

**BABEȘ-BOLYAI UNIVERSITY OF CLUJ-NAPOCA
FACULTY OF ENVIRONMENTAL SCIENCE AND ENGINEERING
DOCTORAL SCHOOL OF ENVIRONMENTAL SCIENCE**

**INVESTIGATING METHANE SOURCES IN URBAN
ENVIRONMENTS: CLUJ-NAPOCA CASE STUDY**

***PhD Thesis
(Summary)***

Thesis supervisor:
Prof. Laurențiu-Călin BACIU

PhD Student:
HMOUDAH Mustafa

**Cluj-Napoca
2026**

Table of Contents

<i>Thesis Table of Contents</i>	3
<i>Table of Contents</i>	2
<i>Chapter 1. Introduction</i>	6
<i>Chapter 2. Literature Review</i>	7
2.1. Methane as a Greenhouse Gas (GHG)	7
2.2. Global Methane Budget.....	8
2.3. Urbanization and CH ₄ Urban Studies.....	10
<i>Chapter 3. Methods and Materials</i>	11
3.1. Study description.....	11
3.2. Instruments	12
3.3. Methodology.....	13
3.3.1. System-Based Methane Measurements (Point-Source)	13
3.3.2. Quantification of Methane Emissions	15
<i>Chapter 4. Results</i>	20
4.1. System-Based Methane Measurements (Point-source)	20
4.1.1. Aquatic Systems (AQ).....	20
4.1.2. Natural Gas End-Use Points (NG)	21
4.1.3. Sewer System Manholes (SE)	21
4.1.4. Building Basements (BS)	22
4.1.5. Traffic Emissions (TE).....	22
4.2. Street-Level Methane Measurements	22
4.2.1. First Street-Level Survey.....	22
4.2.2. Second Street-Level Survey	24
4.3. Quantification of Methane Emissions	25
4.3.1. Aquatic System Emissions (An Artificial Pond)	25
4.3.2. Individual Natural Gas Leak.....	25
4.3.3. Sewer System Emissions	25
<i>Chapter 5. Discussion</i>	26
5.1. System-Based Methane Measurements (Point-Source)	26
5.1.1. Aquatic Systems (AQ).....	26
5.1.2. Natural Gas End-Use Points (NG)	27
5.1.3. Sewer System Manholes (SE)	27
5.1.4. Building Basements (BS)	28
5.1.5. Traffic Emissions (TE).....	28
5.2. Street-Level Methane Measurements	29
5.2.1. First Street-Level Survey.....	29
5.2.2. Second Street-Level Survey	29
5.3. Quantification of Methane Emissions	30
5.3.1. Aquatic System Emissions (An Artificial Pond)	30

5.3.2. Sewer System Emissions	30
Chapter 6. Conclusion and Implications	30
References	32

Thesis Table of Contents

<i>Table of Contents</i>	2
<i>List of Figures</i>	5
<i>List of Tables</i>	9
<i>List of Abbreviations</i>	10
<i>Attestation of Authorship</i>	14
<i>Rezumat</i>	15
<i>Abstract</i>	17
Chapter 1. Introduction and Thesis Objectives	19
1.1. Background.....	19
1.2. Research Gap.....	20
1.3. Thesis Objectives.....	21
1.3.1. General Objective	21
1.3.2. Specific Objectives	22
1.4. Research Questions	23
1.5. Thesis Structure.....	24
Chapter 2. Literature Review	26
2.1. Methane as a Greenhouse Gas (GHG)	26
2.2. Climate Consequences of GHGs and the Impact of CH ₄	28
2.3. International Collaborations and Agreements on Climate Change	28
2.4. Global Methane Budget.....	29
2.4.1. Sources	29
2.4.2. Sinks.....	31
2.4.3. Uncertainty and Imbalance in the Global Methane Budget.....	32
2.5. National Methane Inventory – Romania.....	34
2.6. Urbanization and CH ₄ Urban Studies.....	35
2.6.1. Urban Aquatic Systems (AQ)	40
2.6.2. Natural Gas Distribution Networks (NG)	42
2.6.3. Sewer System (SE).....	43
2.6.4. Traffic-Based Emissions (TE).....	45
2.7. Methane Source Characterization.....	47
2.7.1. Ethane-to-Methane Ratios (C ₂ H ₆ :CH ₄).....	47
2.7.2. Isotopic Analysis for Methane Source Attribution.....	48

Chapter 3. Methods and Materials	52
3.1. Study Area Description	52
3.2. Instruments	53
3.2.1. The Tunable Diode Laser Absorption Spectroscopy (TDLAS)	53
3.2.2. The Mid-Infrared Laser Absorption Spectroscopy (MILAS)	54
3.2.3. Isotopic Ratio Mass Spectrometry (IRMS).....	55
3.2.4. Instruments Calibration and Quality Assurance/Quality Control (QA/QC)	56
3.3. Methodology	57
3.3.1. System-Based Methane Measurements (Point-Source).....	57
3.3.2. Street-Level Methane Measurements.....	76
3.3.3. Quantification of Methane Emissions.....	85
3.4. Statistical Analysis.....	100
3.5. Uncertainty Determination.....	100
Chapter 4. Results	102
4.1. System-Based Methane Measurements (Point-Source)	103
4.1.1. Aquatic Systems (AQ)	103
4.1.2. Natural Gas End-Use Points (NG)	114
4.1.3. Sewer System Manholes (SE).....	117
4.1.4. Building Basements (BS).....	119
4.1.5. Traffic Emissions (TE).....	121
4.2. Street-Level Methane Measurements	128
4.2.1. First Street-Level Survey	128
4.2.2. Second Street-level Survey	134
4.3. Quantification of Methane Emissions	142
4.3.1. Aquatic System Emissions (An Artificial Pond).....	142
4.3.2. Individual Natural Gas Leak	143
4.3.3. Sewer System Emissions	144
Chapter 5. Discussion	149
5.1. System-Based Methane Measurements (Point-Source)	150
5.1.1. Aquatic systems (AQ)	150
5.1.2. Natural Gas End-Use Points (NG)	156
5.1.3. Sewer System Manholes (SE).....	159
5.1.4. Building Basements (BS).....	162
5.1.5. Traffic Emissions (TE).....	163
5.2. Street-Level Methane Measurements	167
5.2.1. First Street-level Survey.....	167
5.2.2. Second Street-Level Survey	175
5.3. Quantification of Methane Emissions.....	181
5.3.1. Aquatic System Emissions (An Artificial Pond).....	181
5.3.2. Sewer System Emissions	182
5.4. Mitigation Opportunities	191
Chapter 6. Conclusions and Implications	192
6.1. General Conclusions	192
6.2. Original Contributions	194

6.3.	Response to Research Questions	195
6.4.	Limitations	199
6.5.	Recommendations for Future Research	200
6.6.	Publications and conference papers	202
6.6.1.	Publications	202
6.6.2.	Conferences	203
<i>References</i>		205

Chapter 1. Introduction

This Ph.D. thesis focuses on the detection and characterization of methane (CH₄) emissions from natural and anthropogenic sources in the urban environment of Cluj-Napoca, Romania. Methane is a potent greenhouse gas (GHG) with a global warming potential approximately 86 times greater than carbon dioxide (CO₂) over a 20-year horizon and an atmospheric lifetime about a decade (IPCC, 2014; Saunio et al., 2025). Since the pre-industrial era, atmospheric CH₄ emissions have more than doubled, primarily driven by anthropogenic activities (IPCC, 2013a, 2023b), highlighting methane as a critical target for near-term climate mitigation.

Urban areas play a key role in the global methane budget. Although they cover less than 2% of the Earth's surface, they host more than half of the global population and concentrate a wide range of emission sources (Crippa et al., 2021; UN DESA, 2019). These include anthropogenic systems such as natural gas distribution networks, wastewater and sewer infrastructure, landfills, and traffic, as well as natural and semi-natural sources like urban aquatic environments. Due to the spatial heterogeneity and temporal variability of these sources, methane emissions in urban areas remain highly uncertain in both magnitude and spatial distribution (Crippa et al., 2021; Satterthwaite, 2008).

At the global scale, methane emissions are commonly categorized into multiple source types, including agriculture, fossil fuel systems, waste and wastewater management, and natural ecosystems. Within urban environments, key potential CH₄ sources include: (i) aquatic systems (rivers, lakes, wetlands); (ii) natural gas distribution networks; (iii) sewer systems and wastewater treatment plants; (iv) landfills; (v) traffic-related emissions; and (vi) industrial activities.

This study focuses on five major urban methane sources in Cluj-Napoca: (i) aquatic systems (AQ); (ii) natural gas distribution networks (NG); (iii) sewer systems (SE); (iv) traffic emissions (TE); and (v) building basements (BS), which may act as accumulation zones for methane originating from natural gas pipeline leaks or in situ microbial activity.

Cluj-Napoca is the second biggest city in Romania with population approximately 286,000 inhabitants (National Institute of Statistics, 2021), has experienced rapid economic and demographic growth in recent decades. Despite this development, methane emissions in Romania

have been predominantly investigated in non-urban contexts, including wetlands (e.g., the Danube Delta), agricultural systems, and fossil fuel-related sources (Baciu et al., 2018; Cuna et al., 2008; Etiope et al., 2009; Popa et al., 2016). Urban methane studies remain limited.

The study aims to (i) identify spatial patterns of methane enhancements, (ii) attribute emissions to their potential sources, and (iii) assess their atmospheric contribution. Additionally, this work includes one of the first direct flux quantifications of methane emissions from urban sewer systems in Romania, using chamber-based measurements combined with geostatistical analysis.

In conclusion, this thesis advances the understanding of methane emissions in complex urban environments and provides a scientific basis for targeted mitigation strategies aligned with international climate objectives, including the Paris Agreement and the European Green Deal.

Chapter 2. Literature Review

2.1. Methane as a Greenhouse Gas (GHG)

Methane (CH_4) is a major greenhouse gas, that substantially contribute to the Earth's radiative balance and climate system. Global GHG emissions have generally increased, particularly since the pre-industrial era, driven by anthropogenic activities since the pre-industrial period. Carbon dioxide (CO_2) accounts for approximately 72% of the total GHG emissions, followed by CH_4 at approximately 21%, nitrous oxide (N_2O) at 5%, and fluorinated gases at around 2% (EC-JRC & IEA, 2024; IPCC, 2013a, 2023b).

Methane is the second most important GHG after carbon dioxide in terms of its contribution to radiative forcing. Despite its lower atmospheric concentration compared to CO_2 , methane has a significantly higher radiative efficiency. Over a 20-year time horizon, methane induces global warming potential approximately 86 times higher than CO_2 , and 28 times over 100-year horizon (IPCC, 2023b; Saunio et al., 2016, 2020).

A key characteristic that distinguishes methane from other long-lived greenhouse is its relatively short atmospheric lifetime., estimated approximately 9-12 years. This short lifetime, combined with its high radiative forcing, makes methane an attractive and target for near-term

climate mitigation strategies, as reductions in methane emissions can yield a tangible climate benefits (Nisbet et al., 2020; Saunois et al., 2025; UNEP, 2021)—a 45% cut of methane emissions by 2030, could lead to a short-term warming drop by approximately 0.3 °C (UNEP, 2021).

Atmospheric methane concentrations have increased dramatically since the pre-industrial era. Ice-core air measurement records indicate 722 parts per billion by volume (ppbv) of concentrations around 1750, compared to recent observations showing approximately 1896 in 2021 (IPCC, 2023b) and 1946 ppbv in 2025 (NOAA, 2026), representing an increase of more than 160%. This unprecedented rise reflects the growing influence of anthropogenic sources such as fossil fuel exploitation, agriculture and waste management (IPCC, 2001, 2013a; Saunois et al., 2025).

For eliminating these global climate change effects, several international collaborations, commitments and agreements have been established. For example, on the global scale, the legislations of the United Nations Framework Convention on Climate Change (UNFCCC), Kyoto Protocols, Paris agreement, Sendai Framework for Disaster Risk Reduction (2015-2030) and the Sustainable Development Agenda (2015-2030) helped in creating global collaboration for the purpose of reporting GHG and to work together in creating certain policies to combat climate change and to mitigate these emissions at national and regional levels (IPCC, 2023b).

On the EU scale, the European Union Green Deal and the European Climate Law stipulates that all member states should reduce GHG emissions by 50% in 2030 the so-called “Fit to 55” and to become neutral by 2050 based on 1990 as a reference year (European Commission. Joint Research Centre., 2023). Therefore, GHG reduction policies don’t only represent a moral responsibility, but also a legislative commitment for Member States.

2.2. Global Methane Budget

Methane emissions can be classified, according to both their formation process and their origin (natural vs. anthropogenic), as shown in **Figure 2.1**. Based on formation mechanisms, methane is mainly categorized into pyrogenic, biogenic, and thermogenic sources. Pyrogenic CH₄ is emitted from incomplete combustion of biomass and fossil fuels. Thermogenic CH₄ originates from the decomposition of organic matter under high temperature and pressure in deep earth layers

and is released naturally through geological seeps (e.g., Sarmasel seeps (Ghiorghiu et al., 2025)) or anthropogenically during fossil fuel extraction and use. Biogenic methane is produced through microbial methanogenesis under anaerobic conditions, primarily in wetlands, waterbodies, and other oxygen-depleted environments (IPCC, 2013a; Saunois et al., 2016, 2025).

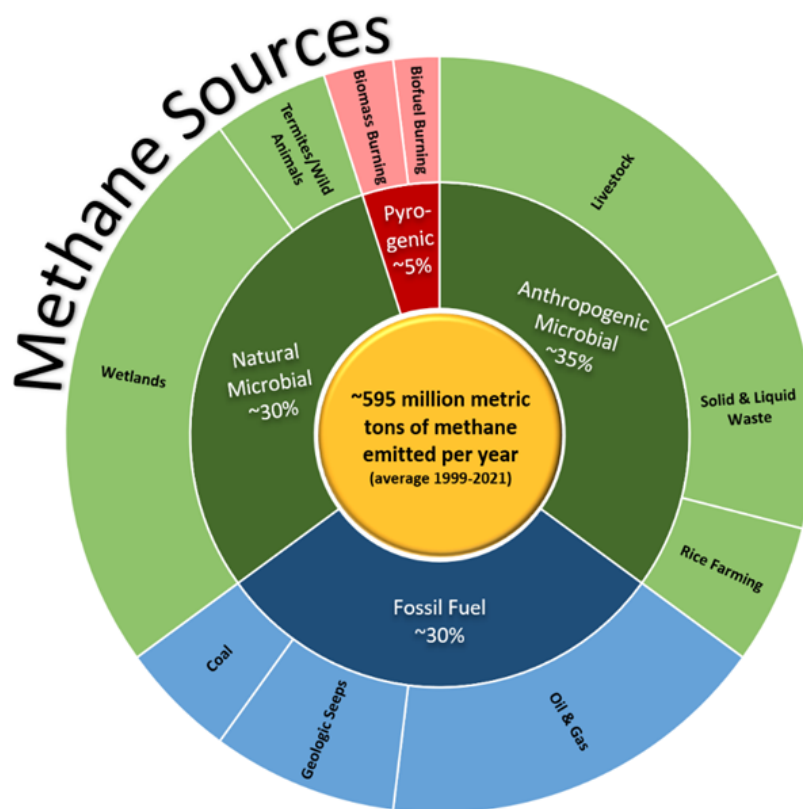


Figure 2.1. Global mean methane emissions (in Mt CH₄ yr⁻¹) between 1999–2021 originating from natural microbial, fossil fuel, pyrogenic, and anthropogenic microbial sources, source: (Oh et al., 2023).

These categories may overlap with the broader classification of methane sources into natural and anthropogenic emissions. Anthropogenic sources are responsible for more than 60% of global CH₄ emissions, while natural sources contribute the remaining 40%, although these estimates may be subject to a high degree of uncertainty (IPCC, 2001, 2013b; Saunois et al., 2020, 2025). The anthropogenic sources come mainly from fossil fuels production and use (coal mining, oil and natural gas extraction and distribution), agriculture and waste sectors, particularly livestock activities, rice paddies, and waste management, and biomass and biofuel burning. Among these

sources, agriculture and waste sectors represent the largest share, followed by fossil fuel. Natural methane emissions are dominated by wetlands accounting for approx. 30–40% of total emissions.

Methane is removed from the atmosphere primarily through chemical oxidation processes, which regulate its atmospheric lifetime and concentration. The dominant sink is the reaction with hydroxyl radicals (OH) in the troposphere, which accounts to approximately 80–90% of total methane removal. This process converts methane into carbon dioxide and water vapor through a series of photochemical reactions (IPCC, 2023a; Saunio et al., 2020, 2025). Additional atmospheric sinks include oxidation in the stratosphere and troposphere involving chlorine (Cl) and oxygen atoms (O), although these contribute only for minor fraction of the global methane sink (IPCC, 2023a; Saunio et al., 2020, 2025).

Methane emissions are commonly estimated using two main approaches: bottom-up (BU) and top-down (TD) estimates. Bottom-up rely on the aggregation of emissions from individual sectors, using activity data and emission factor, and are typically reported through national greenhouse gas inventories under the international frameworks. However, these estimates are associated with significant uncertainty level due to incomplete activity data, variability in emission factors, and methodological assumptions. In contrast, top-down estimates determine methane emissions from atmospheric observations, including surface measurements, aircraft campaigns, and satellite data. These methods provide robust constraints on total emissions at regional to global scales, but are unable to distinguish emitting sources with high certainty (IPCC, 2019; Saunio et al., 2020, 2025).

2.3. Urbanization and CH₄ Urban Studies

Urban areas occupy only a small fraction of the Earth's surface (approximately 2%), yet they host more than half of the global population (Crippa et al., 2021; UN DESA, 2019), and are responsible for a substantial share of GHG emissions usually associated with high degree of uncertainty in the magnitude and the spatial distribution (Crippa et al., 2021; Satterthwaite, 2008). The concentration of population, infrastructure, and economic activity in cities results in intensified energy consumption and resource demand, making urban areas key contributors to anthropogenic emissions.

As global urbanization accelerates, more than 76% of the Romanian population lives in urban areas (PwC, 2023)-projected to reach 83% of the Europe's population by 2050 (UN DESA, 2019)-the demand for energy, infrastructure and resources will likely intensify CH₄ emissions. The potential urban sources of CH₄ include natural gas (NG) distribution networks, landfills, sewer systems, wastewater treatment plants (WWTP) and urban aquatic systems. However, the complexity and the spatial variability of these sources, coupled with limited observational data, contribute to urban CH₄ budget uncertainty (IPCC, 2023b; Saunois et al., 2025).

Urban methane studies increasingly rely on integrated measurement approaches, including in situ monitoring, mobile surveys, and isotopic analysis, to improve source attribution and reduce uncertainty (Gallagher et al., 2015; Plant et al., 2022; Vogel et al., 2024; Xu et al., 2023). These methods are particularly important in complex urban environments, where multiple emission sources coexist and interact.

Overall, the literature demonstrates that urban areas are critical but insufficiently characterized components of the global methane budget, particularly in regions with limited observational data; e.g., Cluj-Napoca. Addressing this gap requires high-resolution, measurement-based studies that are capable to capture spatial variability and source complexity of urban methane emissions.

Chapter 3. Methods and Materials

3.1. Study description

Cluj-Napoca (46° 46'N; 23° 35'E approximate central point) is situated in the heart of Transylvania in the northwestern region of Romania, across a valley area between the Transylvanian Plateau and the Apuseni Mountains (**Fig. 3.1**). The city is the second largest in Romania in terms of population and industrial, commercial, and educational services, with 286,598 residents in 2021, occupying 179.2 km² and making up 1.5% of the total country's population, according to the National Institute of Statistics (INS, 2023).

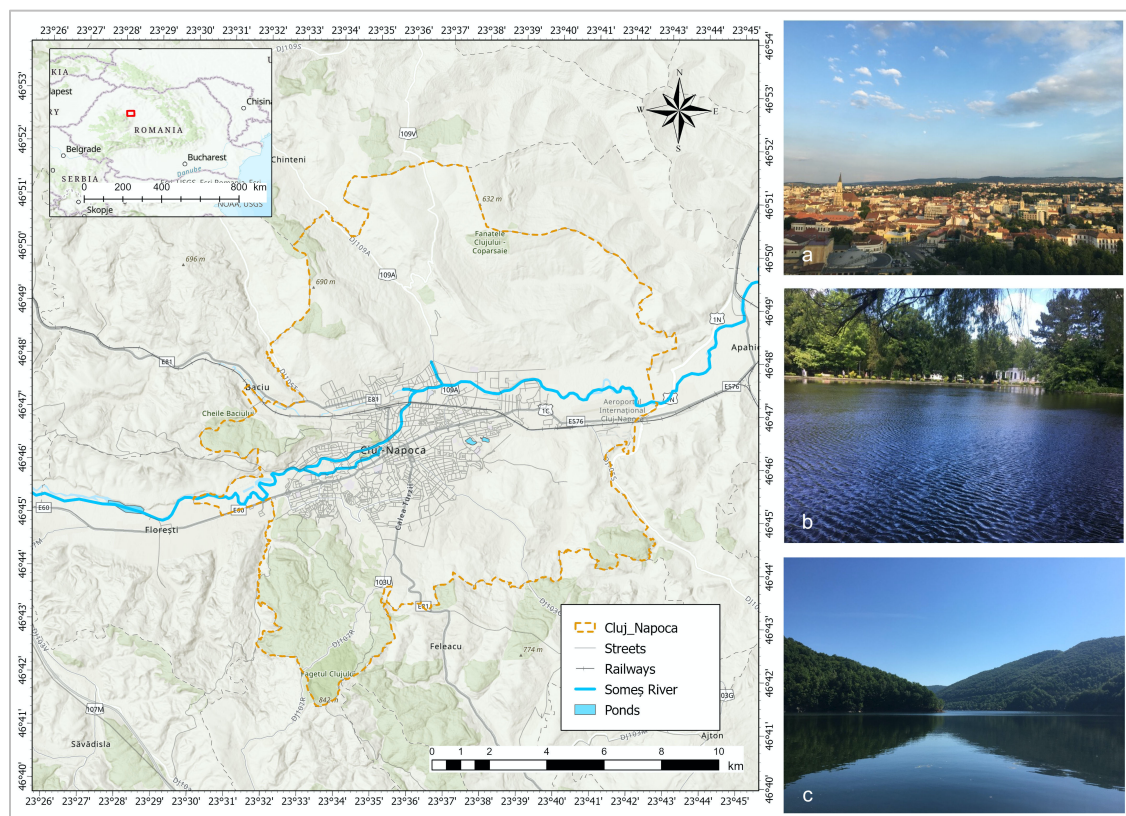


Figure 3.1. The study area of Cluj-Napoca in the north-western of Romania. Photos: a. A view of the city from the north; b. The pond in the central park; and c. Tarnița Lake west to the city.

The Someșul Mic River (SMR) flows through the city from west to east (**Fig. 3.1**). In addition, the city has two major artificial water ponds: Iulius Mall lake and the central park (**Fig. 3.1-b**). Also, an artificial accumulation lake called Tarnița was created on the outskirts of the city, which resulted from the construction of the Tarnița dam to generate energy (**Fig. 3.1-c**). These water ponds and lakes can be a potential source of methane, and will be studied within the category of “aquatic systems” (AQ).

3.2. Instruments

During this study two main detecting sensors were utilized, which support the determination of CH₄ concentration in the atmosphere; the Tunable Diode Laser Absorption Spectroscopy (TDLAS; Gazomat, France) which enables a low detection limit (LDL) of 0.1 ppmv with full scale measurement range from 0 to 100%, 0.1 ppmv precision and resolution, 1 Hz sampling frequency, and 1 ppmv/s methane sensitivity (West Systems, Italy, 2016), and the Mid-infrared Laser

Absorption Spectroscopy (MILAS) measures CH₄ from 10 ppbv to 10000 ppmv, with 1 ppbv precision and 1 Hz frequency, and ethane (C₂H₆) from 1 ppbv to 1000 ppmv and 0.5 ppbv precision and 1 Hz frequency (AERIS Technologies, CA, USA, 2024).

3.3. Methodology

3.3.1. System-Based Methane Measurements (Point-Source)

Based on potential urban sources of CH₄ described in the literature, as explained in the introduction, five main systems in Cluj-Napoca have been investigated: the aquatic system (AQ), the natural gas distribution network (NG), the sewer system (SE), building basements (BS) and vehicle exhausts (VE), illustrated in **Figure 3.2**. Building basements (BSs) were included in this individual survey, which may represent an attractive environment for microbial methane production or an accumulation volume for leaks where gas installations exist.

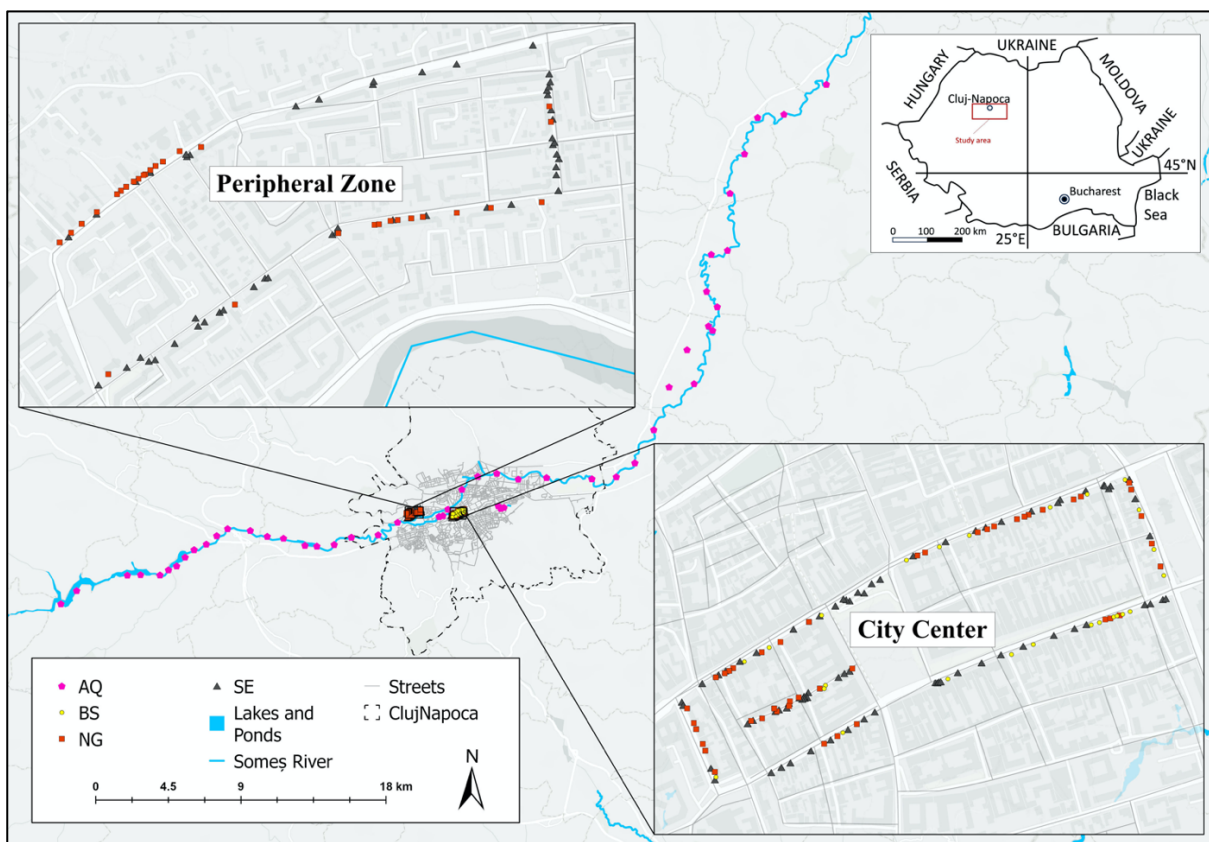


Figure 3.2. Study area of Cluj-Napoca, northwestern Romania, showing the spatial distribution of sampling locations. Aquatic system (AQ) sampling sites are indicated along the river,

accumulation lakes, and artificial ponds. Measuring locations for the natural gas end-use locations (NG), sewer system (SE), and building basements (BSs) are displayed within both the city center (CC) and peripheral zone (PZ).

3.3.1.1. Aquatic Systems (AQ)

Methane was analyzed in the dissolved phase (dCH_4) in Cluj-Napoca's urban aquatic system (river, lakes, and ponds). Someșul Mic River (SMR), which is part of the city's aquatic system, is formed when Someșul Rece River (SRR), which is 49 km long, and Someșul Cald River (SCR), which is 70 km long, meet near Gilău mountain.

In order to acquire a temporal and spatial representation of water samples that were used to determine the dissolved CH_4 in the urban AQ system and for evaluating the contribution of the AQ input into urban CH_4 , while tracking its sources appropriately, the cold and warm seasons were considered. A total of 196 samples distributed over 50 sampling locations over four sampling campaigns with seasonal variations. Surface water was gathered from 0.10 and 0.30 meters deep near the shore. For assessing the temporal changes in dCH_4 while tracking its sources appropriately, the cold and warm seasons were considered. The dissolved methane concentration was measured by equilibration headspace method (Capasso and Inguaggiato, 1998; Jahangir et al., 2012).

3.3.1.2. Urban Infrastructure Systems

In the end of January 2023, in cloudy conditions with temperatures ranging between 2 to 7 °C and wind speeds between 7 and 11 km/h southwest (meteostat.net) via TDLAS, 74 locations were measured at Natural gas distribution end-use points (NG), 126 samples at the sewer system manholes (SE), in two urban areas: the periphery and central area following the CH_4 concentration survey, and 25 samples at the building basements (BS) in the city center. Additionally, Traffic emissions (TE) were determined by inserting a 1/8-inch AERIS Mira-Pico inlet tubing, fitted with an inline 1/4-inch Zemoner filter to reduce pollution from the exhaust smoke to protect the sensor, 0.10 to 0.15 meters inside the exhaust pipe for determining CH_4 and C_2H_6 variations at 1 Hz while the engine is operating in parking mode and then subsequently accelerating. Afterwards, in the urban survey, values > 2.2 ppmv have been considered as zones affected by CH_4 sources.

3.3.1.3. *Street-level Methane Measurements*

Street-level methane measurements were conducted using a walking approach, which is easy to perform in corridors and more flexible in case of traffic agglomeration to maintain approximately the same measurement speed. Second, car-based surveys can affect the detection of gas that might be influenced from the survey own car emissions. Third, the slow speed performed with this walking survey permits to detect and process as much as possible of plumes and to identify potential sources, while also have enough time to observe inducing factors. Walking transects were designed to cover neighborhoods representing different land uses and infrastructure types.

During this approach, the methane atmospheric concentrations were continuously recorded (in ppmv) at 1 Hz, while positioning one meter, 1/8-inch inlet tubing attached to the West System package or the Mira Pico, at 1.5 m above street level. Respectively, a five and three-second delays were added to correct measurements via the West System and the Mira Pico, respectively. The lag time was determined by exposing the sensor inlet to a gas source and calculating the delay between the intake and the display of value by the analyzer.

3.3.2. **Quantification of Methane Emissions**

3.3.2.1. *The Static and Floating Chamber*

The static chamber method has been widely applied for quantifying greenhouse gas emissions from different urban ecosystems (e.g., [Cardellini et al. \(2002\)](#); [Collier et al. \(2014\)](#); [Herrero Ortega et al. \(2019\)](#); [Hu et al. \(2016\)](#); [Lesmeister & Koschorreck, \(2017\)](#); [Mu et al., 2022](#); [Wu et al. \(2018\)](#)).

The static chamber used in our survey was manufactured by West System in Italy with approximately 2.5 kg weight, 0.10 m height, and 0.30 m diameter. The quantity of gas released over time is known as gas flux. The flux is represented by the average change in the concentration of gas inside the chamber over time multiplied by the chamber volume, as expressed in **Equation 1**.

$$F_{CH_4} = k \times V \times S_p \quad (1)$$

where F_{CH_4} = methane flux ($g \cdot d^{-1}$), $k = 10^{-6} \times 86400 \times \frac{16.04}{24.45}$ converts $ppmv \cdot s^{-1} \times L$ to $g \cdot d^{-1}$ ($24.45 L \cdot mol^{-1}$ for $25^\circ C$, at $1 atm$), V = chamber volume (static chamber = $7.07L$, and floating chamber = $21.21L$), Sp = slope of the CH_4 increase in the chamber ($\frac{\Delta CH_4 ppmv}{\Delta t (s)}$), where 10^{-6} converts $ppmv$ to a molar fraction, 86400 converts seconds to days, $16.04 g \cdot mol^{-1}$ is methane molar mass, and $24.45 L \cdot mol^{-1}$ is the molar volume of an ideal gas at $25^\circ C$, at $1 atm$. This formulation converts methane accumulation rates expressed in $ppmv \cdot s^{-1}$ inside the chamber volume into daily mass fluxes ($g \cdot d^{-1}$).

3.3.2.2. *Aquatic System Emissions (An Artificial Pond)*

Measurements at an artificial pond were conducted via the floating chamber at four selected locations on the pond in mid-November 2023. During the sampling period, atmospheric conditions were relatively stable, with temperature of approximately $5^\circ C$ and an average wind speed of $4 m \cdot s^{-1}$ from the northeast (**Figure 3.3**).

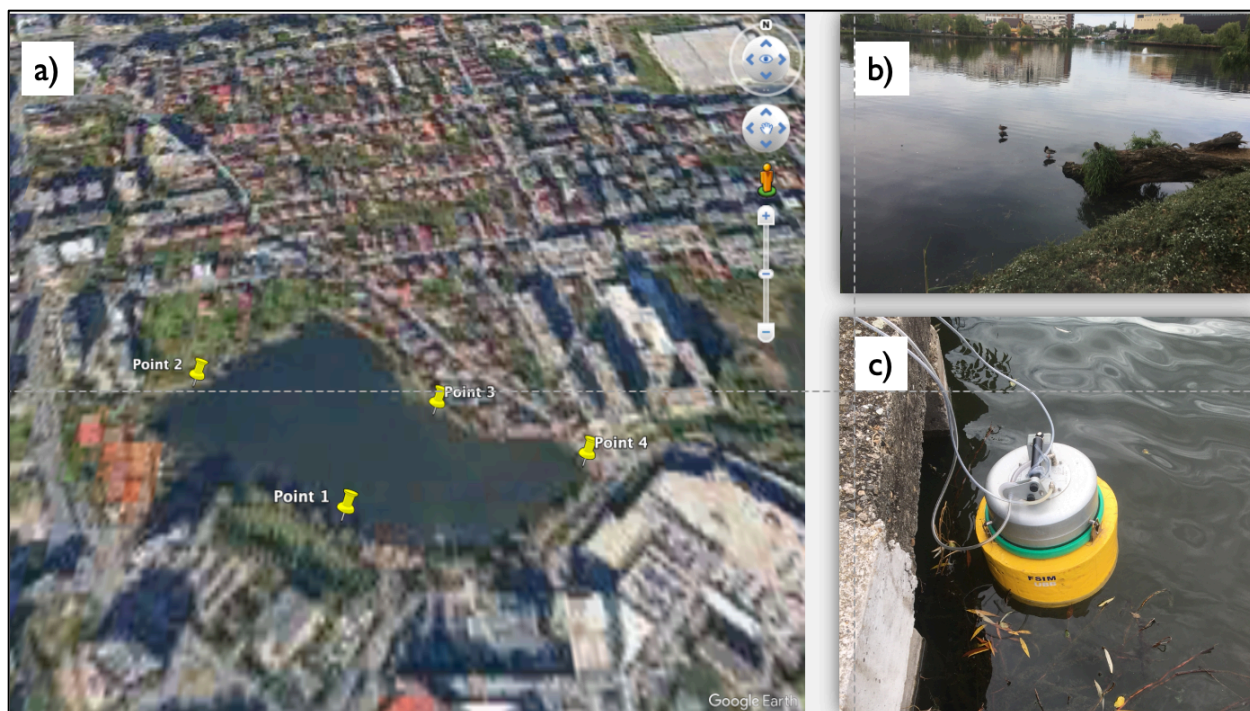


Figure 3.3. *Quantification of methane emissions from an artificial pond. (a) The location of the four sampling locations where the floating chamber was placed, (b) a photo of the lake from southwest, (c) the floating chamber placed at point 1.*

3.3.2.3. *Individual Natural Gas Leak*

During instrument training, localized enhancements in CH_4 mole fraction were detected near a natural gas (NG) compressor station ($46^\circ 46' 06'' \text{ N}$; $23^\circ 33' 08'' \text{ E}$). To identify the leak source precisely, a foam solution (dishwashing detergent and water applied with a sponge) was applied to cover pipeline joints and connections. Bubble formation indicated the leak location (**Figure 3.4**). To estimate the emission, a sealed funnel connected to a 1/4 -inch tubing was placed over the leak and coupled to a closed-chamber system (volume = 7.07 L), sealed at the bottom.



Figure 3.4. Natural gas (NG) compressor pipeline station (a), the leaking point identified by the observed bubbling (b), and the technique of sealing the leaks into the chamber which is isolated from the bottom (c).

3.3.2.4. Sewer System Emissions

In order to establish a uniform representation of the city's sewer system, the static chamber was placed over homogenously distributed manholes during field survey that took into consideration the distance between manholes, their accessibility, and whether or not they were totally sealed off from the atmosphere. In many instances, manholes were situated in the center of busy streets, and some were totally sealed off from the atmosphere. As shown in **Figure 3.5**, the homogenous survey was performed at 228 locations.

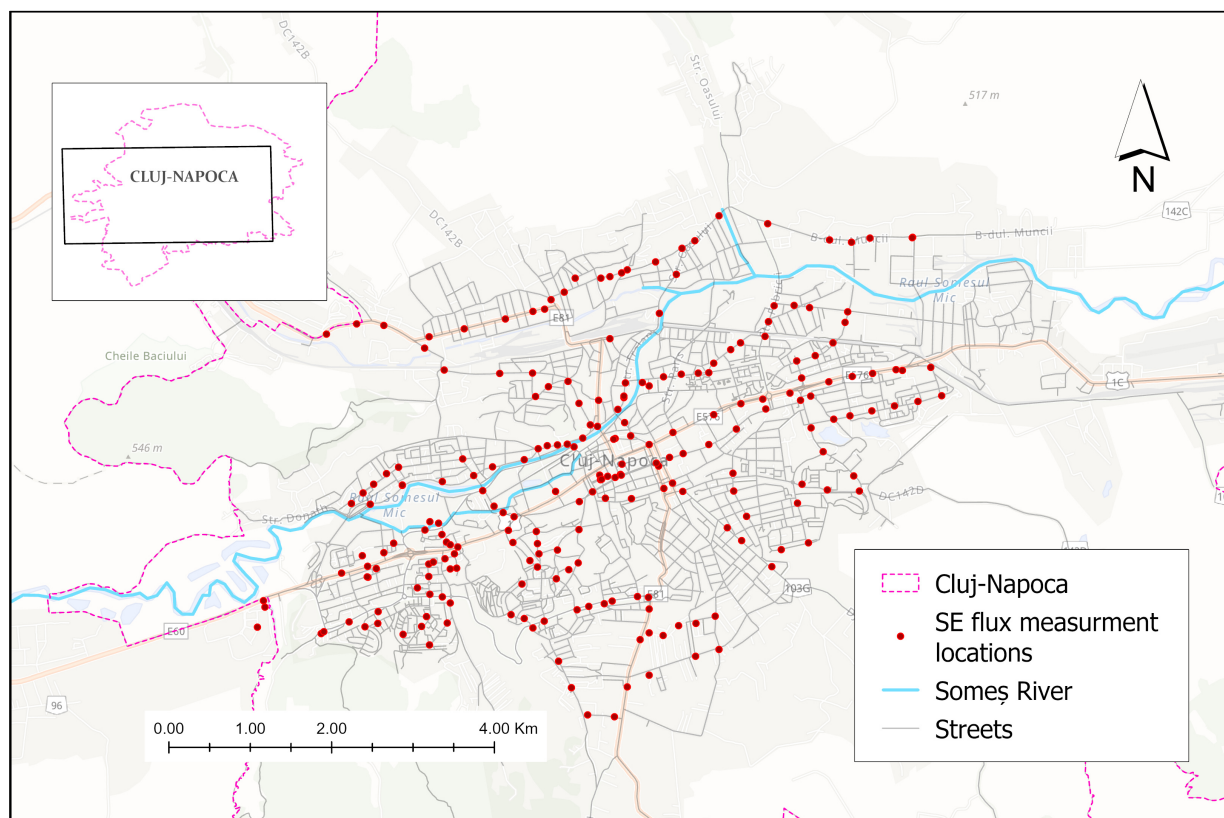


Figure 3.5. Spatial distribution of SE sampling points where CH_4 and C_2H_6 fluxes were determined.

Subsequently, stable isotopic analysis ($\delta^{13}C$ signatures) and mainly ethane-to-methane ($C_2:C_1$) ratios have been used in mobile measurements surveys to separate thermogenic from biogenic sources.

Methane fluxes measured at sewer-related locations were spatially interpolated using the Empirical Bayesian Kriging (EBK) implemented in ArcGIS Pro. 3.2 (Esri Inc., 2022). Prior to interpolation, flux data were $\log_{10}$ -transformed to reduce skewness and improve normality.

Chapter 4. Results

4.1. System-Based Methane Measurements (Point-source)

4.1.1. Aquatic Systems (AQ)

The spatial and seasonal variability of dissolved methane (dCH_4) concentrations are presented in **Figure 4.1** across 50 sampling locations spanning the aquatic system, which includes accumulation lakes, a river stream, and artificial ponds. For analytical clarity, the system was classified into two main components: (1) the hydrologically connected accumulation lakes and river stream, and (2) the isolated artificial ponds.

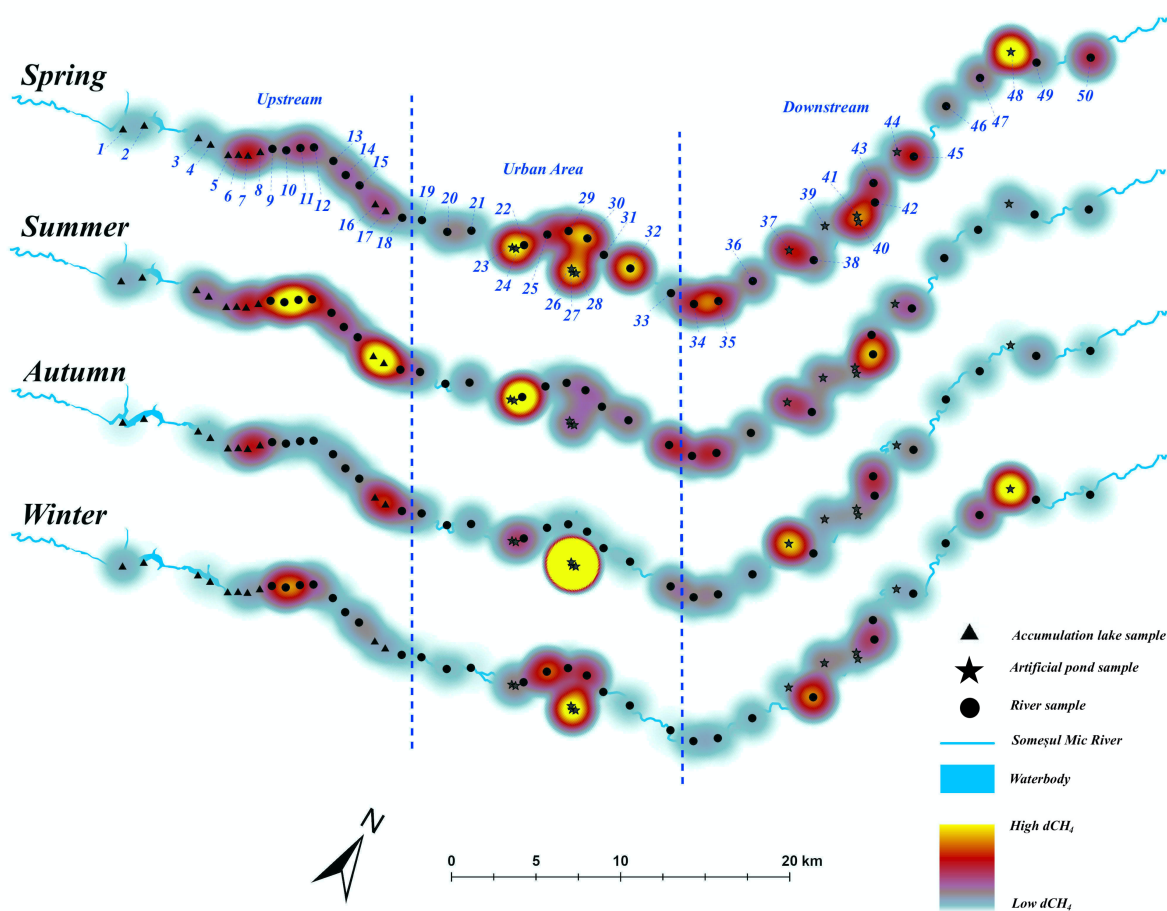


Figure 4.1. Seasonal distribution of dissolved methane (dCH_4) in the urban aquatic system. A triangle represents samples collected from accumulation lake sample, stars for artificial pond samples, and circles for river samples.

Across all locations and seasons, dCH₄ concentrations were consistently oversaturation relative to atmospheric equilibrium (air-saturated water, ASW= 0.003 $\mu\text{mol L}^{-1}$). Measured concentrations ranged from 0.028 to 10.495 $\mu\text{mol L}^{-1}$, corresponding to saturation levels from approximately 900% and over 300,000%. The pervasive oversaturation indicates a clear in situ persistent production of CH₄ within the system.

Overall, higher dCH₄ values were observed during the warmer months, with distinctive decline in winter. In spring (mean temperature $\sim 15^\circ\text{C}$) and summer ($\sim 27^\circ\text{C}$), median dCH₄ concentrations were 0.580 and 0.660 $\mu\text{mol L}^{-1}$, respectively, with corresponding mean $\pm$ standard deviation values of 0.769 ± 0.660 and 0.884 ± 0.751 $\mu\text{mol L}^{-1}$. In contrast, during autumn (10°C) and winter (-2°C), median concentrations declined to 0.337 and 0.264 $\mu\text{mol L}^{-1}$, and mean $\pm$ standard deviation values were 0.409 ± 0.274 and 0.464 ± 0.594 $\mu\text{mol L}^{-1}$, respectively. The seasonal pattern and positive correlation between dCH₄ values with temperature suggest microbial methanogenesis activities during warmer periods, or slow gas exchange dynamics between the aquatic system and the atmosphere.

4.1.2. Natural Gas End-Use Points (NG)

Methane concentrations were measured at 74 interface points between the natural gas (NG) distribution system (end-use points) and the atmosphere, across two urban zones: the city center (CC, $n = 44$), and peripheral zone (PZ, $n = 30$). Through all sites, CH₄ concentrations ranged from 1.5 to 482.0 ppmv, with mean value of 15.4 ± 60.5 . Concentrations in the CC spanned the full range (1.5–482.0 ppmv), whereas values in the PZ were notably lower, ranging from 1.8 to 15.2 ppmv.

4.1.3. Sewer System Manholes (SE)

Methane concentrations were measured in 126 sewer manholes, including 75 samples in the city center (CC) and 51 samples in the peripheral area (PZ). Manhole selection was based on accessibility and availability across the urban sewer network. CH₄ concentrations ranged between 1.5 to 1222.0 ppmv, with an overall mean of 16.4 ± 109.1 ppmv, indicating a wide variability likely driven by possible gas inputs from microbial activities or external sources.

4.1.4. Building Basements (BS)

A total of 25 air samples was determined in the city center (CC). No BS sampling sites were identified in the periphery zone (PZ); therefore, all results relate exclusively to the CC. Methane concentrations within these basements ranged from 1.8 to 12.0 ppmv, with an average $\pm$ standard deviation of 3.9 ± 2.7 ppmv. Approximately 68% of the sampling points showed concentrations between 1.8 and 4.0 ppmv, while 32% displayed elevated values between 4.0 and 12.0 ppmv.

4.1.5. Traffic Emissions (TE)

Direct measurements of CH₄ in vehicle exhaust over 3–5-minute interval for each vehicle revealed elevated concentrations that contribute to atmospheric CH₄ levels. CH₄ concentrations reached up to 162.2 ppmv, with a mean $\pm$ standard deviation of 18.6 ± 32 ppmv, while C₂H₆ concentrations peaked at 23,250 ppbv, with a mean of $2,563.3 \pm 5,597.1$ ppbv. All five tested vehicles exhibited higher CH₄ and C₂H₆ concentrations during engine acceleration compared to idling (i.e., the parking mode with the engine running).

Based on our findings, pyrogenic sources of CH₄ from vehicle exhaust may have a C₂:C₁ ratio ranging between 0.003 and 0.228, which can aid in the attribution of CH₄ concentrations to combustion-related sources.

4.2. Street-Level Methane Measurements

4.2.1. First Street-Level Survey

A total of 3912 atmospheric methane (CH₄) measurements were collected using a walking survey approach employing tunable diode laser absorption spectroscopy (TDLAS) to identify CH₄ street-level concentrations across three separate urban zones: the city center (CC), central park (CP), and peripheral zone (PZ). This survey aimed to capture spatial variability in ambient CH₄ concentrations and to identify localized enhancements potentially indicative of emission sources (Figure 4.2.).

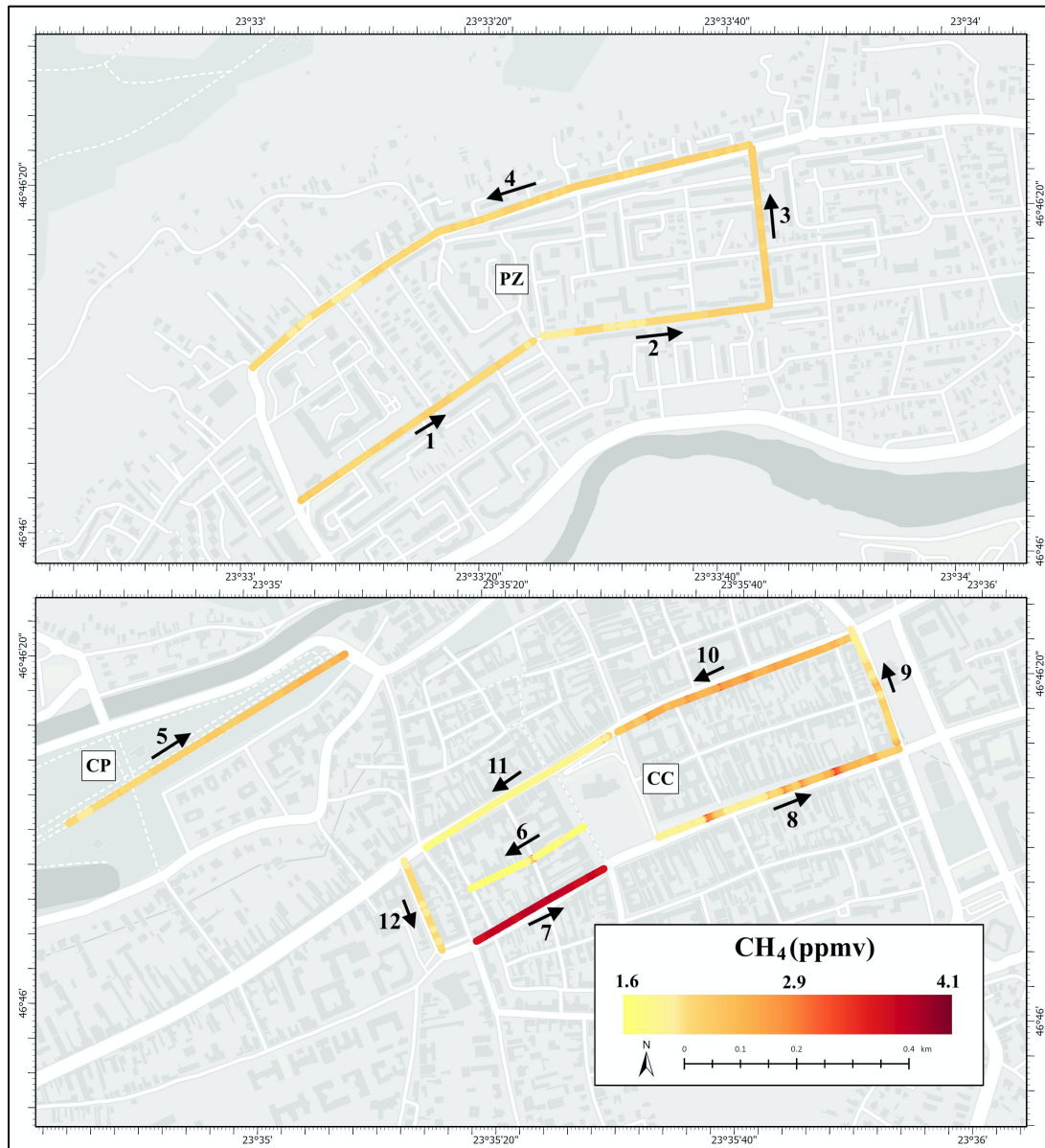


Figure 4.2. *CH₄ concentrations (ppmv) measured 1.5 m above the street in the Periphery Zone (PZ), Centra park (CP), and City Center (CC). Street given codes and measurement directions are indicated.*

Spatially, elevated CH₄ concentrations in the city center (CC) were observed at several discrete street locations, as indicated by high values along these segments. In contrast, CH₄ appeared more uniform across the surveyed segments in the central park (CP) and peripheral zone (PZ). The mapped data reveal clear concentration differences among the three zones, as well as spatial variability within each area.

4.2.2. Second Street-Level Survey

A total of 29,849 ambient air measurements were analyzed during a continuous in situ measurements of CH₄ and C₂H₆. Methane mixing ratio (concentrations) ranged from 1.999 to 5.542 ppmv (**Figure 4.3**), while C₂H₆ ranged from below detection (0.0 ppbv) to 15.1 ppbv. The mean $\pm$ standard deviation for CH₄ was 2.124 ± 0.152 ppmv, and 2.8 ± 3.2 ppbv for C₂H₆.

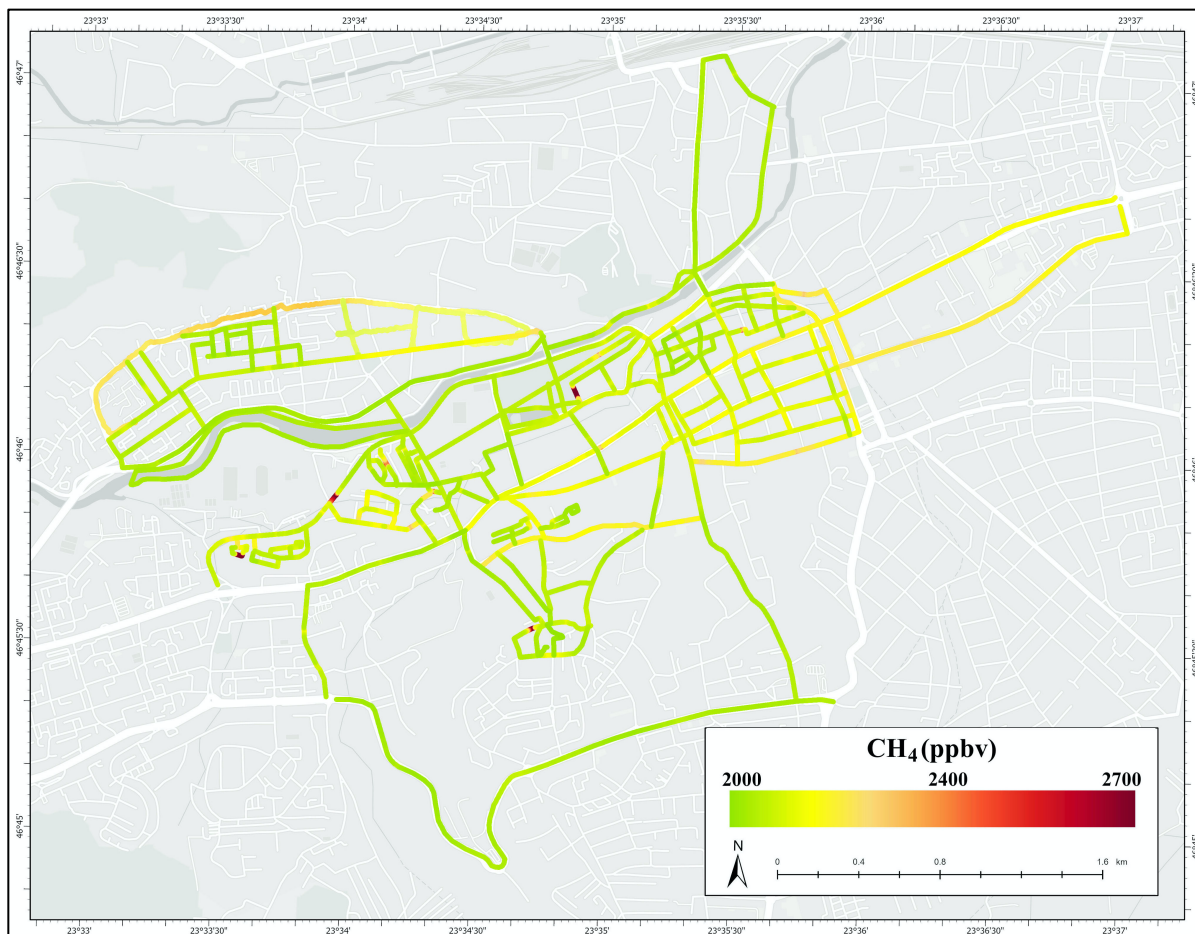


Figure 4.3. The spatial distribution of methane measurements during the walking survey and their values detected in ppbv.

Methane emission rates from individual plumes ranged from 0.07 and 14.40 L min^{-1} , with a mean of 2.04 L min^{-1} across the 14 identified peaks. These rates represent the local leak intensities within the surveyed street network (64.2 km). To estimate city-wide emissions, the fluxes were scaled to the total street network identified from OpenStreetMap (1122 km). The associated

uncertainty was propagated using Monte Carlo resampling, and the scaled total emissions were expressed as $176.5 \text{ t CH}_4 \text{ yr}^{-1}$ (95% CI: $131.0 - 228.4 \text{ t CH}_4 \text{ yr}^{-1}$).

4.3. Quantification of Methane Emissions

4.3.1. Aquatic System Emissions (An Artificial Pond)

At all the four locations, temporal variations in methane concentration inside the floating chamber did not experience a consistent linear increase over time. Consequently, methane fluxes could not be calculated for any of the measurement points.

4.3.2. Individual Natural Gas Leak

The temporal variation of CH_4 mole fractions inside the closed chamber exhibited a linear regression, which was used to determine that the identify leak at the gas pipe is responsible for releasing 10.22 kg yr^{-1} .

4.3.3. Sewer System Emissions

Based on this source characterizations, seven sites ($\sim 3\%$ of total measurements) were identified as NG-related CH_4 sources (Table S1, Supporting Information). These sites exhibited anomalously CH_4 fluxes ranging between 0.022 and 1.310 g d^{-1} . To ensure that subsequent analyses focus exclusively on anthropogenic microbial CH_4 emissions from the sewer system, these NG-attributed data points were excluded from further flux-based statistical evaluation.

Among the 221 sampled manhole sites, 84 sites (representing 38%) exhibited measurable CH_4 fluxes, with an average of 0.0144 g d^{-1} ($\pm 0.0018 \text{ g d}^{-1}$), ranging from 0.0001 to 1.305 g d^{-1} , while the remaining 137 sites (62%) showed zero fluxes.

The EBK interpolation revealed pronounced spatial heterogeneity in CH_4 fluxes across the city (**Figure 4.4**). The citywide assessment yielded a total CH_4 flux of 101.25 g d^{-1} , with a 95% confidence interval of $[96.56, 107.31] \text{ g d}^{-1}$, corresponding to $0.037 [0.035, 0.039] \text{ t CH}_4 \text{ yr}^{-1}$.

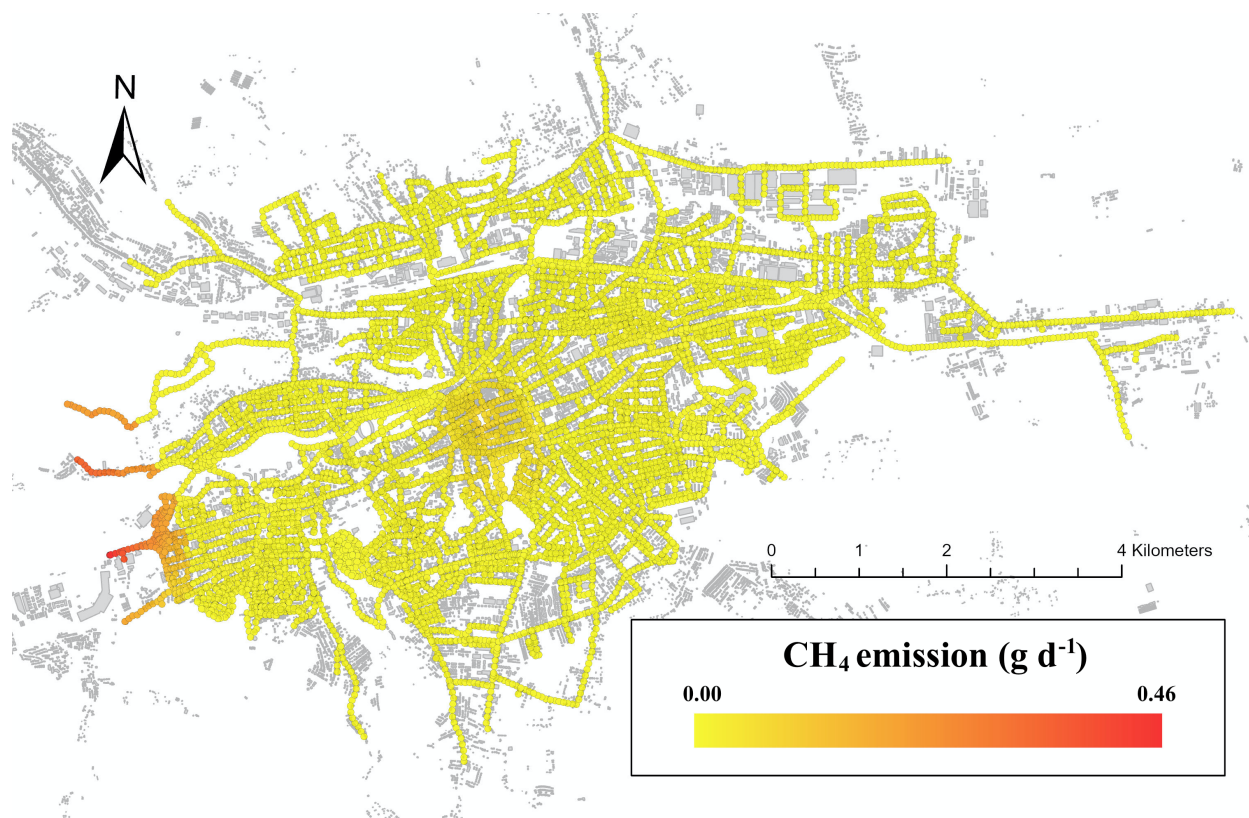


Figure 4.4. City-scale fluxes of CH₄ from the sewer system in Cluj-Napoca of 8801 manhole points whose values extracted from spatial interpolation of the surveyed dataset by Empirical Bayesian kriging approach (Krivoruchko, 2012).

Chapter 5. Discussion

5.1. System-Based Methane Measurements (Point-Source)

5.1.1. Aquatic Systems (AQ)

All water samples collected during the four seasonal campaigns showed significant oversaturation of dCH₄, relative to air-water saturation level (AWS) of 0.003 $\mu\text{mol L}^{-1}$. Measured saturation ranged from 900% to over 300,000%, suggesting active in situ methane production. Comparable findings have been reported in various urban aquatic environments worldwide, as shown in Table 6. For example, saturation levels reached approximately 6,000,000% approximately in the tropical Krishna River, China (Patel et al., 2023), 900,000% in Xiaoyue River in Beijing, China (Wang et al., 2020), and 560,000% in urban ponds in Brussel, Netherlands

(Bauduin et al., 2025). Other high values were reported up to 92,000% saturation in both the Cauvery River (CR), India (Premke et al., 2020), and the River Clyde, Scotland (Brown et al., 2023), and up to 18,000% Yangtze River, China (Leng et al., 2023). These trends highlight global prevalence of CH₄ oversaturation in urban aquatic systems.

In our study, mean and median dCH₄ concentrations in summer and spring were nearly double those recorded in winter and autumn, consistent with the findings of Tang et al. (2023) during dry season conditions. Bauduin et al. (2025) similarly reported elevated dCH₄ levels during warmer seasons in urban ponds in Brussel, with minor diurnal changes driven by wind velocity being negligible compared to seasonal variability.

5.1.2. Natural Gas End-Use Points (NG)

Concluding that measurements were conducted directly at potential end-use points (pipes, valves, meters) at ~0 cm distance from the potential sources. This proximity enhances the accuracy of leak identification, and effectively reduces uncertainties caused by atmospheric dispersion and dilution, which often affect street-level or mobile measurements (e.g., Lamb et al. 2015).

Indeed, wind-driven dispersion and background noise can mask leaks when using indirect measurements (e.g., mobile surveys) at large distances. By contrast, direct individual measurements at end-use points allows a precise localization of emissions at the source and reduces underestimation risks. This is consistent with the findings of Xu et al. (2023), who demonstrated that direct measurements at 1,495 NG end-use points in China (residential and commercial units) revealed emissions of 0.008–0.192 kg CH₄/unit, values that could be easily overlooked by atmospheric sampling alone.

5.1.3. Sewer System Manholes (SE)

Our CH₄ measurements are comparable to the findings from other urban SE networks worldwide. For instance, Fries et al. (2018) measured CH₄ concentrations ranging from 2.1 to 68.8 ppmv across 104 manholes in Cincinnati, Ohio, with microbial sources accounting for nearly half of the observed emissions. Similarly, urban atmospheric studies employing mobile surveys have attributed a significant proportion of detected CH₄ leaks to SE systems, with 33% in Paris (Defratyka et al., 2021) and 63% in Bucharest (Fernandez et al., 2022), but lacked source-specific

validation from thin the infrastructure. Our survey extends these efforts by validating SE CH₄ emissions through direct sampling, offering higher certainty compared to atmospheric methods. In Gwanak district, Seoul, South Korea, [Joo et al. \(2023\)](#) reported that the majority of CH₄ emissions (573 ton. yr⁻¹) originated from microbial processes in the SE network, supported by low C₂H₆:CH₄ ratios (<0.0005).

5.1.4. Building Basements (BS)

Methane concentrations measured in building basements (BS) suggest contributions from both natural gas (NG) leaks and anaerobic microbial production. This dual-source origin was confirmed by isotopic analysis ([van Es et al., 2025](#)), which indicated the absence of traffic-related contaminations, thereby supporting the hypothesis of direct contribution from NG and microbial sources. Among the 25 samples measured in the City Center (CC), 68% of the sites ($n=17$) showed CH₄ concentrations ranging from 1.8 to 4.0 ppmv, while the remaining 32% ranged from 4.0 to 12.0 ppmv. Elevated concentrations were most frequently observed in older, abandoned basements with direct exposure to street runoff and rainwater. These sites were poorly ventilated, creating favorable environment for microbial activities to produce CH₄.

5.1.5. Traffic Emissions (TE)

At the two different traffic locations in Cluj-Napoca, CH₄ concentration varied proportionally with traffic density, although all measured concentrations were below the urban background threshold of 2.2 ppmv. This variation, especially between high and low traffic density sites, suggests a local influence from vehicle activity. However, we cannot determine the actual source of gas due to the absence of source signature, and likely that CH₄ emissions could be driven by wind from far sources.

Several studies have reported contributions of vehicular activities to urban CH₄ emissions. For instance, [Nakagawa et al. \(2005\)](#) stated that high traffic densities can have contribution up to 30% in CH₄ urban budget in Nagoya, Japan. Similarly, [Venturi et al. \(2021\)](#) attributed up to 14% of Florence's CH₄ to a mixed of traffic and household energy, while in Bucharest, [Fernandez et al. \(2022\)](#) reported 5% of urban atmospheric CH₄ originating from pyrogenic sources using mobile-based approach.

5.2. Street-Level Methane Measurements

5.2.1. First Street-Level Survey

The street-level atmospheric CH₄ concentrations revealed a spatial variation in the urban environment that is significantly higher in the City Center (CC) compared to the Periphery Zone (PZ), consistent to CH₄ emission profiles reported in urban centers (Plant et al., 2019; Zazzeri et al., 2016).

The identified CH₄ enhancements in the central zones (CC and CP) were four times more frequent than in the PZ, likely driven by anthropogenic activities such as intense traffic, heating and leaks for the NG distribution network. Remarkably, our findings are consistent with earlier observations reported by Haiduc and Simion (2011) in a site close to the CC, where CH₄ concentrations reached approximately 7.1 ppmv higher than our maximum detected value (4.1 ppmv). Their study also noted a significant decline in atmospheric CH₄ concentrations following rainfall.

5.2.2. Second Street-Level Survey

High CH₄ concentrations were predominantly detected along the main streets in the city center (CC) and peripheral zone (PZ), where co-occurring in C₂H₆ levels were also observed. The co-emission supports the likelihood of fossil fuel-related emissions. The C₂H₆:CH₄ ratio was employed in distinguish between biogenic and non-biogenic (thermogenic or pyrogenic) sources.

In line with prior studies, Lamb et al. (2016) found that C₂:C₁ ratio ≥ 0.046 are typical for NG (thermogenic NG sources), 0.017 for combustion/pyrogenic sources, and ratios < 0.001 for biogenic sources such as sewers. Plant et al. (2019) stated that in six U.S. cities, NG-related emissions had C₂:C₁ ratios between 0.015 and 0.071, assuming no C₂H₆ in non-NG sources.

The estimated CH₄ emissions from NG infrastructure in Cluj-Napoca corresponding to the population ~400,000; 1.8 % of Romania's total 21.7 million according 400 according to National Institute of Statistics (INS, 2025), reveals an amount of 47.30 t CH₄ yr⁻¹ (95% CI). In contrast, our city-scale estimate derived from walking surveys was 176.5 t CH₄ yr⁻¹ (95% CI; 130.7 – 229.0 t yr⁻¹), nearly a factor of four higher than the inventory-based value.

5.3. Quantification of Methane Emissions

5.3.1. Aquatic System Emissions (An Artificial Pond)

The absence of measurable methane fluxes from the artificial pond during mid-November despite dissolved methane oversaturation may come from short-term chamber deployment, and the cold temperature and low surface water turbulence during stable atmospheric conditions that led to not estimating fluxes, even when dissolved methane concentrations are elevated. Herrero Ortega et al. (2019) quantified methane fluxes across multiple urban water bodies in Berlin (Germany) using floating chambers and reported pronounced seasonal variability. Methane emissions were highest during summer months, coinciding with elevated temperatures and enhanced microbial methane production, whereas winter exhibited low or negligible fluxes, corresponding to our findings where minimal methane emissions were detected under cold conditions. Therefore, long-term and diurnal monitoring may solve this issue and provide a more representative assessment of methane emission dynamics.

5.3.2. Sewer System Emissions

The spatial interpolation of CH₄ fluxes revealed that emissions were generally weak across the city during cold measurement period (−3 to 7 °C), consistent with temperature dependence of the microbial methanogenesis, as low ambient temperature likely suppress biological activities and decline the formation of methane in the sewer biofilms and sediments (Beelen & Parker, 2022; Guisasola et al., 2008; L. Liu et al., 2025; Zhao et al., 2019).

Although modest at the urban scale, these fluxes represent a non-negligible source of biogenic methane, particularly given that measurements were conducted during cold-season conditions, when microbial activity is expected to be suppressed (Beelen & Parker, 2022; Foley et al., 2009; Y. Liu et al., 2015).

Chapter 6. Conclusion and Implications

This study presents a comprehensive, multi-scale investigation of methane (CH₄) dynamics in Cluj-Napoca, Romania, integrating high-resolution atmospheric observations with direct, source-specific measurements. The applied methodology combines walking-based mobile surveys

with direct in situ measurements across five key urban systems: aquatic environments (AQ), natural gas distribution end-use points (NG), sewer systems (SE), building basements (BS), and traffic-based emissions (TE). In addition, targeted quantification was conducted using static and floating chamber approaches for selected systems, including an artificial pond, an individual natural gas pipeline leak, and sewer network.

The mobile survey approach enabled extensive spatial coverage and real-time detection of methane enhancements, identifying 31 leak indications (LIs) in the first survey (TDLAS-based) and 37 LIs in the second survey (MILAS-based) above the background levels (>2.2 ppmv), with the latter applying a moving-window background. Hydrocarbon ratio analysis ($C_2:C_1$) revealed a mixed emission profile across the study area. Direct measurements further confirmed the widespread presence of CH_4 across all investigated systems, including consistent oversaturation in aquatic environments, frequent leak indications at NG end-use points (81%) and sewer manholes (48%), detectable methane in all vehicle exhaust samples, and elevated concentrations in the majority of basement measurements.

A strong spatial agreement (approximately 80%) between mobile survey detections and direct source measurements—typically within 160 m—demonstrates the robustness of combining atmospheric and direct system-based approaches. This multi-scale framework enhances source attribution by effectively linking atmospheric signals to specific emission sources, addressing a key challenge in complex urban environments.

Quantification results highlighted contrasting behaviors among sources. No measurable emissions were detected from the investigated artificial pond under the study conditions, whereas the sewer exhibited clear evidence of active microbial CH_4 production despite cold-season measurements. A total of 221 flux measurements using Empirical Bayesian kriging (EBK) to produce a continuous spatial surface of CH_4 emissions across Cluj-Napoca, extended to 8,801 virtual manholes. The estimated total citywide CH_4 flux was 101.3 g d^{-1} (0.037 t yr^{-1} ; 95% CI: $96.6\text{--}107.3 \text{ g d}^{-1}$), revealing pronounced spatial heterogeneity. Elevated emissions were concentrated in the historical urban core and along primary sewer collectors, where aging infrastructure and long hydraulic retention times favour anaerobic methanogenesis.

In contrast, quantification of an individual natural gas pipeline leak yielded emissions of $10.22 \pm 1.06 \text{ kg CH}_4 \text{ yr}^{-1}$ (95% CI), illustrating the disproportionate contribution of localized “supper emitters” to the urban methane budget.

A key outcome of this study is the identification of significant discrepancies between measurement-based observations and inventory-based estimates. Results suggest that methane emissions in urban environments such as Cluj-Napoca may be underestimated by a factor of three to four in conventional bottom-up inventories. This finding aligns with recent studies underlining “missing methane” in urban systems, particularly sewer networks and natural gas infrastructure, emphasizing the importance of integrating high-resolution observational data into national greenhouse gas inventories.

At the system level, the results demonstrate that urban environments function as hybrid methane systems. Aquatic environments act as persistent CH_4 sources primarily driven by biogenic processes. Natural gas distribution networks represent the dominant anthropogenic source, while sewer systems display strong spatial heterogeneity linked to infrastructure and hydraulic conditions. Building basements may reflect overlapping influences from natural gas leakage and microbial activity under low-ventilation settings. Traffic emissions contribute localized and short-lived CH_4 enhancements, particularly under specific operating conditions such as cold starts.

Generally, this thesis demonstrates that urban methane dynamics are governed by complex interaction between biogenic and anthropogenic processes across multiple spatial scales. By integrating mobile surveys, point-source observations, and targeted emission quantification, this research provides a robust framework for improving methane source attribution, refining emission inventories, and identifying priority mitigation targets.

Importantly, this work represents one of the first comprehensive multi-system urban methane assessments in Eastern Europe, addressing a critical geographical research gap. The findings contribute to the development of targeted mitigation strategies and support broader climate objectives aligned with the EU Green Deal and the Paris Agreement.

References

AERIS Technologies, (USA). (2024). *Locate Natural Gas Leaks with Unmatched Sensitivity, Ease-of-Use, and Thermogenic vs. Biogenic Discrimination*. <https://aerissensors.com/wp->

- content/uploads/2024/12/Aeris_Look-Book-Brochure_NoBleed.pdf (accessed on: 04.01.2025)
- Ars, S., Vogel, F., Arrowsmith, C., Heerah, S., Knuckey, E., Lavoie, J., Lee, C., Pak, N. M., Phillips, J. L., & Wunch, D. (2020). Investigation of the Spatial Distribution of Methane Sources in the Greater Toronto Area Using Mobile Gas Monitoring Systems. *Environmental Science & Technology*, 54(24), 15671-15679. <https://doi.org/10.1021/acs.est.0c05386>
- Baciu, C., Ionescu, A., & Etiope, G. (2018). Hydrocarbon seeps in Romania : Gas origin and release to the atmosphere. *Marine and Petroleum Geology*, 89, 130-143. <https://doi.org/10.1016/j.marpetgeo.2017.06.015>
- Bauduin, T., Gypens, N., & Borges, A. V. (2025). Sub-daily variability of carbon dioxide, methane, and nitrous oxide emissions from two urban ponds in Brussels (Belgium). *Journal of Environmental Management*, 373, 123627. <https://doi.org/10.1016/j.jenvman.2024.123627>
- Beelen, B., & Parker, W. (2022). A probabilistic approach to the quantification of methane generation in sewer networks. *Journal of Environmental Management*, 320, 115775. <https://doi.org/10.1016/j.jenvman.2022.115775>
- Brown, A. M., Bass, A. M., Skiba, U., MacDonald, J. M., & Pickard, A. E. (2023). Urban landscapes and legacy industry provide hotspots for riverine greenhouse gases : A source-to-sea study of the River Clyde. *Water Research*, 236, 119969. <https://doi.org/10.1016/j.watres.2023.119969>
- Capasso, G., & Inguaggiato, S. (1998). A simple method for the determination of dissolved gases in natural waters. An application to thermal waters from Vulcano Island. *Applied Geochemistry*, 13(5), 631-642. [https://doi.org/10.1016/S0883-2927\(97\)00109-1](https://doi.org/10.1016/S0883-2927(97)00109-1)
- Cardellini, C., Chiodini, G., Frondini, F., Granieri, D., Lewicki, J., & Peruzzi, L. (2002). Accumulation chamber measurements of methane fluxes : Application to volcanic-geothermal areas and landfills. *Applied Geochemistry*, 18, 45-54.
- Chamberlain, S. D., Ingraffea, A. R., & Sparks, J. P. (2016). Sourcing methane and carbon dioxide emissions from a small city : Influence of natural gas leakage and combustion. *Environmental Pollution*, 218, 102-110. <https://doi.org/10.1016/j.envpol.2016.08.036>
- Collier, S. M., Ruark, M. D., Oates, L. G., Jokela, W. E., & Dell, C. J. (2014). Measurement of Greenhouse Gas Flux from Agricultural Soils Using Static Chambers. *Journal of Visualized Experiments*, (90), 52110. <https://doi.org/10.3791/52110-v>
- Crippa, M., Guizzardi, D., Pisoni, E., Solazzo, E., Guion, A., Muntean, M., Florczyk, A., Schiavina, M., Melchiorri, M., & Hutter, A. F. (2021). Global anthropogenic emissions in urban areas : Patterns, trends, and challenges. *Environmental Research Letters*, 16(7), 074033. <https://doi.org/10.1088/1748-9326/ac00e2>
- Cuna, S., Pendall, E., Miller, J. B., Tans, P. P., Dlugokencky, E., & White, J. W. C. (2008). Separating contributions from natural and anthropogenic sources in atmospheric methane

- from the Black Sea region, Romania. *Applied Geochemistry*, 23(10), 2871-2879. <https://doi.org/10.1016/j.apgeochem.2008.04.019>
- Defratyka, S. M., Paris, J.-D., Yver-Kwok, C., Fernandez, J. M., Korben, P., & Bousquet, P. (2021). Mapping Urban Methane Sources in Paris, France. *Environmental Science & Technology*, 55(13), 8583-8591. <https://doi.org/10.1021/acs.est.1c00859>
- EC-JRC, E. Commission. J. R. Centre., & IEA, I. E. A. (2024). *GHG emissions of all world countries*. Publications Office. <https://data.europa.eu/doi/10.2760/0115360>
- Etiope, G., Feyzullayev, A., & Baci, C. L. (2009). Terrestrial methane seeps and mud volcanoes : A global perspective of gas origin. *Marine and Petroleum Geology*, 26(3), 333-344. <https://doi.org/10.1016/j.marpetgeo.2008.03.001>
- European Commission. Joint Research Centre. (2023). *GHG emissions of all world countries : 2023*. Publications Office. <https://data.europa.eu/doi/10.2760/953322>
- Fernandez, J. M., Maazallahi, H., France, J. L., Menoud, M., Corbu, M., Ardelean, M., Calcan, A., Townsend-Small, A., van der Veen, C., Fisher, R. E., Lowry, D., Nisbet, E. G., & Röckmann, T. (2022). Street-level methane emissions of Bucharest, Romania and the dominance of urban wastewater. *Atmospheric Environment: X*, 13, 100153. <https://doi.org/10.1016/j.aeaoa.2022.100153>
- Foley, J., Yuan, Z., & Lant, P. (2009). Dissolved methane in rising main sewer systems : Field measurements and simple model development for estimating greenhouse gas emissions. *Water Science and Technology*, 60(11), 2963-2971. <https://doi.org/10.2166/wst.2009.718>
- Fries, A. E., Schiffman, L. A., Shuster, W. D., & Townsend-Small, A. (2018). Street-level emissions of methane and nitrous oxide from the wastewater collection system in Cincinnati, Ohio. *Environmental Pollution*, 236, 247-256. <https://doi.org/10.1016/j.envpol.2018.01.076>
- Gallagher, M. E., Down, A., Ackley, R. C., Zhao, K., Phillips, N., & Jackson, R. B. (2015). Natural Gas Pipeline Replacement Programs Reduce Methane Leaks and Improve Consumer Safety. *Environmental Science & Technology Letters*, 2(10), 286-291. <https://doi.org/10.1021/acs.estlett.5b00213>
- Ghiorghiu, E., Ajtai, I., Martonos, I. M., Hmoudah, M., Orban, A., Lupulescu, A., Spulber, L., Cozma, A. I., Șfabu, Ștefan, Moga, R., Baci, C., & Etiope, G. (2025). Long-term emission of methane and ethane to the atmosphere from hybrid natural seepage and well leakage in the Sărmășel gas field (Romania). *Applied Geochemistry*, 195, 106614. <https://doi.org/10.1016/j.apgeochem.2025.106614>
- Guisasola, A., de Haas, D., Keller, J., & Yuan, Z. (2008). Methane formation in sewer systems. *Water Research*, 42(6-7), 1421-1430. <https://doi.org/10.1016/j.watres.2007.10.014>
- Haiduc, I., & Beldean, M. S. (2011). Variation of Greenhouse Gases in Urban Areas-Case Study : CO₂, CO and CH₄ in Three Romanian Cities. In *Air Quality-Models and Applications*. InTech. <https://doi.org/10.5772/17985>
- Herrero Ortega, S., Romero González-Quijano, C., Casper, P., Singer, G. A., & Gessner, M. O. (2019). Methane emissions from contrasting urban freshwaters : Rates, drivers, and a

- whole-city footprint. *Global Change Biology*, 25(12), 4234-4243.
<https://doi.org/10.1111/gcb.14799>
- Hu, Z., Wu, S., Ji, C., Zou, J., Zhou, Q., & Liu, S. (2016). A comparison of methane emissions following rice paddies conversion to crab-fish farming wetlands in southeast China. *Environmental Science and Pollution Research*, 23(2), 1505-1515.
<https://doi.org/10.1007/s11356-015-5383-9>
- INS. (2023, janvier). *Recensământul Populației și Locuințelor, runda 2021—Date provizorii în profil teritorial. National Institute of Statistics (INS)*.
<https://insse.ro/cms/ro/content/recensamantul-populatiei-si-locuintelor-runda-2021-date-provizorii-in-profil-teritorial> (access date 13.02.2024)
- INS. (2025). <https://insse.ro/cms>
- IPCC. (2001). *Climate Change 2001 : Synthesis Report. A Contribution of Working Groups I, II, and III to the Third Assessment Report of the Intergovernmental Panel on Climate Change [Watson, R.T. and the Core Writing Team (eds.)]*. Cambridge University Press, Cambridge, United Kingdom, and New York, NY, USA.
- IPCC. (2013a). *Carbon and Other Biogeochemical Cycles*. In : *Climate Change 2013 : The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- IPCC. (2013b). *Observations : Atmosphere and Surface*. In : *Climate Change 2013 : The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- IPCC. (2014). *Climate Change 2014 : Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, R.K. Pachauri and L.A. Meyer (eds.)]*. IPCC, Geneva, Switzerland.
https://www.ipcc.ch/site/assets/uploads/2018/02/SYR_AR5_FINAL_full.pdf
- IPCC. (2019). *2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, Chapter3 : Uncertainties*.
- IPCC. (2023a). *Climate Change 2021 – The Physical Science Basis : Working Group I Contribution to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change (1^{re} éd.)*. Cambridge University Press. <https://doi.org/10.1017/9781009157896>
- IPCC. (2023b). *Synthesis Report on the IPCC Sixth Assessment Report (AR6). Longer Report : Geneva, Switzerland. IPCC AR6 SYR*.
- Jahangir, M. M. R., Johnston, P., Khalil, M. I., Grant, J., Somers, C., & Richards, K. G. (2012). Evaluation of headspace equilibration methods for quantifying greenhouse gases in groundwater. *Journal of Environmental Management*, 111, 208-212.
<https://doi.org/10.1016/j.jenvman.2012.06.033>

- Joo, J., Jeong, S., Shin, J., & Chang, D. Y. (2023). Missing methane emissions from urban sewer networks. *Environmental Pollution*, 342, 123101. <https://doi.org/10.1016/j.envpol.2023.123101>
- Keyes, T., Ridge, G., Klein, M., Phillips, N., Ackley, R., & Yang, Y. (2020). An enhanced procedure for urban mobile methane leak detection. *Heliyon*, 6(10), e04876. <https://doi.org/10.1016/j.heliyon.2020.e04876>
- Krivoruchko, K. (2012). *Empirical Bayesian Kriging*. <https://www.esri.com/news/arcuser/1012/empirical-byesian-kriging.html>
- Lamb, B. K., Cambaliza, M. O. L., Davis, K. J., Edburg, S. L., Ferrara, T. W., Floerchinger, C., Heimburger, A. M. F., Herndon, S., Lauvaux, T., Lavoie, T., Lyon, D. R., Miles, N., Prasad, K. R., Richardson, S., Roscioli, J. R., Salmon, O. E., Shepson, P. B., Stirm, B. H., & Whetstone, J. (2016). Direct and Indirect Measurements and Modeling of Methane Emissions in Indianapolis, Indiana. *Environmental Science & Technology*, 50(16), 8910-8917. <https://doi.org/10.1021/acs.est.6b01198>
- Lamb, B. K., Edburg, S. L., Ferrara, T. W., Howard, T., Harrison, M. R., Kolb, C. E., Townsend-Small, A., Dyck, W., Possolo, A., & Whetstone, J. R. (2015). Direct Measurements Show Decreasing Methane Emissions from Natural Gas Local Distribution Systems in the United States. *Environmental Science & Technology*, 49(8), 5161-5169. <https://doi.org/10.1021/es505116p>
- Leng, P., Li, Z., Zhang, Q., Koschorreck, M., Li, F., Qiao, Y., & Xia, J. (2023). Deciphering large-scale spatial pattern and modulators of dissolved greenhouse gases (CO₂, CH₄, and N₂O) along the Yangtze River, China. *Journal of Hydrology*, 623, 129710. <https://doi.org/10.1016/j.jhydrol.2023.129710>
- Lesmeister, L., & Koschorreck, M. (2017). A closed-chamber method to measure greenhouse gas fluxes from dry aquatic sediments. *Atmospheric Measurement Techniques*, 10(6), 2377-2382. <https://doi.org/10.5194/amt-10-2377-2017>
- Liu, L., Kawaike, K., Wada, K., Koshiba, T., Chen, X., Han, C., & Matsui, H. (2025). Environmental drivers of sediment accumulation in urban sewer systems : A case study of Kyoto City, Japan. *Water Research*, 268, 122721. <https://doi.org/10.1016/j.watres.2024.122721>
- Liu, Y., Ni, B.-J., Sharma, K. R., & Yuan, Z. (2015). Methane emission from sewers. *Science of The Total Environment*, 524-525, 40-51. <https://doi.org/10.1016/j.scitotenv.2015.04.029>
- Mu, J., Qi, J., Yu, H., Hu, C., Mu, Y., & Qu, J. (2022). Dynamic chamber as a more reliable technique for measuring methane emissions from aquatic ecosystems. *Science of The Total Environment*, 851, 158147. <https://doi.org/10.1016/j.scitotenv.2022.158147>
- Nakagawa, F., Tsunogai, U., Komatsu, D. D., Yamada, K., Yoshida, N., Moriizumi, J., Nagamine, K., Iida, T., & Ikebe, Y. (2005). Automobile exhaust as a source of ¹³C- and D-enriched atmospheric methane in urban areas. *Organic Geochemistry*, 36(5), 727-738. <https://doi.org/10.1016/j.orggeochem.2005.01.003>

- National Institute of Statistics, (INS). (2021). *Romanian Population and Housing Census*. <https://www.recensamantromania.ro/rezultate-rpl-2021/rezultate-definitive/> (date of access 14.11.2023)
- Nisbet, E. G., Fisher, R. E., Lowry, D., France, J. L., Allen, G., Bakkaloglu, S., Broderick, T. J., Cain, M., Coleman, M., Fernandez, J., Forster, G., Griffiths, P. T., Iverach, C. P., Kelly, B. F. J., Manning, M. R., Nisbet-Jones, P. B. R., Pyle, J. A., Townsend-Small, A., al-Shalaan, A., ... Zazzeri, G. (2020). Methane Mitigation : Methods to Reduce Emissions, on the Path to the Paris Agreement. *Reviews of Geophysics*, 58(1), e2019RG000675. <https://doi.org/10.1029/2019RG000675>
- NOAA, N. O. & A. A. (2026). *Global Monitoring Laboratory, Carbon Cycle Greenhouse Gases, Trends in CO₂, CH₄, N₂O, SF₆*. <https://gml.noaa.gov/ccgg/trends/> (accessed on 10.04.2026)
- Oh, Y., Bruhwiler, L., Lan, X., Basu, S., Schuldt, K., Thoning, K., Michel, S. E., Clark, R., Miller, J. B., Andrews, A., Sherwood, O., Etiope, G., Crippa, M., Liu, L., Zhuang, Q., Randerson, J., van der Werf, G., Aalto, T., Amendola, S., ... Xueref-Remy, I. (2023). *CarbonTracker CH₄ 2023*. <https://doi.org/10.25925/40JT-QD67>
- Patel, L., Singh, R., & Thottathil, S. D. (2023). Land use drivers of riverine methane dynamics in a tropical river basin, India. *Water Research*, 228, 119380. <https://doi.org/10.1016/j.watres.2022.119380>
- Phillips, N. G., Ackley, R., Crosson, E. R., Down, A., Hutyra, L. R., Brondfield, M., Karr, J. D., Zhao, K., & Jackson, R. B. (2013). Mapping urban pipeline leaks : Methane leaks across Boston. *Environmental Pollution*, 173, 1-4. <https://doi.org/10.1016/j.envpol.2012.11.003>
- Plant, G., Kort, E. A., Floerchinger, C., Gvakharia, A., Vimont, I., & Sweeney, C. (2019). Large Fugitive Methane Emissions From Urban Centers Along the U.S. East Coast. *Geophysical Research Letters*, 46(14), 8500-8507. <https://doi.org/10.1029/2019GL082635>
- Plant, G., Kort, E. A., Murray, L. T., Maasakkers, J. D., & Aben, I. (2022). Evaluating urban methane emissions from space using TROPOMI methane and carbon monoxide observations. *Remote Sensing of Environment*, 268, 112756. <https://doi.org/10.1016/j.rse.2021.112756>
- Popa, D., Popa, R., Vidu, L., & Nicolae, C. (2016). Emission of Methane from Enteric Fermentation of Cattle and Buffaloes in Romania between 1989-2014. *Agriculture and Agricultural Science Procedia*, 10, 289-298. <https://doi.org/10.1016/j.aaspro.2016.09.066>
- Premke, K., Dharanivasan, G., Steger, K., Nitzsche, K. N., Jayavignesh, V., Nambi, I. M., & Seshadri, S. (2020). Anthropogenic Impact on Tropical Perennial River in South India : Snapshot of Carbon Dynamics and Bacterial Community Composition. *Water*, 12(5), 1354. <https://doi.org/10.3390/w12051354>
- PwC, P. M. C. S. (2023, mai). *Long Term Strategy of Romania*.
- Satterthwaite, D. (2008). Cities' contribution to global warming : Notes on the allocation of greenhouse gas emissions. *Environment and Urbanization*, 20(2), 539-549. <https://doi.org/10.1177/0956247808096127>

- Saunois, M., Bousquet, P., Poulter, B., Peregon, A., Ciais, P., Canadell, J. G., Dlugokencky, E. J., Etiope, G., Bastviken, D., Houweling, S., Janssens-Maenhout, G., Tubiello, F. N., Castaldi, S., Jackson, R. B., Alexe, M., Arora, V. K., Beerling, D. J., Bergamaschi, P., Blake, D. R., ... Zhu, Q. (2016). The global methane budget 2000–2012. *Earth System Science Data*, 8(2), 697-751. <https://doi.org/10.5194/essd-8-697-2016>
- Saunois, M., Martinez, A., Poulter, B., Zhang, Z., Raymond, P. A., Regnier, P., Canadell, J. G., Jackson, R. B., Patra, P. K., Bousquet, P., Ciais, P., Dlugokencky, E. J., Lan, X., Allen, G. H., Bastviken, D., Beerling, D. J., Belikov, D. A., Blake, D. R., Castaldi, S., ... Zhuang, Q. (2025). Global Methane Budget 2000–2020. *Earth System Science Data*, 17(5), 1873-1958. <https://doi.org/10.5194/essd-17-1873-2025>
- Saunois, M., Stavert, A. R., Poulter, B., Bousquet, P., Canadell, J. G., Jackson, R. B., Raymond, P. A., Dlugokencky, E. J., Houweling, S., Patra, P. K., Ciais, P., Arora, V. K., Bastviken, D., Bergamaschi, P., Blake, D. R., Brailsford, G., Bruhwiler, L., Carlson, K. M., Carrol, M., ... Zhuang, Q. (2020). The Global Methane Budget 2000–2017. *Earth System Science Data*, 12(3), 1561-1623. <https://doi.org/10.5194/essd-12-1561-2020>
- Tang, W., Xu, Y. J., Ni, M., & Li, S. (2023). Land use and hydrological factors control concentrations and diffusive fluxes of riverine dissolved carbon dioxide and methane in low-order streams. *Water Research*, 231, 119615. <https://doi.org/10.1016/j.watres.2023.119615>
- UN DESA. (2019). *World Urbanization Prospects : The 2018 Revision*. UN. <https://doi.org/10.18356/b9e995fe-en>
- UNEP. (2021). *Emissions Gap Report 2011 : The Heat Is On—A world of climate promises not yet delivered*. Nairobi.
- van Es, J., van Der Veen, C., Baciuc, C., Hmoudah, M., Menoud, M., Henne, S., & Röckmann, T. (2025). Methane Sources in Cluj-Napoca, Romania : Insights From Isotopic Analysis. *Journal of Geophysical Research: Atmospheres*, 130(18), e2024JD043015. <https://doi.org/10.1029/2024JD043015>
- Venturi, S., Cabassi, J., Tassi, F., Maioli, G., Randazzo, A., Capeccchiacci, F., & Vaselli, O. (2021). Near-surface atmospheric concentrations of greenhouse gases (CO₂ and CH₄) in Florence urban area : Inferring emitting sources through carbon isotopic analysis. *Urban Climate*, 39, 100968. <https://doi.org/10.1016/j.uclim.2021.100968>
- Vogel, F., Ars, S., Wunch, D., Lavoie, J., Gillespie, L., Maazallahi, H., Röckmann, T., Neçki, J., Bartyzel, J., Jagoda, P., Lowry, D., France, J., Fernandez, J., Bakkaloglu, S., Fisher, R., Lanoiselle, M., Chen, H., Oudshoorn, M., Yver-Kwok, C., ... Calcan, A. (2024). Ground-Based Mobile Measurements to Track Urban Methane Emissions from Natural Gas in 12 Cities across Eight Countries. *Environmental Science & Technology*, acs.est.3c03160. <https://doi.org/10.1021/acs.est.3c03160>
- Wang, R., Zhang, H., Zhang, W., Zheng, X., Butterbach-Bahl, K., Li, S., & Han, S. (2020). An urban polluted river as a significant hotspot for water–atmosphere exchange of CH₄ and

- N₂O. *Environmental Pollution*, 264, 114770. <https://doi.org/10.1016/j.envpol.2020.114770>
- West Systems. (2016). *High resolution Methane and Carbon Dioxide diffuse flux meter*. West group news. Portable Fluxmeter. https://www.westgroupnews.com/wp-content/uploads/2016/02/12_Portable_fluxmeter.pdf (access date: 03.02.2024)
- Williams, J. P., Ars, S., Vogel, F., Regehr, A., & Kang, M. (2022). Differentiating and Mitigating Methane Emissions from Fugitive Leaks from Natural Gas Distribution, Historic Landfills, and Manholes in Montréal, Canada. *Environmental Science & Technology*, 56(23), 16686-16694. <https://doi.org/10.1021/acs.est.2c06254>
- Wu, S., Hu, Z., Hu, T., Chen, J., Yu, K., Zou, J., & Liu, S. (2018). Annual methane and nitrous oxide emissions from rice paddies and inland fish aquaculture wetlands in southeast China. *Atmospheric Environment*, 175, 135-144. <https://doi.org/10.1016/j.atmosenv.2017.12.008>
- Xu, X., Zhong, X., Dong, J., Xie, D., & Lu, W. (2023). Measuring methane emissions during the installation of residential and commercial natural gas meters in China. *Science of The Total Environment*, 904, 166629. <https://doi.org/10.1016/j.scitotenv.2023.166629>
- Zazzeri, G., Lowry, D., Fisher, R. E., France, J. L., Lanoisellé, M., Kelly, B. F. J., Necki, J. M., Iverach, C. P., Ginty, E., Zimnoch, M., Jasek, A., & Nisbet, E. G. (2016). Carbon isotopic signature of coal-derived methane emissions to the atmosphere: from coalification to alteration. *Atmospheric Chemistry and Physics*, 16(21), 13669-13680. <https://doi.org/10.5194/acp-16-13669-2016>
- Zhao, X., Jin, X. K., Guo, W., Zhang, C., Shan, Y. L., Du, M. X., Tillotson, M. R., Yang, H., Liao, X. W., & Li, Y. P. (2019). China's Urban Methane Emissions From Municipal Wastewater Treatment Plant. *Earth's Future*, 7(4), 480-490. <https://doi.org/10.1029/2018EF001113>