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Controlled release testing of the static chamber methodology for direct measurements of methane emissions

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Abstract. Direct measurements of methane emissions at the component level provide the level of detail necessary for developing actionable mitigation strategies. As such, there is a need to understand the magnitude of component level methane emission sources and test methane quantification methods that can capture methane emissions from component level sources. The static chamber method is a direct measurement technique that is being applied to measure large and complex methane sources such as oil and gas infrastructure. In this work we compile component level methane emission factors from the IPCC emission factor database to understand the magnitude of component level methane flowrates, review the tested flowrates and measurement techniques from 38 controlled release experiments, and perform 64 controlled release testing of static chambers methodology with mass flowrates of 1.02, 10.2, 102, and 512 grams of methane per hour (g/hour). We vary the leak properties, chamber shape, chamber size, and usage of fans to evaluate how these factors affect the accuracy of the static chamber method. We find that 99% of component level methane emission rates from the IPCC emission factor database are below 100 g/hour, and that 77% of previously-available controlled release experiments did not test for methane mass flowrates below 100 g/hour. We find that the static chamber method quantified methane flowrates with an overall accuracy of $\pm$14%, and that optimal chamber configurations (i.e., chamber shape, volume, usage of fans) can improve accuracy to below $\pm$5%. We find that smaller chambers ($\leq$20 L) performed better than larger volume chambers ($\geq$20 L), regardless of the shape of chamber or usage of fans. However, we found that the usage of fans can substantially increase the accuracy of larger chambers, especially at higher mass flowrates of methane ($\geq$100 g/hour). Overall, our findings can be used to engineer static chamber systems for future direct measurement campaigns targeting a wide range of sources, including landfills, manholes, and oil and natural gas infrastructure.

1 Introduction

Methane is a potent greenhouse gas, and international initiatives such as the Global Methane Pledge have motivated national commitments towards reducing emissions of methane from a variety of sectors from waste to energy to agriculture. In order to materialize methane reductions through actionable mitigation strategies, accurate methane inventories that quantify methane from different sectors and sources are needed. Methane emission sources can be broadly classified as either site or component level emissions, where site level emissions are the sum of multiple emitting components. There are also additional classifications such as facility, regional, continental, and global level (National Academies of Sciences, Engineering) which encompass each preceding classification within a larger agglomeration of methane emission sources. Understanding methane emissions at

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the component level (i.e., the smallest tier of methane emissions sources) is particularly important for developing actionable methane reduction strategies as these data can be used to directly analyze the cost-benefits of mitigation options which allows policy makers to make informed decisions. For example, a carbon crediting system requires that the quantity of methane being emitted from a specific source is known (Kang et al., 2019; IEA, 2021). Overall, it is important that we test and develop methane quantification methods that are capable of measuring methane emissions accurately at the component level.

To select the optimal methane measurement methods, there is a need to understand the expected magnitude of methane emission rates from different component level sources. Some data sources such as the IPCC emission factor database (IPCC-EFDB, 2022) have compiled emission factors for different greenhouse gas sources around the world. However, some emission factors within this database are provided at the site level, and some are provided in alternative forms to methane emission rates (e.g., mass of methane emitted per ton of waste) which makes it difficult to determine the magnitude of expected component level emission rates. As such, our goal is to determine the approximate magnitude of methane emission rates at the component level so that we can conduct tests at appropriate methane flowrate ranges.

There are multiple methods that are used to quantify methane emissions, which we classify here as either indirect or direct methods. Indirect methane quantification methods are based on measurements made away from the source of emissions and can often be conducted without site access. These methods include mobile surveying, stationary tower (e.g., eddy covariance tower) measurements, aerial based surveys, and satellite measurements (Cusworth et al., 2022; Edie et al., 2020; Robertson et al., 2017; Kumar et al., 2022; Riddick et al., 2022; Ravikumar et al., 2017; Ayasse et al., 2019; Cooper et al., 2021; Varon et al., 2018). Direct methane quantification methods are based on quantifying methane emissions directly at the source of emissions and generally require site access. The most common direct measurement methods include optical gas imaging cameras, Hi-Flow samplers, and chamber based methodologies. Indirect measurements can be used to measure a large number of sources quickly and efficiently, but have higher limits of detection when compared to direct methods and additional challenges related to source attribution at the component level. On the other hand, direct measurement methods are labour intensive and typically limited to measuring emissions at a smaller scale, but can quantify and attribute methane emissions at the component level. In terms of testing methane measurement methods for accuracy, the majority of published literature has focused on indirect methods (e.g., (Robertson et al., 2017; Edie et al., 2020; Sherwin et al., 2021; Aubrey et al., 2013)), whereas few studies have tested and quantified the accuracy of direct measurement methods (Riddick et al., 2022; Pihlatie et al., 2013; Christiansen et al., 2011).

Among the direct measurement methods, optical gas imaging cameras and Hi-Flow samplers both have limits of detection at roughly 20 g/hour (Ravikumar et al., 2017; Fox et al., 2019), however the stated uncertainties of optical gas imaging cameras in (Fox et al., 2019) of 3-15% are noted as being complex and likely much higher, and there have been several studies that have highlighted measurement errors attributed to the Hi-Flow sampler (Connolly et al., 2019; Howard et al., 2015). As an alternative, the static chamber methodology is a direct methane measurement method (Riddick et al., 2022; Pihlatie et al., 2013) traditionally used in the measurement of methane and other trace gas emissions emissions from soils (Conen et al., 1998; Raich et al., 1990; Smith et al., 2003). In recent years, the static chamber method has been applied in a wide range of settings such as the quantification of methane emissions from oil and gas wells (Lebel et al., 2020; Williams et al., 2020;

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Kang et al., 2014; el Hachem et al., 2022; Townsend-Small et al., 2016, 2021; Saint-Vincent et al., 2020; Riddick et al., 2019), manholes (Fries et al., 2018; Williams et al., 2022), landfill vents and observation wells (Williams et al., 2022), and natural gas (NG) distribution infrastructure (Williams et al., 2022; Lamb et al., 2016, 2015). All of these sources vary in terms of their leakage properties and structural complexity with regards to the installation of chambers over leaking components. However, there are few studies that have quantified the measurement accuracy of the static chamber method, and even fewer (Riddick et al., 2022; Lebel et al., 2020) that have tested the static chamber method in conditions that mimic the wide range of settings.

Different methane sources can emit methane at the same mass flowrates albeit at different volumetric flowrates depending on the methane concentration of the source. For example, biogas produced from landfills ($\sim$50% methane) will differ in its source methane concentration from NG from a distribution pipeline ($\sim$90% methane). To our knowledge, there have been no studies that have tested the effects of a varying volumetric flowrate of methane as a factor to be considered in measurement accuracy for any methane measurement method. In terms of the structural complexity of these sites, several studies have employed large chambers with sub-optimal shapes to accommodate more complex sites. For example, a study by Lebel et al. 2020 in California targeting oil and gas wells used three static chambers that ranged in size (i.e., 33.8 litres to 32,659 litres) and shape (i.e., cylindrical and rectangular configurations). A key assumption in the static chamber method is that the air/gas within the chamber is well mixed (Kang et al., 2014). If the emission rate is low and the chamber is large, it may be challenging to have the gases in the chamber be well-mixed. Chamber shapes such as rectangular have been shown to have "dead zones" where gases are not well-mixed, thereby lowering the effective volume of the chamber (Christiansen et al., 2011).

In this work we: 1) compile component level methane emission factors and categorize them by source category; 2) investigate prior controlled release testing of direct and indirect methane measurement methods to identify gaps in testing; 3) test the impacts of physical factors such as the chamber shape, size, and usage of fans on the accuracy of methane flowrate estimates; and 4) test the effects of leak properties on the accuracy of chamber measurements. Our results highlight the applicability of the static chamber technique in direct measurements of methane emissions and provide the detail necessary to inform future measurement campaigns.

2 Methodology

We compiled a dataset of methane emission factors from the IPCC emission factor database (IPCC-EFDB, 2022) and categorized them into three source categories: agriculture, forestry, and other land use (AFOLU), energy, and waste. We removed all emission factors that were not related to a direct mass flowrates of methane at the component level. We removed all emission factors presented as methane flux rates (i.e., mass of methane emitted over a given area), and where possible, converted all remaining methane emission factors to component level methane mass flowrate presented in grams of methane emitted per hour based on assumptions outlined in the SI - Table S1.

We performed a literature review of 37 controlled release experiments of methane using both indirect and direct methods to evaluate the range of methane flowrates tested and the methods used. The criteria for the literature review included all studies where methane was released at known mass flowrates of methane from above-ground points and excludes studies related to

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Table 1. Physical descriptions of chambers used for the controlled release experiments. Qualitative descriptions of chamber volume are indicated in parenthesis in the first row.

Chamber ID	A	B	C	D
Chamber size (L)	2,265 (large)	322 (large)	18 (small)	14 (small)
Shape	Rectangular	Cylindrical	Cylindrical	Rectangular
Structure	Collapsible	Collapsible	Solid	Solid
Material	PE tarp	PE plastic	HDPE plastic	HDPE plastic
Aspect ratio	5:4	18:11	1:1	4:5

PE = polyethylene, HDPE = high density polyethylene

methane released in the subsurface, laboratory experiments of methane plume transport through porous media, and studies where the tested mass flowrates of methane were not reported. We also exclude studies where methane quantification methods were tested on in-situ methane sources for validation. We categorized the studies based on the tested measurement platform which we grouped into eight categories: satellite (indirect method), manned aerial vehicle (indirect method), unmanned aerial vehicle (indirect method), stationary tower (indirect method), mobile surveying (indirect method), Hi-Flow sampler (direct method), camera-based (direct method), chamber measurements (direct method), and/or a combination of all the above.

We performed controlled releases of methane for the static chamber method outdoors on the McGill University campus in Montréal, Canada on June 2nd, 8th, and 10th, 2021. The weather for these days was sunny with sparse clouds with an average temperature of 25^{o}C and wind speeds ranging from 5-15 kph (World Meteorological Station ID: 71612) . We designed the controlled release experiments to test a combination of six different factors: mass flowrate, volumetric flowrate, methane percentage of leaking gas, chamber shape (i.e., rectangular versus circular), chamber size (i.e., 14 L, 18 L, 322 L, and 2,265 L), and the usage of the fans within the chamber. For the 322 L and 2,265 L chambers we used four battery-powered equipment cooling fans (airflow: 40 ft^3 of air per minute) installed at the top of the chamber framework and oriented at 45^{o} angles downward into the chamber, and for the smaller chambers we used one fan. For the analysis of chamber size on quantification accuracy, we grouped the results from the 14 L and 18 L chamber together as a single $\leq$20 L category in order to have three different chamber sizes that span three orders of magnitude. The tested chamber shapes were a 2,265 L rectangular chamber, a 322 L cylindrical chamber, a 18 L cylindrical chamber, and a 14 L rectangular chamber (Table 1). In addition, for a qualitative comparison between chamber sizes we define $\leq$20 L chambers as small, and the 322 L and 2,265 L chambers as large. Other factors such as the aspect ratio of the chamber, the rigidity of the chamber material, and the type of chamber material are provided in Table 1.

We tested four different mass flowrates: 1.02 g/hour, 10.2 g/hour, 102 g/hour, and 512 g/hour. In order to provide a qualitative comparison between mass flowrates, we define the mass flowrates of 1.02 and 10.2 g/hour as small flowrates, and the 102 and 512 g/hour releases as high flowrates. At least two different volumetric flowrates and two different methane concentrations were used for each of the mass flowrates we tested. The volumetric flowrates ranged from 0.238 SLPM (standard litres per minute) to 23.8 SLPM for a total of ten unique leaks (Table 2). We controlled mass flowrates of methane using two mass flow

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Table 2. Leak properties of ten different leaks used in controlled release experiments including percentage errors associated with mass flow controllers (MFC). Qualitative descriptions of the leak sizes are shown in parenthesis in the first column.

Methane mass flowrate (g/hour)	Volumetric flowrate (SLPM)	% methane	MFC error
1.02 (small flowrate)	0.238	10%	±1.64%
-	0.476	5%	±1.22%
10.2 (small flowrate)	0.476	50%	±1.64%
-	2.38	10%	±5.00%
-	4.76	5%	±2.90%
102 (large flowrate)	2.38	100%	±5.00%
-	4.76	50%	±2.90%
-	23.8	10%	±1.22%
512 (large flowrate)	11.9	100%	±1.64%
-	23.8	50%	±1.22%

SLPM = Standard litres per minute, MFC = Mass flow controller

controllers (Masterflex Mass Flowmeter Controller) with volumetric flow ranges of 50 to 0.5 SLPM and 1 to 0.01 SLPM (error of ±0.8% of reading and ±0.2% of full-scale range). Both mass flow controllers were factory calibrated prior to use for these experiments. Four different methane standards, prepared by Linde Canada, were used in our study: 100%, 50%, 10%, and 5% methane (±0.5%) all with a gas balance of air.

We performed the controlled release tests by releasing methane through Tygon tubing connected to the chamber. We oriented the tubing to the center of the chamber and secured it to the ground with tape to orient the flow upwards. We measured methane concentrations within the chamber continuously using a Sensit Portable Methane Detector which has a range of 0-100% methane, precision of 1 ppm, sampling frequency of 1 Hz, pump flow of 1 L per minute, and a reported accuracy of ±10%. The analyzer was located outside the chambers with the analyzer inlets and outlets connected to the chamber ports in a closed loop with Tygon tubing of equal lengths for the inlet and outlet. Chambers were equipped with a 2 meter coil of 1/8" diameter Tygon tubing to allow for pressure equalisation between the chamber and the atmosphere (Christiansen et al., 2011). The duration of each controlled release was 5 minutes, with the exception of releases where fans were used within the chamber and methane concentrations were expected to reach the lower explosive limit of methane (i.e., 5% methane) before the 5 minute mark. Since the fans were not intrinsically safe, these experiments were terminated when the methane concentration within the chamber reached 35,000 ppm (i.e., 70% LEL). For this same reason, we did not test mass flowrates of 102 and 512 g/hour with the smaller chambers (i.e., ≤20 L) with fans present. When larger volume chambers were used, we were able to maintain methane levels within the chamber at safe limits.

Mass flowrates were calculated from the rate of methane build-up within the chamber over time multiplied by the volume of the chamber (1): where M is the mass flowrate of methane, dc/dt is the change in methane concentration over time, and V is

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the volume of the chamber.

$$M = \frac{dc}{dt}V \tag{1}$$

We summarized the results of each controlled test as an absolute percentage error (2): where E is the error in (%), Q_i is the estimated methane flowrate and Q is the actual methane flowrate. We calculated the bias of measurements as the average of the raw percentage errors to determine whether tests were biased more towards the under- or overestimation of methane flowrates.

$$E = |\frac{Q_i - Q}{Q}| * 100 \tag{2}$$

3 Results

3.1 Prior controlled methane releases and component level methane emissions

We compiled a total of 1,142 component level methane emission factors from the IPCC emission factor database (IPCC-EFDB, 2022). A total of 718 emission factors were from the AFOLU sector, 291 were from the energy sector, and 133 were from the waste sector. The emission factors ranged from 9.8×10^{5} to -1.1×10^{-2} g/hour. We found that 1% of emission factors were above 100 g/hour, 5% of emission factors were above 10 g/hour, and 45% of emission factors were above 1 g/hour. Within the energy sector, we found that the highest component level emission factors were associated with liquid unloadings of storage tanks, flowback events for unconventional oil and gas wells, and fugitive emissions from flaring and venting at oil and gas wells which ranged from 9.8×10^{5} to 1.6×10^{5} g/hour. For the waste sector, we found that the highest component level emission factors were associated with leachate collections wells, pump stations, and sludge pits from landfills which ranged from 4.3×10^{3} to 2.4×10^{3} g/hour. For the AFOLU sector, we found that no component level emission factors were above 100 g/hour, but the highest component level methane emissions we observed from the AFOLU sector were from enteric fermentation from dairy cattle which emitted in the range of 10 g/hour (Figure 1).

We analyzed a total of 38 controlled release studies spanning from 2011 to 2022 (Figure 2). We found that 30 of the 38 (i.e., 79%) controlled release tests had upper methane emission ranges that exceeded 1,000 g/hour, with the highest tested flowrate at 1.03×10^{6} g/hour for a manned aircraft based platform (Sherwin et al., 2021). We also found that 28 of the 38 (i.e., 74%) controlled release tests had a lower methane emission range that exceeded 100 g/hour. We found the majority of controlled releases focused on indirect sampling methods, especially with mobile surveying (i.e., 42%) and manned aircraft (i.e., 31%) based measurement platforms (Figure 2). Other indirect methods that were tested less frequently in our review were unmanned aircraft (i.e., 19%), stationary tower (i.e., 11%), and satellite (i.e., 3%) based methods. For direct measurement methods, we found that camera-based methods were tested the most frequently (i.e., 11%). We only found three studies we found conducted controlled methane releases for chamber based methodologies (Riddick et al., 2022; Pihlatie et al., 2013; Christiansen et al., 2011). We found that eight studies performed controlled releases using multiple measurement methods, with two studies (Singh et al., 2021; Riddick et al., 2022) employing five different methodologies. Overall, we found that the

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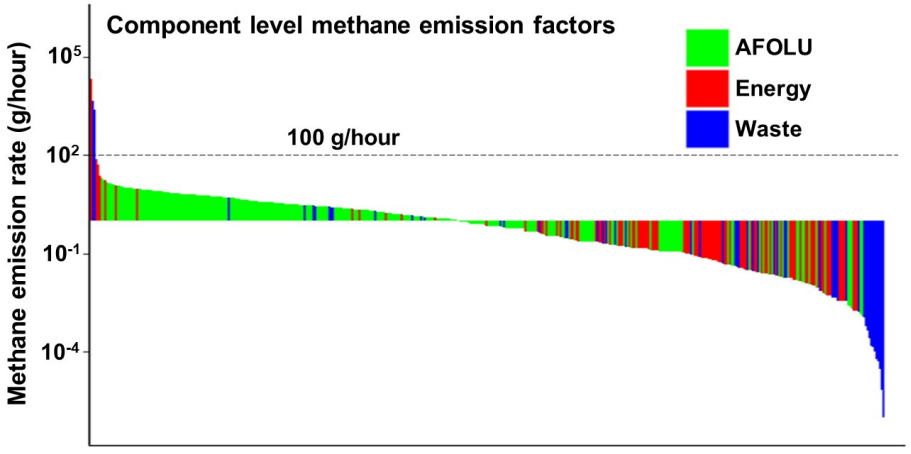

Figure 1. Component level methane emission factors from the IPCC emission factor database. Emission factors are categorized according to their respective IPCC source category. All emission factors were converted to methane mass flowrates based on assumptions outlined in the SI-Section 1.1.

majority of controlled release tests we analyzed focused on indirect sampling methods, and tested methane emission ranges of $\geq$ 100 g/hour. Therefore, the testing we present here (1.02 g/hour to 512 g/hour) fills this gap and provides guidance for measuring a wide range of component level methane sources.

3.2 Controlled releases of methane

The median absolute error of our 64 controlled release experiments was $\pm$14% with a standard deviation of 20%. The lowest error we observed was 0.2%, and 25 of 64 controlled release tests (i.e., 39%) had percentage errors lower than $\pm$10%. Based on testing for bias, we found that the average percentage difference between actual and measured mass flowrates to be -4%, implying a small bias towards the underestimation of methane flowrates.

3.2.1 Chamber volume

We found that the median percentage errors decreased with smaller chamber volumes (Figure 3). The $\leq$20 L chambers had the lowest median percentage errors at $\pm$6% with an error standard deviation of 10%. The 322 L chamber had a higher median percentage error of $\pm$16% with a standard deviation of 22%. Our highest errors were measured from the largest 2,265 L chamber with a median error of $\pm$19% and a standard deviation of 26%. We observed that the median value of the percentage error was lower than the mean for all chamber volumes, indicating an extreme distribution in error values. We analyzed all three chamber sizes for bias and found that the $\leq$20 L chambers showed a slight tendency for underestimation of flowrates

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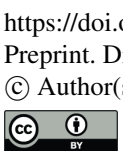

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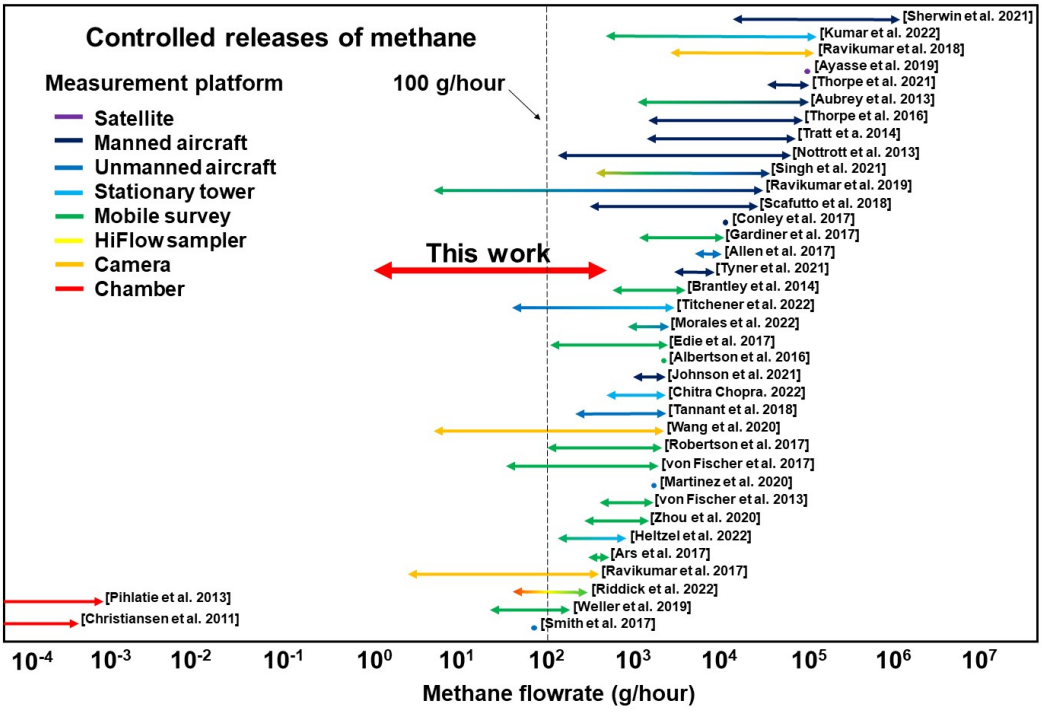

Figure 2. Summary of published literature of controlled releases of methane showing the range of methane emissions being tested and coloured according to the measurement platform used to quantify emissions.

with an average bias of -2%, the 322 L chamber showed a stronger tendency towards the underestimation of flowrates at -19%, and the 2,265 L chamber showed a slight bias towards overestimating flowrates at +6%.

3.2.2 Chamber shape

We found that the cylindrical chambers were more accurate than the rectangular chambers, showing a median percentage error of ±13% and a standard deviation of 18% (Figure 3). We found that the rectangular chambers showed a median percentage error of ±15% with a standard deviation of 22%. Similar to the chamber volume, we found that the median percentage error was smaller than the average error for both chamber shapes, which indicates an extreme distribution in percentage errors. We analyzed both chamber shapes for bias and found that the cylindrical chambers were biased towards the underestimation of methane flowrates with an average bias of -14% whereas the rectangular chambers showed a small bias towards the overestimation of methane flowrates with an average bias of +5%.

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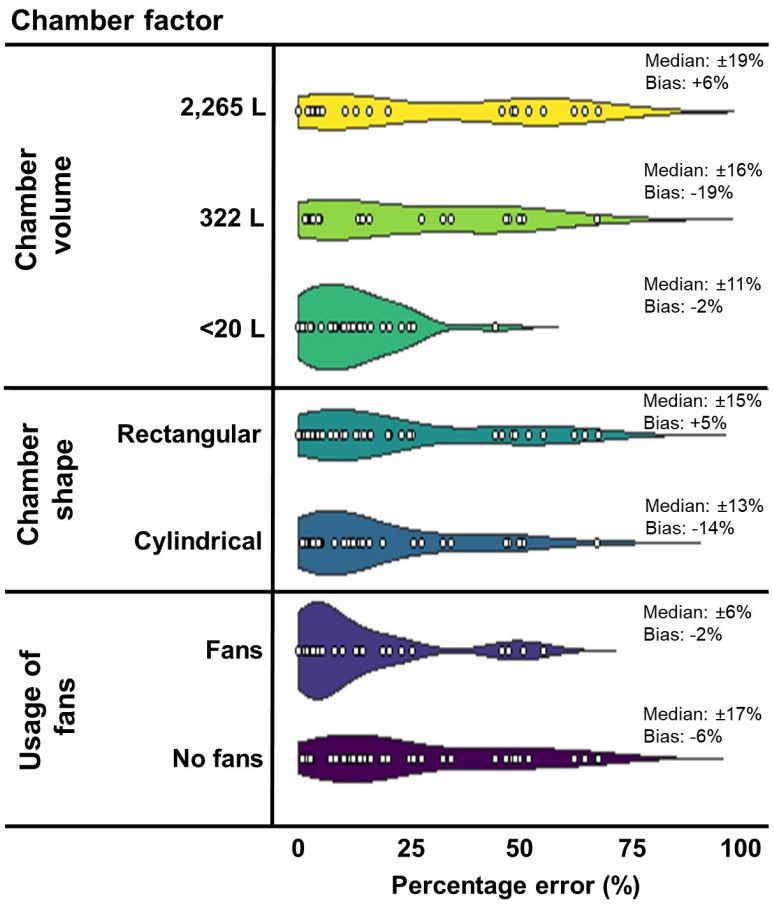

Figure 3. Violin plots of percentage errors of controlled release experiments for static chambers with different chamber volumes (top), different chamber shapes (middle), and with and without fans for interior chamber mixing (bottom). Median percentage errors and bias are for each violin plot.

3.2.3 Usage of fans

195 We found that chambers with fans present were more accurate than chambers without fans with a median percentage error of $\pm 6\%$ with a standard deviation of 17% (Figure 3). We found that chambers without fans had a median percentage error of $\pm 17\%$ with a standard deviation of 22%. For both data-sets we observed median values lower than the mean indicating a skewed data-set. We analyzed both data-sets for bias and found that both chambers with and without fans showed slight biases towards the underestimation of methane flowrates at -6% and -2% respectively.

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3.3 Effects of leak properties

3.3.1 Mass flowrate

We tested four different mass flowrates for our controlled release tests: 1.02 g/hour, 10.2 g/hour, 102 g/hour, and 511 g/hour (Figure 4). We found that the lowest errors were measured from the 10.2 and 102 g/hour mass flowrates each with median percentage errors of $\pm 10\%$. The highest median percentage error of $\pm 26\%$ was attributed to the highest mass flowrate of 512 g/hour. We found that the 1.02, 10.2, and 102 g/hour mass flowrates all had negative biases of -11%, -2%, and -8% respectively. The mass flowrate of 512 g/hour had a slight bias of +2% towards the overestimation of mass flowrates. We observed a positive correlation between the mass flowrates and average percentage errors with an R^2 value of 0.52, implying a medium correlation between the accuracy of chamber measurements and the mass flowrate of methane.

3.3.2 Volumetric flowrate

We analyzed six different volumetric flowrates for the range of methane flowrates we tested: 0.238 L/min, 0.476 L/min, 2.38 L/min, 4.76 L/min, 11.9 L/min, and 23.8 L/min (Figure 4). We found that the highest percentage errors were attributed to the highest and lowest volumetric flowrates with median percentage errors of $\pm 26\%$ and $\pm 20\%$ respectively. We found lower average percentage errors were associated for volumetric flowrates of 11.8, 4.76, 2.38, and 0.476 SLPM with median percentage errors ranging from $\pm 10\%$ to $\pm 15\%$. Similar to the mass flowrates, we also found a positive correlation between the median percentage errors and volumetric flowrates, albeit with a low correlation coefficient (R^2 = 0.32).

3.3.3 Methane percentage of leaking gas

We analyzed four different percentages of methane in the leaking gas for the controlled releases (Figure 4). We found that the highest percentage errors were attributed to the 5% methane gas with a median percentage error of $\pm 17\%$. We found lower average percentage errors were associated for gases with methane concentrations of 10%, 50%, and 100% with median percentage errors of $\pm 11\%$, $\pm 14\%$, and $\pm 11\%$ respectively. Unlike the mass and volumetric flowrates, we found negative correlation between the methane percentage of the leaking gas and the median percentage error with a weak correlation coefficient (R^2 = 0.25).

3.4 Optimizing the static chamber method for accuracy

For consistency, we define release rates of 1.02 and 10.2 g/hour as small flowrates, and releases of 102 and 512 g/hour as high flowrates. In addition, we define chamber volumes $\leq$20 L as small, and chamber volumes of 322 L and 2,265 L as large. We found that chamber configurations (i.e., chamber volume, usage of fans, chamber shapes) can be optimized to increase the accuracy of methane flowrate estimates. In general, we found that smaller sized chambers produced the lowest errors. Only one measurement from a smaller sized chamber produced a percentage error above $\pm 30\%$, which was for a flowrate of 10.2 g/hour in a rectangular chamber without fans (Figure 5). We also found that smaller chambers performed similarly if fans

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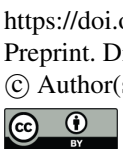

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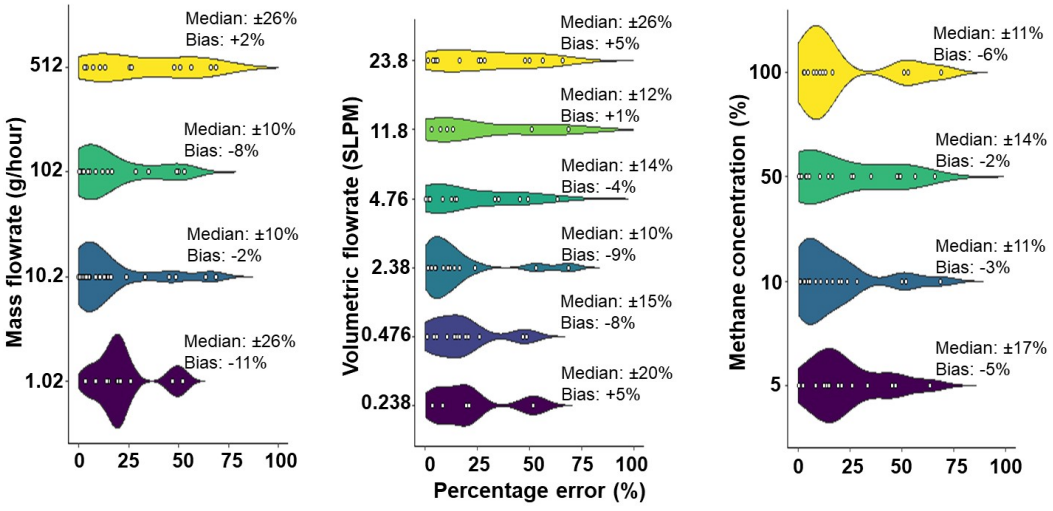

Figure 4. Violin plots of the percentage errors of true versus measured methane flowrates under varying mass flowrates (left), volumetric flowrates (middle), and gas concentrations (right) of methane. Median percentage errors and bias are for each violin plot.

were present or not, with smaller chambers with fans producing a median percentage error of $\pm 9\%$ and smaller chambers without fans producing a median error of $\pm 12\%$ (Figure 5). We also found that smaller chambers performed slightly better if the chambers were cylindrical, with a median percentage error of $\pm 10\%$ compared to smaller rectangular chambers that had a median percentage error of $\pm 14\%$. For larger sized chambers (i.e., $\geq$20L), we found that the usage of fans was critical for reducing measurement error. Larger chambers with fans produced a median percentage error of $\pm 6\%$ compared to large chambers without fans which produced a median percentage error of $\pm 49\%$. Therefore, although smaller chambers generally have lower errors than larger chambers, the errors in the larger chambers can be comparable to the smaller chambers when fans are used.

We found that chamber configurations could also be optimized according to the mass flowrate of methane. At low mass flowrates of methane (i.e., $\leq$ 100 g/hour), we found that smaller sized chambers were more accurate than larger chambers, with median percentage errors of $\pm 10\%$ and $\pm 16\%$ respectively. We found that the usage of fans had little impact on the accuracy of smaller sized chambers at these low flowrates, with smaller chambers with fans producing a median percentage error of $\pm 9\%$ and smaller chambers without fans producing median percentage errors of $\pm 13\%$. In contrast, we found that the usage of fans was important for the accuracy of larger chambers at these lower mass flowrates, with larger chambers with fans producing a median percentage error of $\pm 10\%$ and larger chambers without fans producing a median percentage error of $\pm 27\%$. In terms of chamber shape, we found that at low flowrates smaller cylindrical chambers produced a median percentage error of $\pm 8\%$ compared to small rectangular chambers which produced a median percentage error of $\pm 14\%$. For larger chambers at low mass flowrates, we found a contrasting result with large rectangular chambers producing a median percentage error of $\pm 14\%$ and large cylindrical chambers producing a median percentage error of $\pm 33\%$. Overall, we found

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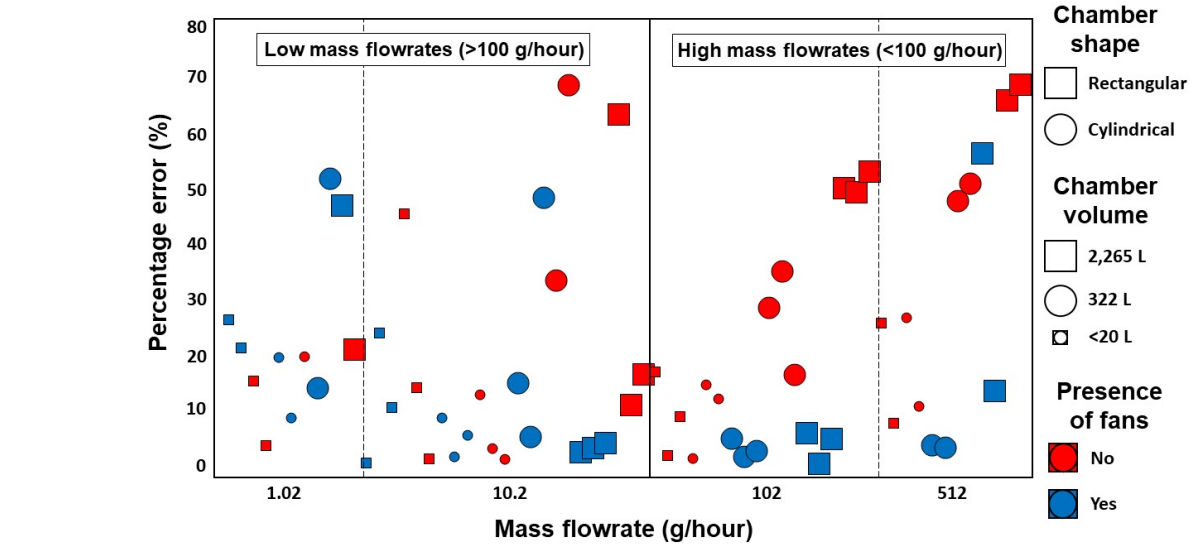

Figure 5. Results of all controlled release experiments of methane sectioned by mass flowrates. Points are sized according to the volume of the chamber, coloured according to whether fans were used or not, and assigned a shape corresponding to the shape of chamber used.

that at these smaller mass flowrates of methane, small cylindrical chambers with fans produced the lowest median percentage error of $\pm 10\%$ compared to $\pm 16\%$ from large chambers.

We observed similar results for optimizing chamber configurations for high methane mass flowrates (i.e., $\geq$100 g/hour). We found that smaller chambers ($\leq$20 L) performed better than larger chambers with a median percentage error of $\pm 11\%$ and $\pm 22\%$ respectively. We observe that the usage of fans was critical for measurement accuracy for larger sized chambers at these higher mass flowrates of methane. Larger chambers with fans had a median percentage error of $\pm 4\%$ compared to larger chambers without fans which had a median percentage accuracy of $\pm 50\%$. For chamber shapes, we found that cylindrical chambers were more accurate than rectangular chambers with median percentage errors of $\pm 13\%$ compared to $\pm 17\%$ from rectangular chambers. At these higher mass flowrates of methane, we found that large cylindrical chambers with fans produced the lowest average percentage errors of $\pm 3\%$.

4 Discussion

Our compilation of component level methane flowrates from the IPCC emission factor database showed that 99% of the component level emission rates fall below the 100 g/hour level. Therefore, it is important to develop and test methane quantification methods for these lower methane flowrates (i.e., $\leq$100 g/hour). Quantification of methane emissions at the component level provides a level of detail necessary to develop actionable mitigation strategies through the clear identification of emitting components. Most controlled release studies focus on indirect sampling methods which are effective in measuring methane

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emissions at the site and/or facility level scale. While these data are important for validating greenhouse gas inventories and quantifying emissions from super-emitting methane sources (Brandt et al., 2016; Ravikumar et al., 2017), emissions data at the component level are also needed to construct actionable mitigation strategies. Many of the component level sources we consider such as manholes, livestock, abandoned oil and gas wells, and NG pipeline leaks have all been shown to be significant methane sources at municipal, provincial/state/territorial, and national levels (Williams et al., 2022, 2020; el Hachem et al., 2022; Seiler et al., 1983; Kang et al., 2016; Hendrick et al., 2016). These sources are all characterized by low methane emissions rates below 100 g/hour range on average, which are challenging to measure using indirect methods. Several studies have highlighted the super-emitting nature of methane emission sources, particularly from the NG sector (Brandt et al., 2016). However, the upper range of super-emitting methane sources varies depending on the source being measured. For example, a study of methane emissions from Montreal, Canada, found that both residential NG meter-sets and manholes were significant sources of methane for the city despite having maximum methane emission rates of 4.2 and 33 g/hour respectively (Williams et al., 2022). While many controlled release studies focus on a higher range of methane emissions, it is still important that methods are developed and tested for lower methane emitting sources.

In addition to the factors we tested, there are several other sources of uncertainty in the static chamber method that we do not investigate. The methane concentration measurement method is one aspect of the static chamber method that will affect both the measurement accuracy and sensitivity of the method. In this work we use a portable greenhouse gas analyzer to continuously measure methane concentrations within the chamber. Uncertainty related to the frequency of methane concentration measurement and the accuracy and precision of the greenhouse gas analyzer are all important factors related to uncertainty. Furthermore, portable greenhouse gas analyzers can generally be classified as either measuring a full range of methane concentrations at the cost of precision at lower methane concentrations (i.e., $\leq$10 ppm methane), or measuring methane with high precision at the cost of an upper measurement range (i.e., 1,000 ppm). Therefore, the selection of the greenhouse analyzer can also be optimized according to the methane source being measured to improve accuracy. Other factors such as the release point of the emitted gas; presence of multiple emission sources; environment; chamber rigidity; method and strength of interior chamber mixing; and position of the gas sampling points are all factors that could also impact measurement uncertainty.

Our results show that the static chamber methodology can quantify methane emissions ranging from 1.02 g/hour to 512 g/hour with a median percentage error of $\pm 14\%$. Overall, we found a small bias towards the underestimation of methane flowrates which is similar to prior studies (Lebel et al., 2020; Pihlatie et al., 2013). For the larger chambers we find that the usage of fans is critical for maximizing accuracy, which is expected given the larger volume of air that is required to be mixed. We also find that chamber shape is more important for larger chambers than smaller chambers, with the large cylindrical chamber performing better than the large rectangular chamber. Ideally static chambers should be constructed to minimize potential "dead zones" where gases can accumulate (Christiansen et al., 2011), and cylindrical, or even spherical chambers, should facilitate easier mixing of air.

At higher methane flowrates ($\geq$100 g/hour) we found that our large cylindrical chamber with fans quantified methane emissions with the highest accuracy of any chamber we used throughout this study. In addition, a methane source such as an abandoned oil and gas well can have multiple emitting components (e.g., pipe flanges, valves, surface casing vents, soil

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gas migration) which could be missed if using smaller sized chambers. Methane concentrations within a smaller chamber can also rapidly reach explosive levels which can pose safety concerns if the environment is not intrinsically safe (Riddick et al., 2022), but these risks can be minimized at little cost to accuracy if fans are omitted. Furthermore, intrinsically safe methods of chamber mixing such as external pumps could be used to mix air within chambers, regardless of the size of chamber. Overall, our findings indicate that small chambers (i.e., $\leq$20 L), regardless of the chamber shape and usage of fans, can be used to quantify component level methane flowrates with an accuracy of $\pm 11\%$ for methane flowrates ranging from 1.02 to 512 g/hour. If larger chambers are required/desired, optimal configurations (i.e., fans present and cylindrical shapes) will produce errors $\pm 3\%$ for high methane flowrates (i.e., $\geq$100 g/hour).

5 Conclusions

Our results have shown that the static chamber methodology can be an effective and accurate method for the quantification of component level methane flowrates. While indirect sampling methods have been tested extensively, there is a need to test direct sampling methods given their ability to quantify methane emissions at the component level, which is important for developing actionable mitigation strategies. The static chamber method is logistically simple to implement and adaptable to multiple methane sources, making it a viable measurement option for many component level emission sources. Going forward, there are opportunities to improve the static chamber design to reduce measurement uncertainties. Our work provides the testing and design information for the static chamber methodology, thereby contributing to the range of measurement tools needed to quantify methane emission rates from all sources.

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Competing interests. The authors declare no competing interests

Data availability. Excel files of the IPCC emission factor database compilation are available for the AFOLU, Energy, and Waste sectors. Conversions to component level emission factors and justifications are provided within each excel file.

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