a city with a relatively new gas pipeline network. To do this, we measured the carbon ($\delta^{13}\text{C}$) and hydrogen ($\delta^2\text{H}$) stable isotopic composition of CH₄ to distinguish between biogenic CH₄ from sewer gas and thermogenic CH₄ from leaking natural gas pipelines and measured CH₄ and N₂O flux rates and concentrations at sites from a previous study of street-level CH₄ enhancements (77 out of 104 sites) as well as additional sites found through surveying sewer grates and utility manholes (27 out of 104 sites). The average isotopic signatures for $\delta^{13}\text{C}\text{-CH}_4$ and $\delta^2\text{H}\text{-CH}_4$ were $-48.5\text{‰} \pm 6.0\text{‰}$ and $-302\text{‰} \pm 142\text{‰}$. The measured flux rates ranged from 0.0 to 282.5 mg CH₄ day⁻¹ and 0.0 to 14.1 mg N₂O day⁻¹ (n = 43). The average CH₄ and N₂O concentrations measured in our study were 4.0 ± 7.6 ppm and 392 ± 158 ppb, respectively (n = 104). 72% of sites where fluxes were measured were a source of biogenic CH₄. Overall, 47% of the sampled sites had biogenic CH₄, while only 13% of our sites had solely thermogenic CH₄. The other sites were either a source of both biogenic and thermogenic CH₄ (13%), and a relatively large portion of sites had an unresolved source (29%). Overall, this survey of emissions across a large urban area indicates that production and emission of biogenic CH₄ and N₂O is considerable, although CH₄ fluxes are lower than those reported for cities with leaky natural gas distribution systems.

Summary:

In Cincinnati, a city with low levels of natural gas leaks from distribution pipes, the sewer system is a significant source of street level biogenic methane as well as nitrous oxide.

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Keywords

Methane; nitrous oxide; greenhouse gas; sewer gas; natural gas

Introduction

Atmospheric concentrations of the greenhouse gases methane (CH₄) and nitrous oxide (N₂O) are increasing as a result of human activities (Ciais et al., 2013; NOAA, 2016). Methane has a global warming potential 34 times greater than carbon dioxide (CO₂) over 100 years, and 86 times greater than CO₂ over 20 years (Myhre et al., 2013). N₂O has a global warming potential 298 times greater than CO₂ over 100 years (Myhre et al., 2013); N₂O is also the dominant ozone-depleting gas emitted by human activities (Ravishankara et al., 2009). Both CH₄ and N₂O have unique urban point and nonpoint sources. Examples of urban point sources of N₂O include wastewater treatment plants, fertilized landscapes, and industrial processes; whereas fertilized landscaping soils and, to a lesser extent, vehicle emissions, are diffuse or nonpoint sources of urban N₂O (Townsend-Small et al., 2011a; 2011b; USEPA 2015a; 2015b). Urban areas have discrete sources of CH₄ from landfills, dairies, wastewater treatment plants, and power plants, but natural gas pipelines and end uses such as homes, power plants, and customer meters are more diffuse CH₄ sources in cities (Lamb et al., 2015; 2016; Townsend-Small et al., 2012; 2016b).

Overall, the oil and natural gas supply chain is the largest anthropogenic CH₄ source nationally, accounting for approximately 30% of U.S. CH₄ emissions (USEPA, 2015a), and is likely the largest anthropogenic source globally (Saunio et al., 2016). The lack of quantitative data on this source in urban areas has motivated research on street-level CH₄ emissions from the underground natural gas distribution pipelines in roadways (Phillips et al., 2013; Jackson et al., 2014; Gallagher et al., 2015; Hendrick et al., 2016; von Fischer et al., 2017). For example, Phillips et al. (2013) and Jackson et al. (2014) mapped street-level CH₄ enhancements (~ 2.50 ppm) over urban roadways in Boston, MA and Washington, D.C., respectively. Both studies suggested that a majority of street-level CH₄ enhancements were from a thermogenic source, such as natural gas distribution pipelines. Using similar methods, Gallagher et al. (2015) surveyed three East Coast cities (Manhattan, NY, Cincinnati, OH, and Durham, NC) and found that cities with accelerated natural gas pipeline replacement programs, such as Durham and Cincinnati, had fewer street leaks per kilometer of roadway (0.14 leaks km⁻¹ and 0.29 leaks km⁻¹, respectively) than metropolitan areas with slower pipeline replacement programs such as Manhattan, Boston, and Washington, D.C., with 2.64 leaks km⁻¹ (Gallagher et al. 2015), 2.66 leaks km⁻¹ (Phillips et al., 2013), and 2.44 leaks km⁻¹ (Jackson et al., 2014), respectively. Similarly, von Fischer et al. (2017) showed that cities with older, more corrosion-prone distribution gas lines had higher leak rates of natural gas than those with more rapid pipeline replacement programs.

Although oil and gas systems are a large contributor to CH₄ emissions at a variety of spatial scales, all together, biological CH₄ production is the largest contributor to both natural (e.g., wetlands, lakes, and soils) and anthropogenic (e.g., agriculture and waste) emissions of CH₄ globally (USEPA, 2015a; Saunio et al., 2016). On city streets, CH₄ enhancements could

evolve from sewer and natural gas pipelines, both of which can leak from cracks, corrosion, or joint leakage as well as through vents, grates, and infrastructure access points such as manholes. Previous studies have indicated that sewer mains could be a source of atmospheric CH₄ (Guisasola et al., 2008; Liu et al., 2015; Chamberlain et al., 2016; Hopkins et al., 2016a) and/or N₂O (Short et al., 2014). The nutrient-rich wastewater carried in sewer pipelines encounters environmental conditions that produce both biogenic CH₄ and N₂O (Doorn et al., 2006; Townsend-Small et al., 2011a; US EPA, 2015a). The close placement of underground sewer and natural gas conveyances can result in the mixing of biogenic CH₄, N₂O, and natural gas, all of which are lighter than air and travel upwards along pressure gradients to vent as combined emissions into the atmosphere, either through infrastructure access points or via soil diffusion. Therefore, biogenic CH₄ produced in the wastewater collection system could be contributing to overall street-level CH₄ emissions, such that not all CH₄ enhancements are street leaks from the natural gas distribution pipelines. Biogenic CH₄ and thermogenic CH₄ can be distinguished by the carbon ($\delta^{13}\text{C-CH}_4$) and hydrogen ($\delta^2\text{H-CH}_4$) stable isotopic composition of CH₄ (Townsend-Small et al., 2012; 2015), or by analysis of other source apportionment tracers that are co-emitted with thermogenic CH₄, such as ethane or larger alkanes (Simpson et al., 2012; Hopkins et al., 2016b), or with biogenic CH₄, such as N₂O or ammonia (Leytem et al., 2011; Schneider et al., 2015).

The objective of this study was to determine the contribution of biogenic sources to street-level CH₄ and N₂O enhancements and emissions in Cincinnati, OH. We measured $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ and made measurements of CH₄ and N₂O emission rates and concentrations from utility manholes, sewer grates, and CH₄ hotspots identified in a previous study (Gallagher et al., 2015) as well as a variety of other locations on city streets.

Material and methods

Study Area –

All sampling took place between May and September 2016 within the city limits of Cincinnati, OH, a metropolitan area situated on the north bank of the Ohio River in southwestern Ohio. The city is located within Hamilton County, the primary county of operation for the Metropolitan Sewer District of Greater Cincinnati (MSD) to collect and treat wastewater. The MSD operates seven wastewater treatment plants (WWTP), and maintains approximately 5,000 kilometers of sewer pipeline (MSD, 2017). Our study area (Figure 1) covers 54% of the entire MSD wastewater collection system (Pittinger and Chen, 2017), and sites selected for sampling were located in the Mill Creek and Little Miami WWTP service areas. Cincinnati has combined sewer infrastructure, where storm sewers are combined with sanitary sewers during high runoff events. However, all sampling in the current study was conducted during dry conditions to avoid sampling combined sewers.

Site Selection –

Most of our sampling sites (77 out of 104 total; Table S1) were previously identified as CH₄ enhancements during a street-level survey of CH₄ concentration in Cincinnati (Gallagher et al., 2015); this represents a randomly selected subset (33%) of the 233 CH₄ enhancements originally identified by Gallagher et al. (2015). The remainder of our sites were either

located near sites identified in the Gallagher et al. (2015) study; qualitatively identified as emitters of CH₄ by the characteristic odor of mercaptan, the odorizer used in natural gas or the smell of septic sewage; or selected due to the known location of a combined sewage outfall or pipeline. Because 27 out of our 104 sites were selected this way, our emission rate measurements may be skewed high and may not be representative of the true range of emissions across the city. Most samples were collected from sewer grates or manholes (both utility access manholes and sewer manholes), with a small number of samples collected directly from streets or lawns where CH₄ enhancements were identified (Table S1).

Sample Collection –

Direct measurements were made from city streets within the study area (Figure 1). Each site was qualitatively screened with a Gas-Rover™ (Bascom-Turner Instruments, Inc., Norwood, MA; detection limit = 10 ppm CH₄) to indicate the presence or absence of elevated CH₄ levels. We then collected gas samples for CH₄ and N₂O concentration levels and analysis of $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$, although not all samples were analyzed for isotopic composition (see further discussion below). We also collected samples of natural gas and sewer gas for analysis of $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ endmembers. Natural gas samples were taken from one residential stove in Cincinnati and from the laboratory in the Department of Geology at University of Cincinnati. We also took samples from throughout a wastewater treatment plant in Cincinnati with preliminary, primary, secondary, and sludge digestion processes.

Air samples were collected by inserting a 100 mL syringe with stopcock that was fitted with a 66-cm long piece of plastic tubing into the manhole or sewer grate. The plastic tubing reached approximately 60 cm into the grate opening to ensure that sewer gas was being sampled. The syringe was filled and cleared three times before filling vials to ensure that sample gas, not ambient air, was sampled, and that the syringe and tubing were cleared between sampling events. This sample was then transferred using a hypodermic needle into a 20 mL pre-evacuated glass vial with gray butyl rubber septa and aluminum crimps for later analysis. Gas samples were taken as described above and transferred into 12 mL pre-evacuated glass vials (Exetainers®, Labco Ltd., Buckinghamshire, UK) for stable isotope analysis. At sites located at ground level (i.e., not in a sewer grate or manhole; Table S1), samples were taken from the spot previously identified in Gallagher et al. (2015) without inserting the tubing underground.

We also measured CH₄ and N₂O emission rates at a subset of sites (n = 43) where access was safe and which were located in easily accessible, low traffic areas; this accounted for 41% of the sampled sites. We used two chambers constructed in our laboratory from readily-available plastic containers to measure emissions from manholes (volume = 79.5 L; Figure S1) and sewer grates (volume = 55.6 L; Figure S2). We measured fluxes from 14 sewer grates and 29 manholes. For both chambers, a single hole was drilled at the top and fitted with an airtight Swagelok fitting with a rubber septum as a portal for direct gas measurements. A plastic skirt was added to the inside of each chamber and weighed down by a heavy chain to prevent external gas exchange with the sampling chamber. Battery operated fans were attached to the interior to ensure a well-mixed gas sample, as per Hendrick et al. (2016). Chambers were placed over each sampling site for ten minutes and

headspace samples were collected at two-minute intervals through the septa with a 100 mL syringe fitted with stopcock and needle and placed in pre-evacuated 20 mL glass vials with gray butyl rubber septa and aluminum crimps. These headspace samples were then analyzed for CH₄ and N₂O concentrations to generate a concentration time series to calculate the CH₄ and N₂O flux rates. Most fluxes were measured only once; at three sites, fluxes are presented as an average of two measurements taken on two separate days.

To calculate the fluxes, we used linear regression to determine the degree of correlation for the plotted chamber data of both CH₄ and N₂O. Sites that had a r^2 value of 0.80 or above were considered significant, and the flux rate for that site was calculated. Chamber measurements with an r^2 value of below 0.80 were defined as a flux of zero. To calculate the flux, we used:

$$F_P = S_P \times (0.0001\% \text{ ppm}^{-1}) \times (60 \text{ min h}^{-1}) \times (24 \text{ hr d}^{-1}) \times (1 - 100\%) \times V \times (0.035 \text{ ft}^3 \text{ L}^{-1})$$

Where F_P is the flux rate ($\text{ft}^3 \text{ d}^{-1}$), S_P is the slope of the concentration time series of the efflux measurements (ppm min^{-1}) and V is the volume (L) of the chamber (Hendrick et al., 2016). We then converted F_P from volume of gas to mass of gas for both CH₄ ($1 \text{ ft}^3 \text{ CH}_4 = 18.58 \text{ g CH}_4$) and N₂O ($1 \text{ ft}^3 \text{ N}_2\text{O} = 50.94 \text{ g N}_2\text{O}$) at 1 atm and 25°C.

Sample Analysis –

All samples were analyzed for CH₄ and N₂O using a GC-PAL AOC 5000 autosampler connected to a Shimadzu GC-2014 greenhouse gas analyzer (Shimadzu Corporation, Japan) with a flame ionization detector and an electron capture detector. Known CH₄ and N₂O standards bracketing the peak areas of samples were analyzed alongside the unknown samples to calibrate the instrument. We generally use three standards for calibrating air samples and flux chamber samples ranging in concentration from below-ambient CH₄ and N₂O levels (2.18 ppm CH₄ and 293 ppb N₂O) to above-ambient (3.64 ppm CH₄ and 393 ppb N₂O); these standards were purchased from our carrier gas supplier and calibrated with a primary standard purchased from the National Oceanic and Atmospheric Administration Earth Science Research Laboratory. We also use standards for CH₄ with concentrations of 0.1%, 1%, and 10% to calibrate the GC for measurements of natural gas. The day-to-day precision of GC measurements is about 5 ppb for N₂O and about 0.001 ppm for CH₄, with a minimum detection limit for our flux measurement of about 0.2 mg N₂O d⁻¹ and 0.4 mg CH₄ d⁻¹.

Methane isotopic composition was measured only in samples that had elevated CH₄ concentrations based on our laboratory analysis via GC (> 2.5 ppm) and could therefore be corrected for background levels of CH₄ (as described in Townsend-Small et al. (2012)). Samples were analyzed for $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ via continuous flow isotope ratio mass spectrometry (Thermo Fisher Delta V) using gas chromatography combined with combustion/pyrolysis (Yarnes, 2013) at the University of Cincinnati. Calibrated CH₄ isotopic standards that bracketed the isotopic composition of the samples were analyzed concurrently. Standards were purchased from Isometrics, Inc. (Victoria, British Columbia) and cross-calibrated with standards from University of California, Davis (Yarnes, 2013) and

University of California, Irvine (Tyler et al., 2007; Townsend-Small et al., 2012). Samples are calibrated using a two, three, or four point curve using standards ranging in $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ ranging from -66.2‰ to -28.5‰ and -247‰ to -156‰ , respectively. The reproducibility of this method is 0.2‰ for $\delta^{13}\text{C-CH}_4$ and 4‰ for $\delta^2\text{H-CH}_4$ (Yarnes, 2013) and we routinely analyze multiple standards at atmospheric concentrations and pressures that meet or exceed this precision.

Source apportionment –

We defined CH_4 sources as biogenic, thermogenic, mixed, or unresolved in this study using CH_4 concentration, endmember isotopic composition, and isotopic composition thresholds from supporting literature (Townsend-Small et al., 2012; Phillips et al., 2013; Jackson et al., 2014; Gallagher et al., 2015; Hendrick et al., 2016) and the known composition of natural gas (Zumberge et al., 2012; Townsend-Small et al., 2015; Speight, 2017). Each sampling site was assigned a source type according to the following hierarchy, depending on the availability of each type of information for each site: 1), $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ stable isotopic composition; 2), CH_4 and N_2O flux rates; 3), and CH_4 and N_2O concentration enhancements above background atmospheric concentrations.

We used the ranges reported in Townsend-Small et al. (2012) for the isotopic composition endmembers for biogenic and thermogenic CH_4 (Table 1). Our results for isotopic endmembers of natural gas and wastewater treatment plant CH_4 in Cincinnati fell within these ranges (see below). We also assumed that the N_2O content of natural gas is negligible (Zumberge et al., 2012; Townsend-Small et al., 2015), and therefore that the presence of a positive N_2O flux indicated a biogenic source, and the absence of N_2O with a positive CH_4 flux indicated a thermogenic source (Table 1).

For sites without isotopic and/or efflux measurements, we used CH_4 and N_2O concentration enhancements above background levels in our samples to define the source (Table 1). During the sampling months, the average background CH_4 and N_2O concentrations we measured during the study period in Cincinnati, OH were 2.3 ppm, and 329 ppb, respectively. We defined CH_4 enhancement as a concentration at or above 2.5 ppm (as measured by the gas chromatograph), which is consistent with previous work (Phillips et al., 2013; Jackson et al., 2014; Gallagher et al., 2015; Hendrick et al., 2016). An N_2O enhancement was defined as a concentration at or above 339 ppb, which is 10 ppb above the background N_2O concentration. We defined sites that had an elevated CH_4 concentration (≥ 2.5 ppm), but no significant N_2O concentration (< 339 ppb) as thermogenic, and sites that had an elevated N_2O concentration (≥ 339 ppb), but no significant CH_4 concentration (< 2.5 ppm) as biogenic.

Since not all samples fell within these exact ranges, we defined sites that fell in between these known ranges as mixed (Table 1). Some “mixed” sources had a $\delta^{13}\text{C-CH}_4$ signature in the biogenic range and a $\delta^2\text{H-CH}_4$ signature in the thermogenic range. Other sites defined as “mixed” had $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ isotopic signatures indicating a thermogenic CH_4 source but exhibited a positive N_2O flux rate, which indicated that both natural gas and sewer gas contribute to greenhouse gas emissions at that site. Because not all sites had isotopic data, efflux measurements, or CH_4 and N_2O concentration enhancements, we

defined the remainder of the sites as “unresolved” (Table 1). In other words, unresolved sites did not have elevated levels of CH₄ and N₂O, and we did not measure flux rates or CH₄ isotope ratios at these sites.

Results

Greenhouse gas concentrations measured in this study are shown in Figure 2 and included in Table S1. The CH₄ concentrations ranged from 2.1 to 68.8 ppm of CH₄, with an average of 4.0 ± 7.6 ppm ($n = 104$), while the N₂O concentrations ranged from 298 to 1589 ppb of N₂O, with an average of 392 ± 158 ppb ($n = 104$) (Figure 2). The supplemental table also indicates which sites were re-sampled from the Gallagher et al. (2015) study, which pinpointed CH₄ concentrations on city streets (at an elevation of 30 cm) of 2.5 ppm or above. Of the 77 sites from the Gallagher study that we re-visited, 48 had a CH₄ concentration less than 2.5 ppm (measured via GC-FID and sampled mostly from underground as described above) (Table S1). The Gallagher et al. (2015) study points out that Cincinnati has a rapid natural gas pipeline replacement and leak repair program, and our results appear to confirm this. We found that 40 of our 104 sites had CH₄ concentrations at or above 2.5 ppm and N₂O concentrations above 350 ppb. It should be noted that concentrations measured in the current study were largely measured in samples taken underground, as described above, whereas the Gallagher et al. (2015) study measured CH₄ concentrations ~30 cm above the road surface.

Fluxes were measured at 43 of the 104 sites in our study. Methane flux rates ranged from 0.0 to 282.5 mg CH₄ d⁻¹, with an average rate of 18.3 mg CH₄ d⁻¹, while N₂O flux rates ranged from 0.0 to 14.1 mg N₂O d⁻¹, with an average rate of 1.8 mg N₂O d⁻¹ (Figure 3). For sites that were measured twice, some sites were highly variable over time and some were not. Variability in N₂O flux within one month ranged from 0.2 mg N₂O d⁻¹ to 11.9 mg d⁻¹ (the most extreme variability observed), whereas N₂O flux at one site measured over a two-day period ranged from 0.4 to 0.7 mg N₂O d⁻¹. The average standard deviation of flux measurements was 3.9 mg N₂O d⁻¹ and 7.3 mg CH₄ d⁻¹. Of sites where flux measurements were made, 51% of sites exhibited a combination of CH₄ and N₂O fluxes into the atmosphere, 26% exhibited only an N₂O emission, 14% exhibited only a CH₄ emission, and 9% were not a positive source of either constituent (Figure 3; Table S1). Emission rates of both CH₄ and N₂O showed a skewed distribution, where most sites are a small or zero source and the largest emissions are from a small number of sites (Figure 3).

Stable isotopic composition of samples taken during this study is shown in Figure 4. Only 37 of our 104 sites were measured for stable isotopic composition of CH₄ (Figure 4). We found that natural gas in Cincinnati had an average $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ of -39.8‰ and -168‰ , and that samples collected within the wastewater treatment plant had a $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ of -52.3‰ and -325‰ , respectively (Figure 4). These samples fall within the previously reported biogenic and thermogenic ranges for $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ (Townsend-Small et al., 2012), shown in Figure 4. The majority of the 37 samples measured for isotopic composition in our study indicated a biogenic CH₄ source ($n = 21$), whereas a small portion ($n = 3$) were from a thermogenic CH₄ source (Figure 4; Table S1). Thirteen

samples measured for isotopic composition were classified in the “mixed” category (see further discussion below).

Considering the isotopic data (Figure 4), the CH₄ and N₂O flux rates (Figure 3) and the CH₄ and N₂O concentration enhancements (Figure 2), we determined that 49 out of 104 (47%) of all sampled manholes and sewer grates contained biogenic CH₄; 13 out of 104 (13%) were attributed to a thermogenic CH₄ source; 13 out of 104 (13%) were attributable to a mixed CH₄ source; and 29 out of 104 (29%) had CH₄ concentrations below 2.5 ppm and N₂O concentrations below 350 ppb and were therefore attributed to an unresolved source (Table S1). Of the 43 sites where flux measurements were taken, 31 fell into the biogenic category (based on either isotopic or concentration enhancement data, depending on the availability of data for each site), 8 into the thermogenic category, 2 in the mixed category, and 2 in the unresolved category (Figure 3; Table S1). Of the 43 sites, 28 were sites identified by Gallagher et al., (2015) during their drive-around study and 5 of those fell fully into the thermogenic category (Figure 3).

Sites categorized as “mixed” generally fell into two categories. There were two sites that had fluxes of both CH₄ and N₂O, which would indicate biogenic sewer gas emissions, but had $\delta^{13}\text{C-CH}_4$ signatures indicative of natural gas and $\delta^2\text{H-CH}_4$ signatures indicative of biogenic sewer gas (Table S1). The other 10 sites in the “mixed” category did not have greenhouse gas flux measurements. These sites either had isotopic values outside of the known ranges for thermogenic and biogenic CH₄ or a $\delta^{13}\text{C-CH}_4$ value indicative of one source and a $\delta^2\text{H-CH}_4$ value indicative of another source (Figure 4). Some mixed sites also had thermogenic CH₄ isotopic signatures and elevated N₂O concentrations indicating both sources of CH₄ may be present (Table S1).

Discussion

We found that most street-level CH₄ emissions or elevated concentrations observed in Cincinnati during this study were associated with biogenic CH₄, perhaps from sewer pipelines, rather than thermogenic CH₄ from natural gas distribution pipeline leaks. Our results show that 72% of sampled sites that are a positive source of CH₄ were associated with a biogenic source (Figure 3), as were 47% of sites with CH₄ enhancements above background atmospheric concentrations (Figure 2). This suggests that street-level CH₄ enhancements should not be labeled as a natural gas leak without investigation of CH₄ source. Indeed, a previous study in Boston found that 34% of the street-level CH₄ enhancements had a biogenic $\delta^{13}\text{C-CH}_4$ signature (Phillips et al., 2013) and another study of CH₄ enhancements on streets in Ithaca, NY found that sewer gas could contribute to “false positives” (Chamberlain et al., 2016). Other studies have sampled a subset of CH₄ enhancements on city streets for isotopic composition and found similar isotopic composition to pipeline natural gas, including in Washington, D.C. and the previous study in Cincinnati (Jackson et al., 2014; Gallagher et al., 2015). Our study suggests that not all sites on city streets with positive CH₄ flux rates and CH₄ enhancements are solely from a thermogenic CH₄ source.

CH₄ Source –

We found that 13% of all surveyed sites in Cincinnati were from a thermogenic CH₄ source and another 13% were potentially from a combination of thermogenic and biogenic sources, while in Boston, MA, Phillips et al. (2013) found that 66% of sites were from a thermogenic CH₄ source. However, our study design may be somewhat biased toward biogenic sources, and we also assessed some sites without a concentration enhancement above street level, unlike the Boston study. The accelerated natural gas pipeline replacement program in Cincinnati likely reduced the number of identified thermogenic CH₄ enhancements in the city and prevented us from locating some natural gas leaks identified in 2014 (Gallagher et al., 2015). We re-visited 77 sites from the previous study (Gallagher et al., 2015) and found that many of them no longer had detectable CH₄ enhancements, and of the sites that did have CH₄ enhancements, some emitted biogenic CH₄ (Table S1; Figure 3). This is in sharp comparison to Boston, which has a much slower replacement program and a higher proportion of old cast iron distribution pipes (Gallagher et al., 2015; Lamb et al., 2015). Therefore, we may expect to see similar findings in other cities like Cincinnati with accelerated pipeline replacement programs, such as Durham, NC (Gallagher et al., 2015). We predict that as cities replace their natural gas distribution pipelines, the proportion of thermogenic CH₄ street leaks will decline, and biogenic CH₄ emissions from the wastewater collection system will contribute to street-level CH₄ enhancements.

The current study suggests that street-level CH₄ enhancements should not all be defined as natural gas leaks without measurement of source apportionment tracers. Previous measurements of a subset street-level CH₄ enhancements found a $\delta^{13}\text{C}\text{-CH}_4$ value of $-42.8\text{‰} \pm 1.3\text{‰}$ (Phillips et al., 2013) and $-38.2\text{‰} \pm 3.9\text{‰}$ (Jackson et al., 2014) for Boston, MA and Washington, D.C., respectively, both of which are within the known isotopic range for thermogenic CH₄ ($\delta^{13}\text{C}$: -45‰ to -30‰ ; Townsend-Small et al., 2012) and similar to the isotopic value of natural gas in Cincinnati ($\delta^{13}\text{C}\text{-CH}_4 = -39.8\text{‰}$, Figure 4). Measurement of $\delta^{13}\text{C}\text{-CH}_4$ using cavity ringdown spectroscopy at seven or eight sites with CH₄ enhancements in Cincinnati found an average $\delta^{13}\text{C}\text{-CH}_4$ of $-36.1\text{‰} \pm 2.6\text{‰}$, somewhat more enriched than our value for natural gas (Gallagher et al., 2015). However, since WWTPs are a known biogenic CH₄ source and sewer pipelines are placed in close proximity to natural gas pipelines, these sources can mix with natural gas sources. For example, we found a more depleted average $\delta^{13}\text{C}\text{-CH}_4$ value of $-48.5\text{‰} \pm 6.0\text{‰}$ for CH₄ sampled in Cincinnati, which falls within the general range for biogenic CH₄ ($\delta^{13}\text{C}$: -60‰ to -45‰ ; Townsend-Small et al., 2012) and closely resembles previously identified $\delta^{13}\text{C}\text{-CH}_4$ values from a WWTP in Southern California (-47.0‰ to -46.7‰) (Townsend-Small et al., 2012). We also measured CH₄ in a WWTP in Cincinnati with a $\delta^{13}\text{C}\text{-CH}_4$ of -52.3‰ (Figure 4). Future studies should be sure to incorporate source apportionment tracers such as stable isotopes into studies investigating street-level CH₄ enhancements.

Data for comparison among biogenic CH₄ sources using $\delta^2\text{H}$ in urban areas is sparse. A study in Los Angeles, CA observed a $\delta^2\text{H}\text{-CH}_4$ value of -298‰ at a sewage treatment plant (Townsend-Small et al., 2012). In the current study, the average $\delta^2\text{H}\text{-CH}_4$ value was $-302\text{‰} \pm 142\text{‰}$, which falls within the known isotopic ranges for biogenic CH₄ ($\delta^2\text{H}$: -350‰ to -275‰ ; Townsend-Small et al., 2012) and close to the $\delta^2\text{H}$ of CH₄ measured in the

Cincinnati WWTP (-325‰; Figure 4). The range in $\delta^2\text{H}$ in our study was much broader than expected (Figure 4), and suggests the possibility of isotopic exchange in the wastewater in pipelines prior to gas evasion (Whiticar, 1999), which deserves further attention. We sampled during normal sewer operations, not combined sewer overflows (which do occur in Cincinnati), but sanitary sewer water was present in pipes during our sampling events.

Using CH_4 and N_2O flux rates (Figure 3), we were able to further discern source for sites without isotopic data. Soils underlying city streets and sidewalks are not expected to be a significant source of N_2O because they are typically unsaturated and nitrogen poor (Raciti et al., 2012). The composition of refined natural gas ranges from 90% to 99% CH_4 , and does not contain N_2O (Speight, 2017). Depending on the reaction energies and lability of carbon resources, wastewater in sewer pipelines will be transformed through a number of physical and biochemical processes (Butler and Davies, 2004), and can produce biogenic CH_4 and N_2O (US EPA, 2015a), likely in varying proportions. In this study, we found that 33 out of 43 (77%) of sites either emitted both CH_4 and N_2O , or had just a positive N_2O flux rate; which together strongly suggest a biogenic source. These can, of course, be co-emitted with thermogenic CH_4 from leaking natural gas pipelines. We assumed that N_2O flux or concentration without a concomitant CH_4 flux or concentration indicated a biogenic sewer gas source, but the ideal method would be to measure stable isotopes of CH_4 along with CH_4 and N_2O flux or concentration at each site to determine whether thermogenic CH_4 is emitted with biogenic N_2O .

Lastly, we defined CH_4 source for sites without an isotopic or flux measurement using CH_4 and N_2O concentration enhancements above background atmospheric concentrations (Figure 2). In this study, 80 out of 104 (77%) of sites had either both CH_4 and N_2O enhancements, or just an N_2O enhancement (Figure 2; Table S1). These N_2O concentrations also indicate that sewer gas is widespread in Cincinnati, and suggest that sewers may be a source of CH_4 . Therefore, we suggest that measurement of N_2O may be a useful tool to determine CH_4 source in future studies, or at least, may indicate the presence of sewer gas while not ruling out the presence of natural gas CH_4 . Future studies should consider measurement of spatial and temporal variation in $\text{CH}_4/\text{N}_2\text{O}$ ratios in sewer gas.

CH_4 Emissions –

The largest point source of CH_4 enhanced emissions near Cincinnati, the Rumpke landfill, emitted approximately 25 million tons of CH_4 per year in 2015 (US EPA, 2015b) (actually, the Rumpke Landfill is the largest reported CH_4 source in the state of Ohio for 2015). We measured an average CH_4 emission rate for manholes and sewer grates in Cincinnati of $18.3 \text{ mg } \text{CH}_4 \text{ d}^{-1}$ (this estimate may be biased high, given our site selection approach). Applying this to the approximately 84,000 manholes and sewer grates within the Cincinnati Metropolitan Sewer District collection system (Pittinger and Chen, 2017), we estimate that approximately 0.07 ± 0.03 tons of CH_4 emissions per year come from the wastewater collection system. In other words, the landfill contributes approximately 37 million times more CH_4 to the atmosphere than the sewer system in Cincinnati. While the wastewater collection system may not be a prominent CH_4 source in Cincinnati, these manholes and sewer grates still contribute to local atmospheric CH_4 emissions and elevated street-level

CH₄ concentrations and should be considered as a nonpoint source, which may concentrate gases in certain parts of the wastewater service area.

The national average emission rates for natural gas distribution mains fall in the range from 432 to 1728 g CH₄ d⁻¹, per leak (Lamb et al., 2015). In Cincinnati, the CH₄ flux rate from the wastewater collection system is several orders of magnitude below this range (0.0 to 0.28 g CH₄ d⁻¹), which could be due to sampling only manholes and sewer grates and few natural gas leaks (Figure 3). By comparison, CH₄ emissions on Boston city streets are at the higher end of the national emission rate (4.0 to 23,000 g CH₄ d⁻¹; Hendrick et al., 2016), which could be due to sampling all of the detected, and likely thermogenic, street-level CH₄ enhancements, and not from sewer grates as in the current study.

Despite the different sampling designs, the differences in CH₄ flux rates between Cincinnati and Boston may also be due to different natural gas pipeline replacement and leak repair programs in each city (Gallagher et al., 2015). However, our study was focused on determining whether sewers could be responsible for some of the street-level CH₄ enhancements previously identified by Gallagher et al. (2015) and at getting a first-order estimate of CH₄ emission rates from sewers. Our results may be skewed towards higher-emitting sites, since we picked some sites that we thought would be a large CH₄ source, and may not accurately represent the variability in city-wide CH₄ emissions from all the different interfaces between underground utility conveyances and the atmosphere. Future work should also take care to characterize spatial and temporal variability in efflux, particularly diurnal and seasonal variability, as Cincinnati has combined sewers that likely contribute to high water, C, and N loading in sewers during storm events, which could fuel methanogenesis.

N₂O Emissions –

Our findings identify the wastewater collection system as a nonpoint source of N₂O in urban areas (Short et al., 2014). Other urban sources of N₂O include landscaped or agricultural soils, urban aquatic ecosystems, and WWTPs (Townsend-Small et al., 2011a; 2011b; McPhillips et al., 2016), but studies are sparse. We estimate that the approximately 84,000 sewer grates and manholes in Cincinnati contribute N₂O to the atmosphere at an average rate of 1.8 ± 3.9 mg N₂O d⁻¹ each, or 151.2 ± 326 g N₂O d⁻¹ for the city. It is difficult to put these numbers in context due to the small number of other studies for comparison. One previous study measured dissolved N₂O concentrations in sewage influent in New South Wales, Australia and determined an emission factor of about 1.7 g N₂O person⁻¹ yr⁻¹ (Short et al., 2014). Townsend-Small et al. (2011a) estimated N₂O emissions from southern California WWTPs to be ~27 kg N₂O d⁻¹, which is ~200 times greater than our estimates for the sewer system in Cincinnati. Wastewater and WWTPs are not the only N₂O sources in urban areas. Eutrophic aquatic ecosystems in the Cincinnati area are a source of N₂O, including the Ohio River (up to 15 mg N m⁻² d⁻¹; Beaulieu et al., 2010) and Harsha Lake, a flood control reservoir in the western suburbs (0.24 mg N m⁻² d⁻¹; Smolenski, 2013; Beaulieu et al., 2014). Townsend-Small et al. (2011b) found annual N₂O emission rates for urban lawns and athletic fields to be 0.0002 mg N m⁻² d⁻¹ in Los Angeles, CA, lower than the range of our per-site average emission rate of 1.8 mg N₂O d⁻¹. McPhillips et al. (2016)

estimated a N_2O flux rate of $0.07 \text{ mg N m}^{-2} \text{ d}^{-1}$ from suburban roadside ditches catching road runoff in upstate New York. However, in order to accurately compare the urban greenspace N_2O emissions from the studies mentioned above to the sewer fluxes in this study, we need to investigate landscape-level emission factors from different land uses in Cincinnati, and an estimate of greenspace area to scale the sewer emissions to the city area. Further investigation is required to better understand the magnitude of sewer N_2O emissions in urban areas to frame the overall significance of this source.

Implications –

In Indianapolis, IN, Lamb et al. (2016) estimated total urban CH_4 emissions by using top-down and bottom-up techniques. They quantified all known urban CH_4 sources in the city including a landfill, two WWTPs, a steam and power plant, interstate highways, and a variety of natural gas systems, including measurements from known leaking natural gas distribution pipelines. They found that the top-down emissions estimations were 1.4 to 2.8 times greater than bottom-up estimations, and suggest that a widespread diffuse CH_4 source similar to currently measured emissions from natural gas pipeline leaks might account for this gap between the estimation techniques (Lamb et al., 2016). It is possible that sewers are contributing to urban CH_4 emissions but are overlooked in estimation techniques. Our study found that the wastewater collection system in Cincinnati is an urban, nonpoint CH_4 source, suggesting that CH_4 emissions from manholes and sewer grates could help close the CH_4 estimation gap found in Indianapolis and potentially other cities (Lamb et al., 2016). However, further research on the contribution of CH_4 emissions from the wastewater collection system is necessary to fully understand city-wide CH_4 emissions. In particular, our study does not address the heterogeneity of biogenic greenhouse gas emissions from sewers, which is the essential next step in scaling-up of this emissions source. Leaking natural gas pipelines are an accepted part of the urban CH_4 budget (e.g., Lamb et al., 2015), and leaking sewer and other water conveyance systems are known to contribute to groundwater and surface water budgets in cities (Townsend-Small et al., 2013): here we demonstrate that sewers may also contribute to atmospheric CH_4 emissions in cities, albeit likely at lower levels than natural gas systems.

We found that underground sewers can co-emit biogenic CH_4 and N_2O , as both are produced in wastewater carried by sewer pipelines. Since the N_2O content is negligible in natural gas (Zumberge et al., 2012; Townsend-Small et al., 2015), positive N_2O flux rates and concentration enhancements may be a useful tracer method for determining CH_4 source in future studies, although not bulletproof as N_2O from sewer gas can be co-emitted with thermogenic CH_4 from natural gas sources. Since stable isotope measurements are typically done in the laboratory rather than in the field, measuring N_2O levels with real-time gas analyzers alongside CH_4 concentration (Arévalo-Martínez et al., 2013; O'Reilly et al., 2015) could be an easy and more cost-effective alternative for quickly determining the source of CH_4 emissions in urban roadways, or, at the very least, for pinpointing locations for gas sampling for later isotopic analysis.

This study appears to be the first to estimate street-level N_2O emissions from the wastewater collection system in the United States. Due to the substantial N_2O emissions and

concentrations we measured in Cincinnati, the findings suggest that ventilated manholes and sewer grates could be a potentially overlooked urban N₂O source (Short et al., 2014). Even though urban areas provide conditions for N₂O emissions in wastewater collection and treatment systems, N₂O contributions to urban greenhouse gas budgets are not well understood and require further investigation.

Conclusions

Direct measurements of CH₄ and N₂O concentrations were taken from a total of 104 manholes and sewer grates within the city limits of Cincinnati, OH to determine whether the wastewater collection system is a significant source of these powerful greenhouse gases. We resolved CH₄ source at 77 previously identified sites with CH₄ enhancements (Gallagher et al., 2015) and 27 additional sites with measurements of $\delta^{13}\text{C}\text{-CH}_4$ and $\delta^2\text{H}\text{-CH}_4$ isotopic compositions (n=37, 36% of sites), calculating the CH₄ and N₂O flux rates (n=43, 41% of sites), and identification of CH₄ and N₂O concentration enhancements. Overall, we found that the wastewater collection system in Cincinnati is a nonpoint, urban source of both CH₄ and N₂O. Of the sites where emission rate was measured, most sites (31 of 43 total) emitted biogenic CH₄, while only 8 out of 43 indicated a thermogenic CH₄ leak. The remaining sites were either from a mixed source of both biogenic and thermogenic CH₄ (2 out of 43) or an unresolved CH₄ source (2 out of 43). Of all the 104 sites in the study, 49 had biogenic CH₄ present. Our study shows the importance of further investigation into street-level CH₄ enhancements by determining the source of CH₄ to fully understand urban CH₄ emissions and create accurate city-wide CH₄ budgets in the future.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

The study area within the city limits of Cincinnati, OH with the locations of all sampled sites from this study (n=104) and the previously identified CH₄ enhancements determined by Gallagher et al. (2015). The colors identify the wastewater treatment plant (WWTP) basins within Cincinnati.

Figure 2.

CH₄ (left) and N₂O (right) concentrations measured at each site in our study (n=104). Data are also available in Table S1.

Figure 3.

The CH_4 (top panel) and N_2O flux rates (bottom panel) ($n=43$) measured in the current study shown as histograms organized in rank order according to emission rate. For CH_4 emissions, emissions are color coded according to the CH_4 source as indicated in the text. The x -axis of each graph also indicates which sites are from the Gallagher et al. (2015) study.

Figure 4.

$\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ of samples taken from city streets in Cincinnati, in gray circles ($n=37$). Also shown is natural gas from Cincinnati, in red diamond, and wastewater CH_4 from Cincinnati, in blue triangle, as well as previously published ranges of biogenic (blue) and thermogenic (red) CH_4 sources reported by Townsend-Small et al. (2012).

Table 1.

A summary of the parameters that were used with each method in this study to delineate between biogenic, thermogenic, mixed, and unresolved CH₄ sources (see methods). Methane source was assessed at each site according to the following hierarchy where data were available: 1), stable isotope data; 2), relative CH₄ and N₂O flux rates; and 3), CH₄ and N₂O concentrations.

CH ₄ Source	Method Type					
	Stable Isotopes ^a (‰)		Flux Rates (mg day ⁻¹)		Concentrations	
	δ ¹³ C-CH ₄	δ ² H-CH ₄	CH ₄ Flux	N ₂ O Flux	CH ₄ (ppm)	N ₂ O (ppb)
Biogenic	-65 to -45	-350 to -275	> 0.0 <i>OR</i> Zero Flux	> 0.0	< 2.5	> 339
Thermogenic	-45 to -30	-275 to -100	> 0.0	0	> 2.5	< 339
Mixed	-65 to -45 -45 to -30	-275 to -100 -350 to -275	0.0 + thermogenic isotopes	0.0	> 339 + thermogenic isotopes	
Unresolved	nd	nd	nm or 0.0	nm or 0.0	< 2.5	< 339

^a = Ranges reported in Townsend-Small et al., 2012, corrected for the presence of background air

nm = not measured

nd = not determined