Locating and quantifying CH$_4$ sources within a wastewater treatment plant based on mobile measurements

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Abstract. Wastewater treatment plants (WWTPs) are substantial contributors to greenhouse gas (GHG) emissions because of the high production of methane (CH$_4$) and nitrous oxide (N$_2$O). A typical WWTP complex contains multiple functional areas that are potential sources for GHG emissions. Accurately quantifying GHG emissions from

these sources is challenging due to the inaccuracy of activity~~emission~~ data, the ambiguity of emission sources, and the absence of monitoring standards. Locating and quantifying WWTPs emission sources using~~in combination with~~ measurement-based GHG emission quantification method~~s~~ is~~are~~ crucial for evaluating and improving traditional emission inventories. In this study, CH_4 mobile measurements were conducted within a WWTP complex in the summer and winter of 2023. We utilized a multi-source Gaussian plume model combined with the genetic algorithm inversion framework, designed to locate major sources within the plant and quantify the corresponding CH_4 emission fluxes. We identified 13~~2~~ main ~~point~~ sources in the plant and estimated plant-scale CH_4 emission fluxes of 68.78 ± 17.40 kg h^{-1} (603.33 ± 152.66 t a^{-1}) for the summer and 47.76 ± 21.39 kg h^{-1} (418.95 ± 187.59 t a^{-1}) for the winter. The predominant sources of CH_4 emissions were the screen and primary clarifier, contributing 55 % and 67 % to the total emissions in summer and winter, respectively. The comparison revealed that summer CH_4 emissions were 2.8 times higher than inventory estimates, while winter emissions were twice the inventory values.~~The comparison against traditional emission inventories revealed that the CH₄ emission fluxes in the summer were 2.8 times greater than the inventory estimates, and in the winter, emissions were twice the inventory values. Our flux inversion method achieved a good agreement between simulations and observations (correlation > 0.6 and a root mean square error (RMSE) < 0.7 mg m⁻³).~~ This study demonstrated that mobile measurements, combined with the multi-source Gaussian plume inversion framework, are a powerful tool to locate and quantify GHG sources in a complex site, with the potential for further refinement to accommodate different types of factories and gas species.

1 Introduction

~~Greenhouse gas (GHG) emissions exacerbate the greenhouse effect, causing adverse~~

impacts on human health, ecosystems, and the environment (IPCC, 2023). Methane (CH_4) is the second-largest contributor to climate change, with the global warming potential 27.9 times that of carbon dioxide (CO_2). Reducing CH_4 emissions is essential for mitigating climate change and progressively achieving the global target of limiting warming to 1.5 °C (IPCC, 2023). The latest observational study from the WMO Global Atmospheric Watch network indicated that the global annual average concentration of CH_4 in 2022 was 1923 ± 2 ppb, representing a 264 % increase from pre-industrial levels (WMO, 2023). The International Energy Agency (IEA)'s 2024 Global Methane Tracker report suggests that global CH_4 emissions reached 580 Mt in 2023, with anthropogenic CH_4 emissions accounting for 60 %. The complexity of CH_4 emission processes, lack of monitoring systems, and limitations of emission estimation models present challenges in accurately estimating anthropogenic CH_4 emissions.

The quantification of CH_4 emission fluxes is typically achieved through a bottom-up inventory method. However, due to the difficulties in obtaining actual emission factors activity data used for actual emission factors, and specific information on different emission sources, there is considerable uncertainty in the assessing of the emission inventory method (Lin et al., 2021). In contrast, a top-down method that estimates CH_4 emissions by monitoring atmospheric concentration has been increasingly applied in recent years (Sun et al., 2019; Cusworth et al., 2024; Han et al., 2024; Maazallahi et al., 2023; Riddick et al., 2017). The monitoring technology mainly includes satellite (Zhang et al., 2021; Liang et al., 2023; Jacob et al., 2022) and airborne (Allen et al., 2019; Abeywickrama et al., 2023; Cui et al., 2017) remote sensing, as well as ground-based monitoring such as vehicle-based mobile monitoring (Albertson et al., 2016; Al-Shalan et al., 2022; Caulton et al., 2018), station monitoring (Dietrich et al., 2021; Hase et al., 2015; Heerah et al.,2021) and tower monitoring (Richardson et al., 2017; Balashov et al., 2020). Emission flux inversion methods also include isotope tracer method (Jackson et al., 2014; Zimnoch et al., 2018), cross-sectional flux method (Luther et al., 2019; Makarova et al., 2021), and atmospheric diffusion model inversion method (Kumar et

al., 2021; Yacovitch et al., 2015). Atmospheric transport models with varied degrees of complexity, including Gaussian diffusion models (Stadler et al., 2021), Lagrangian models (Mckain et al., 2015), and Eulerian models (Bergamaschi et al., 2018), are used in the inversion to relate GHG concentrations with emissions. Optimization methods, such as Bayesian optimization (Karion et al., 2019) and linear regression models (Kumar et al., 2021), are applied to achieve accurate inversion results. Furthermore, some studies incorporate carbon isotope observations to better attribute the contribution of different CH_4 emission sources (Maazallahi et al., 2020). Numerous studies use satellite remote sensing, unmanned aerial vehicle (UAV) monitoring, and vehicle-based mobile monitoring techniques to measure CH_4 emissions (Sun et al.,2023). However, satellite spatiotemporal resolution is limited and UAVs have short endurance, making vehicle-based mobile monitoring a better choice for measuring CH_4 emissions at wastewater treatment plants (WWTPs). Vehicle-based mobile monitoring can perform continuous real-time monitoring and precise identification of emission sources, and hence have been applied to urban (von Fischer et al., 2017; Defratyka et al., 2021) and plant-scale (Zhao et al., 2021; Jin et al.,2010) monitoring of GHG concentrations and emission fluxes. Vogel et al. (2024) used high-precision fast-response GHG analyzers to investigated CH_4 leaks in 12 cities across 8 countries., using high-precision fast-response GHG analyzers combined with the mobile survey methodology (von Fischer et al., 2017). Chen et al. (2020) utilized the multiple-Gaussian-plume model and a forward modeling approach for mobile measurements of CH_4 emissions during the Munich Oktoberfest. Shi et al. (2023) proposed a CO_2/CH_4 emission quantification model (EMISSION-PARTITION) and conducted mobile measurements with vehicle-based monitoring system at chemical, coal washing, and waste incineration plants in two cities and one industrial park in China. , assuming different numbers of emission sources for quantitative assessment. Wang et al. (2022a; 2022b) employed the Environmental Protection Agency's Other Test Method 33A (OTM 33A) for monitoring downwind of fueling stations to estimate the CH_4 emission fluxes of nine

compressed natural gas (CNG) stations and five liquefied natural gas (LNG) stations in Eastern China. Emission flux inversion methods also include isotope tracer method (Jackson et al., 2014; Zimnoch et al., 2018), cross-sectional flux method (Luther et al., 2019; Makarova et al., 2021), and atmospheric diffusion model inversion method (Kumar et al., 2021; Yacovitch et al., 2015). Atmospheric transport models with varied degrees of complexity, including Gaussian diffusion models (Stadler et al., 2021), Lagrangian models (Mckain et al., 2015), and Eulerian models (Bergamaschi et al., 2018), are used in the inversion to relate GHG concentrations with emissions. Optimization methods, such as Bayesian optimization (Karion et al., 2019) and linear regression models (Kumar et al., 2021), are applied to achieve accurate inversion results. Furthermore, some studies incorporate carbon isotope observations to better attribute the contribution of different CH_4 emission sources (Maazallahi et al., 2020).

As a significant source of GHG emissions, wastewater treatment plants (WWTPs) generate substantial amounts of CH_4, N_2O, and CO_2 during the collection, treatment, and discharge of sewage and sludge, contributing 3 % of the global total GHG emissions (Bai et al., 2022). The estimation of CH_4 emission fluxes from WWTPs has increasingly attracted widespread attention. Li et al. (2024) developed a plant-level and technology-based CH_4 emission inventory for municipal WWTPs in China, estimating the CH_4 emissions for 2020 to be 150.6 Gg. Wang et al. (2022) systematically considered process technological differences in wastewater treatment, constructing a high-resolution greenhouse gas emission inventory for Chinese WWTPs from 2006 to 2019. Delre et al. (2017) measured the CH_4 and N_2O concentrations downwind of five WWTPs in Scandinavia using tracer gas dispersion, which obtained a range of CH_4 emission fluxes from 1.1 ± 0.1 to 18.1 ± 6.3 kg h^{-1}. Moore et al. (2023) employed an integrated Gaussian plume model with a Bayesian framework for CH_4 mobile measurements of CH_4 emissions from 63 WWTPs in the United States, pointing to a significant underestimation in the CH_4 emission inventories. However, most studies lack comparisons between measured and simulated concentrations, resulting in

significant uncertainty in the results. We present a mobile measurement investigation of a WWTP in Hangzhou 2023. To analyze the mobile data, we construct a multi-source Gaussian plume model combined with the genetic algorithm inversion framework, which assists us to locate and quantify CH_4 emission sources, based on the concentration distribution measured within the WWTP. Additionally, we compare CH_4 emission fluxes from the measurements with the bottom-up estimates of emission inventories. A sensitivity analysis is performed to elucidate the discrepancies arising from variations in emission source locations. Our results provide insight into formulating and evaluating emission reduction measures for WWTPs.

2 Instruments and methods

2.1 Site selection

The monitoring site was chosen at a WWTP in Hangzhou, a megacity in East China. This WWTP is a large-scale plant located in Hangzhou, processing up to 1.5 million tons of domestic wastewater daily. ~~The plant roads were flat and wide, suitable for vehicle-mounted CRDS (Cavity Ring Down Spectrometer~~Spectroscopy) to conduct monitoring along the internal roads of the plant to monitor various functional areas within the plant.~~ The chosen WWTP~~s processes ~~typically ~~encompass mechanical treatment, biological treatment, sedimentation, advanced treatment, disinfection, and sludge treatment. As illustrated in Fig. 1, we divide the WWTP into 14 functional areas according to treatment processes. ~~For instance, a~~Areas associated with primary treatment were labeled as coarse screens and primary sedimentation tanks, while those linked to secondary treatment were indicated as aeration tanks and secondary sedimentation tanks. ~~Mobile measurements were conducted by driving around the outer periphery and internal functional areas of the wastewater treatment plant, with each monitoring experiment involving circling the functional areas 1-2 times. 10 days of~~

163 ~~experiments were carried out from June to December 2023. This yielded 8 valid sets of~~

164 ~~monitoring data, including 3 days of summer data and 5 days of winter data.~~ We

165 performed one monitoring experiment per day, with each experiment entailing 1-2

166 rounds of mobile measurements along external roads and internal functional areas roads.

167 Additionally, we conducted repeated mobile measurements and fixed measurements on

168 roads with high concentrations to calculate average concentration data. Over 10 days

169 of experiments from June to December 2023, we obtain 8 days of complete monitoring

170 data, including 3 days in summer and 5 days in winter. On the other two experimental

171 days, internal facility maintenance restricted access to certain roads, resulting in

172 incomplete monitoring data.

173

Figure 1. Distribution of functional areas of the WWTP. The yellow mark represents the simulated location of the line source. Solid lines show the roads measured by the mobile vehicle. Map data are from ESRI.

2.2 Instrumentation

The monitoring instruments consisted of a vehicle-mounted Cavity Ring-Down Spectrometer (CRDS) monitoring system (Zhao et al., 2024) and a portable meteorological station. The vehicle-mounted CRDS system was anchored by the CRDS analyzer (Picarro G2201-i, Picarro 2010), accompanied by GPS and meteorological instruments. ~~The CRDS analyzer measures $^{12}CO_2$, $^{13}CO_2$, $^{12}CH_4$, $^{13}CH_4$ and H_2O, t~~The volume fraction of CH_4 is measured with an accuracy of 5 ppb ± 0.05 % ~~(Picarro 2010)~~. CRDS measurements have the advantages of strong interference resistance, high sensitivity and accuracy, making them widely employed in research focused on monitoring GHG emissions (Rella et al., 2015; Lopez et al., 2017).

In this study, the CRDS analyzer was ~~securely~~ placed inside the monitoring vehicle~~, with the sampling probe mounted on the roof to mitigate the effects of vehicular emissions.~~ to measure CH_4 concentrations in the WWTP. The sampling probe was

placed near the roof along the window of the car to avoid interference from vehicle exhaust due to the low position. ~~The system was powered by a battery, drawing in ambient air through a pump, and displaying real-time monitoring data on a screen.~~ The mobile meteorological instrument was placed on the roof of the vehicle to gather meteorological data. In addition, the GPS unit was integrated to record the location of sampling points during the measurement period. Two portable meteorological stations (Hangzhou Pengpu Technology SWS-500) were positioned adjacent to the main entrance and atop the filter tank at the WWTP. Capable of measuring ~~key~~ meteorological parameters ~~such as~~ (wind speed, direction, temperature, humidity, and atmospheric pressure)~~, this station provided essential climatic data for the monitoring experiments. Mobile measurements were performed by the monitoring vehicle along the entire roads of the WWTP, as well as the internal roads, to pinpoint the locations of emission sources, scrutinize variations in emission concentrations. The concentration data was subsequently integrated with an inversion model to estimate the CH4 emission fluxes.~~

2.3 Inventory accounting method

We used the methods suggested by the IPCC Guidelines for National Greenhouse Gas Inventories (2006) to calculate the amounts of CH_4 emissions from wastewater. The formula for calculating the amounts of CH_4 emissions from wastewater is described as:

$$E_{CH_4} = (TOW - S \cdot a) \cdot EF_{CH_4} - R_{CH_4} \tag{1}$$

Where E_{CH_4} denotes the direct CH_4 emissions from the wastewater treatment plant, tCH_4 a^{-1}. TOW is defined as the total organic pollutant load in the influent wastewater, $tCOD$ a^{-1}. S refers to the annual production total of dry sludge, t a^{-1}. The parameter a signifies the organic matter content in the dry sludge, $tCOD$ t^{-1}. EF_{CH_4} is the CH_4 emission factor, tCH_4 $tCOD^{-1}$. R_{CH_4} quantifies the annual recovery of CH_4 from

219   anaerobic treatment processes, t a^{-1}.

220   Operational data of the WWTP examined in this study is derived from the Urban

221   Drainage Statistical Yearbook, an annual publication of urban water supply and

222   drainage systems in China. This data set includes details such as the water treatment

223   volume, sludge production, and the concentrations of six pollutants (COD_{Cr}, BOD, SS,

224   NH_3-N, TN, and TP) in both influent and effluent. The Total Organic Waste (TOW) is

225   ~~deduced from the yearbook's foundational data~~ calculated by the amount of treated

226   water and COD influent concentration of the WWTP provided in the yearbook, while

227   the annual sludge production (S) is extracted directly from ~~it~~the yearbook. The organic

228   matter content in dry sludge is estimated at an empirical 40 %, assuming a sludge

229   moisture content of 75 %, leading to a value of 0.1 (Guo et al., 2019). EF_{CH_4} is selected

230   based on the recommended value for Zhejiang province, 0.0046 (Cai et al., 2015).

231   Given the infrequency of anaerobic treatment in wastewater, R_{CH_4} is set to 0.

232

233   **2.4 Inversion method**

234   We developed an inversion framework for ~~CH₄~~ emission fluxes designed for plant-

235   level applications. The framework used ~~CH₄ concentration~~ mobile measurements data,

236   ~~specific~~ locations of emission sources, and initial emission estimates, alongside wind

237   speed and direction data, as inputs to the ~~multi-point and line source~~ multi-source

238   Gaussian diffusion models. The preliminary localization of the emission sources was

239   chiefly contingent upon the concentration distribution along the roads within the

240   internal functional areas. Meanwhile, the initial emission estimates for each source were

241   determined by integrating the concentration data from these areas with an improved

242   empirical equation (Weller et al., 201~~8~~9). Based on the comparison of measurement and

243   model simulation results (Fig. S1), it is determined that the plant exhibits multiple point

244   sources and line source diffusion patterns. Fig. S1 illustrates that the CH₄ concentration

245   curve presents distinct peak distributions in point source diffusion patterns, while the

CH₄ concentration distribution in line source diffusion patterns consistently maintains higher levels. ~~These inputs were fed into a multi-source Gaussian plume model that simulates the concentration patterns of CH₄ given multiple point and line sources.~~ We then used a genetic algorithm to iteratively optimize source emission fluxes and their locations. The inversion framework simulation dictated the placement of 12 main point sources throughout the WWTP, specifically within Aeration Tank ①②③④⑤, Primary Clarifier ③④⑤, Screen ①, Secondary Clarifier ①②, and the Sludge Treatment ② (Fig. 1). ~~The inclusion of a Gaussian line source model was determined based on the actual emission conditions.~~ Within this study, a uniform line source was established, with the assumed location along the road between the Screen ① and the Primary Clarifier ① (Fig. 1 yellow mark). This assumption was grounded in the CH₄ concentration distribution observed within this road segment and was substantiated through model validation. ~~, confirming the existence of a line source emission pattern.~~ The remaining emission flux inversion processes followed the same procedure as the point source simulation. Adjustments to the source locations within the model narrow the gap between simulated and measured concentrations, thus enhancing the accuracy of inversion. This section delineates each model incorporated into the inversion framework.

2.4.1 Empirical equation for estimating initial emissions

We used the improved empirical equation to estimate the initial emissions of emission sources (von Fisher et al., 2017; Weller et al.,2019). This method was primarily utilized for urban CH₄ leakage source emissions estimation (Defratyka et al., 2021; Maazallahi et al., 2020). The empirical equation is as follows:

$$ln\left(M_{CH_4}\right) = -0.988 + 0.817 \times ln\left(CH_4 \ emission \ rate\right) \quad (2)$$

The M_{CH_4} is the maximum enhancement value of CH₄ concentration, ppm. The

271   *CH₄ emission rate* represents the CH₄ emission flux, L min⁻¹.

272 **2.4.2 Multiple-point-source Gaussian plume model**

273   We developed a multiple-point-source Gaussian plume model to relate CH₄

274 concentration enhancement to CH₄ emissions. This method approximates atmospheric

275 dispersion of CH₄ from an individual source as a Gaussian plume under uniform and

276 stable wind conditions (Nassar et al., 2017), which is usually good for describing

277 average atmospheric transport tens to hundreds of meters downwind the source, making

278 the Gaussian plume model a useful tool to study emissions from industrial and traffic

279 sources.

280   The mass concentration enhancement (C, mg m⁻³) is computed as superposition of

281 Gaussian plumes from multiple point sources.

282 $$C(x, y, z) = \sum_{i=1}^{n} \frac{Q_i}{2\pi \bar{u} \sigma_{i,y} \sigma_{i,z}} exp\left(-\frac{(y-y_i)^2}{2\sigma_{i,y}^2}\right) \left\{ exp\left[\frac{-(z-z_i)^2}{2\sigma_{i,z}^2}\right] + exp\left[\frac{-(z+z_i)^2}{2\sigma_{i,z}^2}\right] \right\} \quad (23)$$

283   The variables x, y, and z denote the downwind, crosswind distances, and the height

284 above the ground from the source, m. Q_i signifies the emission rate from the i_{th} point

285 source, mg/s mg s⁻¹, for i = 1, 2, 3……N, where N represents the total count of point

286 sources. The average wind speed is indicated by $\bar{u}$, m s⁻¹. The x_i, y_i and z_i are

287 represented as the spatial position of the i_{th} point source, m. $\sigma_{i,y}$ and $\sigma_{i,Z}$ are the

288 horizontal and vertical dispersion parameters of the i_{th} point source, respectively, which

289 are given by the formula below:

290 $$\sigma_{i,y} = \gamma_1 \cdot (x - x_i)^{\alpha_1}, \text{ when } x > x_i \quad (34)$$

291 $$\sigma_{i,z} = \gamma_2 \cdot (x - x_i)^{\alpha_2}, \text{ when } x > x_i \quad (45)$$

292   The power functions, known as the Pasquill's curves, associates with the downwind

293 distance x and the prevailing atmospheric stability (Briggs et al., 1973). Atmospheric

294 stability is determined based on the Pasquill stability classes recommended in the

295 Technical Principles and Methods for Formulating Local Air Pollution Emission

296 Standards (GB3840-83). During the observation, the CH₄ concentrations were obtained

2.4.3~~2~~ General Finite Line Source Model

Our analysis of measurement at WWTPs indicates that multiple-point-source Gaussian plume model is insufficient to capture the observed CH_4 concentrations. The entire road between the Screen ① and the Primary Clarifier ① shows high distribution of CH_4 concentrations. ~~To match the observations, we further consider a line source based on observed concentration distribution. The line source model is used to confirm that the road concentration distribution is consistent with line source emissions (Fig. S1).~~ The contribution of a line source to CH_4 concentration is given by the General Finite Line Source Model (GFLSM) (Luhar et al., 1989; Venkatram et al., 2006), which represents the line source as an ensemble of point sources:

$$C = \frac{Q}{2\pi \bar{u} \sigma_y \sigma_z} \left\{ exp\left[\frac{-(z-H)^2}{2\sigma_z{}^2} \right] + exp\left[\frac{-(z+H)^2}{2\sigma_z{}^2} \right] \right\}$$

$$\cdot \left[erf\left(\frac{\sin\theta\left(\frac{L}{2}-y\right) - x\cos\theta}{\sqrt{2}\sigma_y} \right) + erf\left(\frac{\sin\theta\left(\frac{L}{2}+y\right) + x\cos\theta}{\sqrt{2}\sigma_y} \right) \right] \qquad (\tilde{5}6)$$

x, y, and z correspond to the downwind, crosswind distances, and the altitude above ground level from the source, m. Q_i is the emission fluxes of the unit source, mg s^{-1}. $\bar{u}$ is the average wind speed, m s^{-1}. H_i is the effective emission height of the line source, with the length of the line source represented by L, m. The angle between the line source and the wind direction is given by θ. The horizontal and vertical dispersion parameters are characterized by σ_y and σ_z, respectively.

2.4.4 Genetic algorithm

Genetic algorithms, which mimic the evolutionary process of biological systems, serve as optimization search algorithms. The algorithms encode practical problems into binary genetic coding. Through the simulation of natural selection, crossover, and mutation processes, these algorithms are in a constant state of evolution and iteration, all in the pursuit of the optimal solution (Katoch et al., 2021). We deployed genetic algorithms to enhance the source emission flux outcomes modeled by the Gaussian plume model.

The process of inverting multi-source CH_4 emission fluxes utilizing genetic algorithms involves a series of steps. Initially, the emission flux of each source is treated as a gene, with binary-encoded gene sequences randomly assigned to a set number of individuals within the predefined range of a priori emission fluxes. Subsequently, the formulation of a fitness function is based on the defined optimization goals and constraints. This function serves as a critical tool for assessing the relative merits of each individual within the population. In this study, the objective of the optimization is centered on minimizing the aggregate absolute discrepancy between the values predicted by the model and those obtained from measurements. Ultimately, the population is subjected to the processes of selection, crossover, and mutation. Individuals with elevated fitness values, as determined by the fitness function, are chosen for the generation of new individuals. Through an iterative process, the optimal solution is refined, representing the emission fluxes for each source. Genetic algorithms are distinguished by the parallel computation capabilities, the propensity for identifying global optima, and the commendable stability and reliability (Harada et al., 2020).

2.4.5 Uncertainty analysis

To quantify the uncertainty in the inversion results, we have considered the uncertainties associated with the input parameters of the inversion model, including

wind speed, wind direction, and instrument measurements. The uncertainty in the CH_4 emission fluxes (ε_t) is derived using the error propagation formula as follows:

$$\varepsilon_t = \sqrt{\varepsilon_s{}^2 + \varepsilon_d{}^2 + \varepsilon_m{}^2} \tag{7}$$

ε_s and ε_d denote the uncertainties in wind speed and direction, which are determined by the standard deviation of the wind speed and direction measurements from two fixed meteorological stations during the observation period. ε_m represents the uncertainty in instrumental measurements. This uncertainty is derived from data provided by the manufacturer Picarro, which indicates a concentration measurement uncertainty of approximately 1 ppb for a 10-second integration time (Picarro 2010).

3 Results and discussion

3.1 Concentration mapping

The closed-path mobile measurements were conducted by vehicle-mounted CRDS monitoring system along the external roads encircling the WWTP, with further monitoring conducted along the internal roads. This strategy depicts the distribution of CH_4 concentrations within an WWTP, allowing for identification of specific CH_4 emission sources. Based on 8 days of CH_4 monitoring experimental data, the CH_4 concentration range on the overall roads was determined to be 1.98-17.13 ppm. The CH_4 concentration distribution indicated higher levels downwind, with the highest concentrations consistently recorded at the Screen ① throughout mobile experiments.

Due to the consistencysimilarity of concentration measurement methods, we chose 29th June and 13th December as a typical example for measuring the spatial distribution of CH_4 and evaluating the seasonal variability of WWTP. Figure 2 illustrates measured CH_4 concentration enhancement distributions on 29th June (summer) and 13th December (winter) 2023 (other days are shown in Figures S32-S87). The CH_4

concentration enhancements depicted ~~within the figures~~ were calculated by subtracting the background concentrations from the measured values, with the background determined as the mean of the bottom 10 % of the concentration data. Specifically, the background concentrations register at 1.98 ppm on 29th June and at a slightly elevated 2.11 ppm on 13th December. The analysis indicates that the shallower boundary layer in winter causes CH_4 to accumulate near the surface, resulting in a higher background concentration. Moreover, increased concentrations are detected in the regions surrounding the Screen ①, Primary Clarifier ④, and Aeration Tank ③ during these two days. The complete concentration maps , which include the internal roads, reveal that the experiment on 29th June exhibits heightened concentrations at the Screen ①, Secondary Clarifier ②, and Primary Clarifier ②④. The Screen ① exhibits the highest CH_4 concentration, with an enhancement of 14.83 ppm. On 13th December, the concentration enhancements are noted in proximity to the Secondary Clarifier ① and Primary Clarifier ② , with the Primary Clarifier ② showing the highest CH_4 concentration at 4.79 ppm.

CH_4 concentrations in summer surpass those observed in winter, consistent with a previous study on WWTPs (Masuda et al., 2015). The screen, primary clarifier and aeration tank are identified as sources with notably higher concentrations. Analysis of concentration distributions reveals that Screen ① shows a peak concentration reaching 14.83 ppm, which is 7.5 times the background concentration. The four primary clarifiers record high concentrations between 4.79 and 10.88 ppm. The high value measured by aeration tanks is mainly detected in Aeration Tank ③ at 4.60ppm. The screen in this study includes coarse and fine screens and a grit chamber, constituting preliminary wastewater treatment to capture larger suspended solids and particulates. The anaerobic environment of the sewer network promotes the production of CH_4 from organic compounds in municipal wastewater. As this wastewater enters the WWTP, the

influent contains dissolved CH_4 that originated in the sewer network. During primary treatment, wastewater is elevated through riser mains, facilitating the release of CH_4 into the atmosphere (Guisasola et al., 2008; Bao et al., 2016). Flow velocity, hydraulic design and detention times in these facilities may affect CH_4 production and release (Alshboul et al., 2016; Yin et al., 2024). The primary clarifier physically removes suspended solids from wastewater through sedimentation, while organic matter undergoes anaerobic microbial degradation to the substantial production of CH_4 (Masuda et al., 2017). In the aeration tank, operated under anaerobic and anoxic conditions, complex organic compounds are converted to CH_4 by facultative and anaerobic bacteria through biological processes (Yoshida et al.,2014). In contrast, Kupper et al. (2018) identified sludge storage tanks as the primary source of CH_4 emissions in Swiss WWTPs, accounting for 70 % or more of the total emissions. Stadler et al. (2022) monitored CH_4 concentrations inside and around wastewater treatment facilities ranging from 2.04-32.78 ppm, with elevated CH_4 levels predominantly measured near sludge treatment tank, the digesters and secondary clarifiers. CH_4 emissions from various WTTPs are affected by a range of factors, including specific processes, pipeline design, and equipment aging, the mobile monitoring can better reflect the actual emission distribution.

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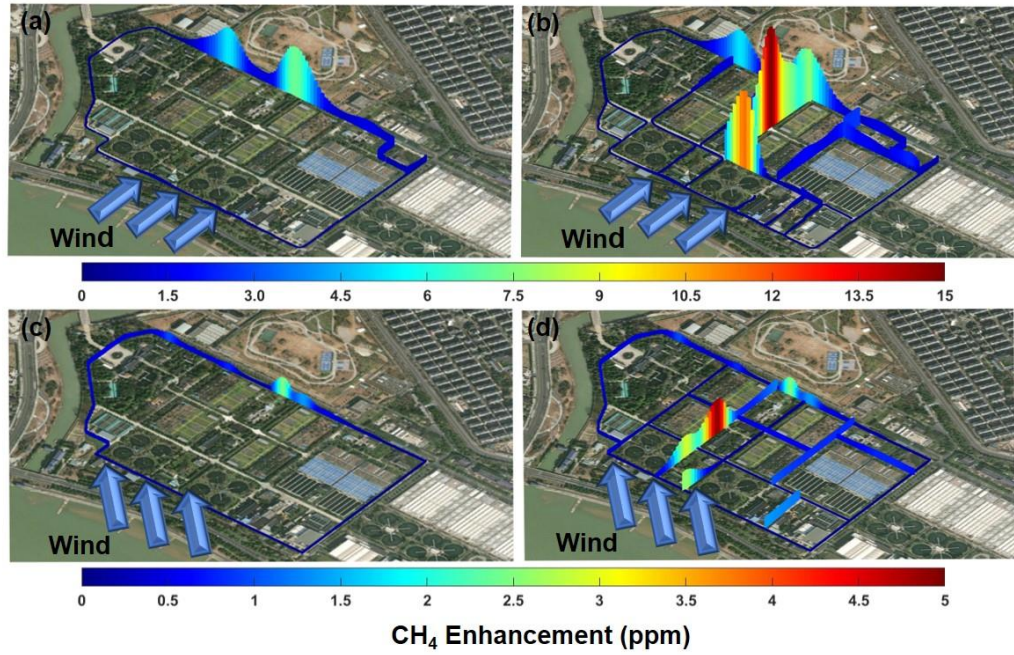
Figure 2. CH$_4$ concentration maps in the WWTP. The concentration maps for the external roads for 29th June (a) and 13th December (c). The corresponding complete concentration maps that include the internal roads for 29th June (b) and 13th December (d). Map data are from ESRI.

3.2 Emission quantification

The mobile measured CH$_4$ concentrations were employed in combination with the inversion framework to achieve the quantification of CH$_4$ emissions and localization of the emission sources within the WWTP. Figures 3 and 4 show the locations of identified point sources and the comparison between measured~~monitored~~ and simulated concentration distribution~~s for the point source locations at the WWTP on the dates of~~ ~~29th June and 13th December~~. The experiment conducted on 29th June finds the Screen ① to be the most significant contributor to CH$_4$ point source emissions at 18.26 kg h^{-1}~~160.19 t a^{-1}~~, and the Secondary Clarifier ② as the least significant at 1.23 kg h^{-1}~~10.78 t a^{-1}~~. The correlation coefficient R^2 for the measured~~monitored~~ and simulated

concentrations is 0.63, with an RMSE of 0.70 mg m^{-3}. On 13th December, the Aeration

Tank ⑤ is the largest point source of CH$_4$ emissions at 3.93 kg h^{-1}34.48 t a^{-1}, and the

Primary Clarifier ⑤ is the smallest at 0.55 kg h^{-1}4.82 t a^{-1}, with a correlation

coefficient R^2 of 0.70 and an RMSE of 0.28 mg m^{-3}. The enhanced correlation between

winter measurementmonitoring and simulation data, as well as the improved fit of the

measurementmonitoring and simulation value curves, is attributed to the shorter

monitoring cycle and more stable meteorological conditions.

In addition, when employing the multi-source Gaussian diffusion model combined with a genetic algorithm framework for iterative optimization to pinpoint point sources, we were able to locate external sources. As shown in Fig. S2 (a) and (c), external sources are primarily located along the main roadway to the south of the WWTP. Moreover, the estimated emissions vary across different days, which indicates that external source emissions are influenced by traffic vehicles. Fig. S2 (b) and (d) compare measured and simulated CH$_4$ concentrations before and after accounting for external sources, demonstrating that simulations are significantly closer to the measurements when external sources are included.
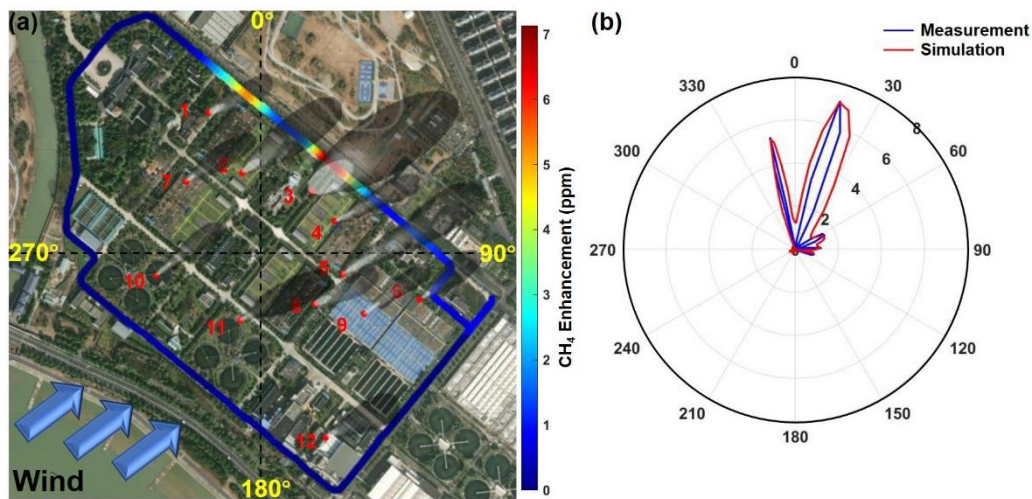
Figure 3. The emission distribution for the source locations (a) and the comparison between measuredmonitored and simulated CH$_4$ concentrations (b) at the WWTP on 29th June. Map data are from ESRI.

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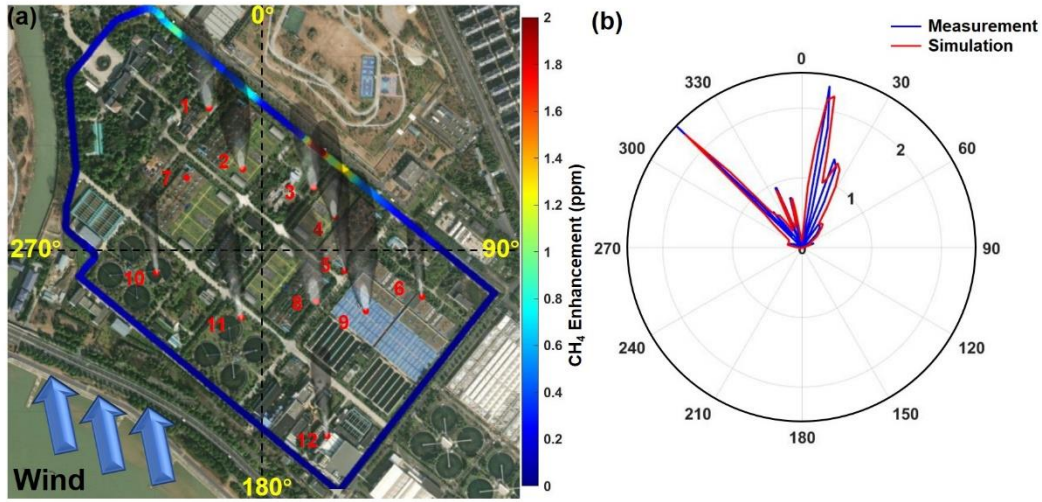
452

453 **Figure 4.** The emission distribution for the source locations (a) and the comparison

454 between measured~~monitored~~ and simulated CH$_4$ concentrations (b) at the WWTP on

455 13th December. Map data are from ESRI.

456

457 Table 1 displays the CH$_4$ emission fluxes (Q), Wind speed and direction data (W$_s$,

458 W$_d$), the horizontal diffusion coefficient (γ_1, α_1) and the vertical diffusion coefficient

459 (γ_2, α_2) from the 8-day monitoring experiment. Wind speed and direction data are the

460 average wind speed and direction during the monitoring time, and the CH$_4$ emission

461 fluxes are obtained by the inversion of the average concentration, wind speed and

462 direction data as input of the inversion framework.~~Table 1 displays the CH$_4$ emission~~

463 ~~fluxes, meteorological data, and the coefficients of the power function expressions for~~

464 ~~diffusion parameters from the 8-day monitoring experiment.~~ The emission flux values

465 of CH$_4$ emission sources (12 point sources and 1 line source) for all experimental days

466 are detailed in Tables S1 and S2. It is observed that the summer average CH$_4$ emission

467 flux (68.78 $\pm$ 17.40 kg h^{-1}~~603.33 $\pm$ 152.66 t a^{-1}~~) surpasses the winter average CH$_4$

468 emission flux (47.76 $\pm$ 21.39 kg h^{-1}~~418.95 $\pm$ 187.59 t a^{-1}~~). This seasonal disparity in

469 emissions is primarily attributed to the aeration tank, followed by the screen and

470 primary clarifier. The activated sludge in the aeration tank contains a higher population

of methanogens, whose CH_4 production capability intensifies with rising temperatures

(Vítěz et al., 2020). Notably, the seasonal variance in the aeration tank is predominantly

driven by the performance of the Aeration Tank ④. However, the substantial variation

in the emissions from the three summer experiments of the Aeration Tank ④ suggests

a degree of emission instability. Conversely, the uniformity in the low emissions from

the five winter experiments might be associated with the meteorological conditions and

the actual operational status of the plant on those days. At lower wind speeds, the CH_4

emissions show only slight differences when compared to emissions on days with

higher wind speeds. This suggests that the inversion results are less influenced by wind

speed and are primarily associated with seasonal variations.

~~Analysis of emission source data from Tables S1 and S2 reveals that t~~The screen and

primary clarifier are the predominant emission sources at the WWTP. Specifically, these

sources emit 37.50 kg h^{-1}~~329 t a^{-1}~~ in the summer and 31.92 kg h^{-1}~~280 t a^{-1}~~ in the winter,

accounting for 55 % and 67 % of the total emissions. ~~The study hypothesizes that~~

~~emissions are boosted by p~~Pipeline leaks near the ~~emission sources in the~~ screen and

primary clarifier~~,~~ lead~~ing~~ to the ~~more~~ CH_4 release. Previous research has similarly

examined major emission sources at WWTPs. Yin et al. (2024) conducted offline

monitoring of WWTPs in Beijing and Guiyang, identifying the primary treatment zone

as the primary source of CH_4, accounting for 60.1 % and 35.8 % of the respective total

emissions. Masuda et al. (2017) analyzed CH_4 emissions from different processes at

three WWTPs in Japan, concluding that primary clarifiers are one of the major sources

of CH_4 emissions. He et al. (2023) compiled CH_4 emission proportions for different

processes in WWTPs based on reported data, finding percentages of 7 %-12 % for grit

chamber, 8.2 %-68.1 % for primary clarifier, and 18.3 %-86.4 % for aeration tank.

Table 1. CH_4 emission fluxes (Q), Wind speed and direction data (W_s, W_d), the

horizontal diffusion coefficient (γ_1, α_1) and the vertical diffusion coefficient (γ_2, α_2)

498 from the 8-day monitoring experiment. ~~CH₄ emission fluxes, meteorological data and~~

499 ~~diffusion parameter power function expression coefficients from the 8-day monitoring~~

500 ~~experiment.~~

Date	Q ($kg\ h^{-1}$ ~~$t\ a^{-1}$~~)	W_s ($m\ s^{-1}$)	W_d (°)	γ_1	α_1	γ_2	α_2
0601	61.85 ± 20.41	2.3	248.5	0.28	0.91	0.13	0.94
0629	74.92 ± 35.21	1.9	238.3	0.28	0.91	0.13	0.94
0711	69.58 ± 32.70	0.9	225.8	0.28	0.91	0.13	0.94
1213	49.19 ± 21.15	1.6	175.7	0.28	0.91	0.13	0.94
1214	43.29 ± 27.28	1.2	209.9	0.28	0.91	0.13	0.94
1220	49.99 ± 25.00	3.8	342.3	0.18	0.92	0.11	0.92
1221	48.17 ± 17.34	2.7	342.6	0.43	1.10	0.08	1.12
1222	48.15 ± 21.67	3.0	342.5	0.43	1.10	0.08	1.12

501

502 An alternative top-down approach known as the tracer gas dispersion method (TDM),

503 which has been applied to estimate CH_4 emissions from city streets (von Fischer et al.,

504 2017; Weller et al., 2018), WWTPs (Yoshida et al., 2014; Delre et al., 2017; Delre et

505 al., 2018), biogas plants (Reinelt et al., 2017; Scheutz et al., 2019; Fredenslund et al.,

506 2023) and landfills (Rees-White et al., 2019; Kissas et al., 2022). TDM involves

507 releasing tracer gases like nitrous oxide and acetylene near the source and measuring

508 their concentrations along with CH_4 downwind using a mobile platform. The similar

509 diffusion patterns of CH_4 and the tracer gases result in a stable concentration ratio after

510 atmospheric mixing, enabling the calculation of CH_4 emission rates with a better

511 accuracy (Mønster et al., 2014).

512 Moreover, the TDM was employed to validate and compare other model inversion

513 methods. Moore et al. (2023) proposed that the Gaussian dispersion modeling demands

514 less experimental equipment, site access, and manpower than the TMD, which allows

515 for swifter data gathering. Yacovitch et al. (2015) utilized a five-day dataset of tracer

516 gas release in the Barnett shale region to evaluate the Gaussian dispersion flux

quantification method. The results indicated a 95% confidence interval, with a lower bound factor of 0.334 and an upper bound factor of 3.34. von Fischer et al. (2017) performed three controlled release experiments to validate the reliability of leak rate algorithm in Fort Collins, CO, which indicated a very significant correlation between known and estimated leak rates ($p < 0.0001$, $r^2 = 0.43$). Compared to the method employed in the study, the TDM offers advantages such as simpler formula calculations. Nonetheless, it also presents several drawbacks, including complex experimental procedures, safety hazards associated with the release of tracer gases, which require access permits from industrial facilities.

3.3 Comparison with IPCC method

The ~~direct~~ CH_4 emissions ~~from WWTP~~ were also calculated using the IPCC method, with data sourced from the Urban Drainage Statistical Yearbook of 2017. ~~By applying the formula to the basic information of the WWTP outlined in the yearbook, t~~The emission flux of 213.95 ± 128.37 t a^{-1} was determined, with the uncertainty (60%) derived from the data summarized in the research (Lin et al., 2021). Figure 5 shows the contrast between the emission inversion results from the monitoring experiment and the emission inventory. The uncertainty of the inversion results was determined by accounting for the uncertainties in wind speed, wind direction, and instrument measurements, following the method presented in Section 2.4.5. The uncertainties in emission fluxes inversion ranged from 33% to 63% on individual days. Notably, the uncertainty associated with wind speed contributes approximately 44% to 94% of the uncertainty range. The summer average inversion emission flux (603.33 ± 152.66 t a^{-1}) was calculated to be 2.8 times that of the inventory, and the winter average (418.95 ± 187.59 t a^{-1}) was twice as much. It is posited that the discrepancy may stem from significant uncertainties in the emission factors associated with the WWTPs or the lack of updated activity level data, as the statistical yearbook provided data only up to 2017,

544 the emission inventory might have underestimated the actual emissions.

545   Furthermore, other studies have also investigated the comparison between CH_4

546 emissions obtained from different measurement methods at WWTPs and IPCC

547 inventory estimates. The majority of these studies indicate that the measured

548 values exceed the inventory values. Wang et al. (2021) conducted a measurement-

549 based assessment of CH_4 emissions (46.58 t a^{-1}) in Wuhu City, revealing a 46.71 %

550 higher than those calculated using the IPCC method. Moore et al. (2023)

551 employed mobile monitoring to evaluate CH_4 emissions at 63 WWTPs across the

552 United States. ~~The study showed that the estimates based on the IPCC guidelines~~

553 ~~underestimated the emissions from most of the measured plants.~~ Specifically, CH_4

554 emissions from centrally treated domestic wastewater in the U.S. amount to 4.64×10^5 t

555 a^{-1}, which is 1.9 times greater than the EPA inventory. Song et al. (2023) investigated

556 CH_4 emissions from municipal wastewater treatment in the U.S at $(4.36 \pm 2.8) \times 10^5$ t

557 a^{-1}.~~sewer systems and water resource recovery facilities. Utilizing a collected dataset,~~

558 ~~they employed the Monte Carlo analysis method to determine the CH_4 emissions from~~

559 ~~municipal wastewater treatment in the U.S. at $(4.36 \pm 2.8) \times 10^5$ t a^{-1}.~~ This value was

560 approximately twice the estimates provided by the IPCC. Our estimated results are

561 generally consistent with the previous studies. The lower estimated results provided by

562 the IPCC method can be attributed to the neglect of certain potential emission sources

563 from the emission inventories, including emissions from equipment in sludge treatment

564 facilities and leaks from pressure relief valves.

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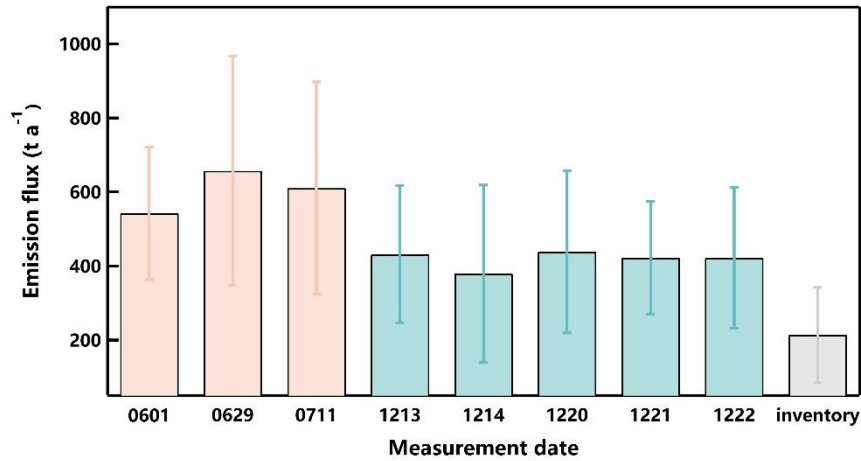
Figure 5. Comparison of CH_4 emission fluxes from the monitoring experiment and emission inventory in the WWTP.

3.4 Sensitivity analysis

In this section, we evaluated the stability of the inversion framework through sensitivity analysis and explored the impact of different point source locations on the inversion of emission concentrations. The precise identification of emission sources can enhance the accuracy of emission flux inversion, making a sensitivity analysis of the source location essential. We applied the method of controlling variables to perform a sensitivity analysis on the location of a single point source. The central position of the plant was taken as the reference origin, the positions of 12 emission sources were determined to analyze the variation in error between measured and simulated concentrations within a 200 m × 200 m range around each emission source. We sequentially modified the source position parameters in the model input to analyze the congruence between the simulated concentrations and the observed measurements, quantifying the fit with RMSE. The change in concentration error serves as an indicator of the accuracy of the emission source localization.

Figures 6 and 7 describe the error variation between monitored and simulated concentrations when the point source location is subject to change within a 200 m × 200 m range from the monitoring experiment on 29th June and 13th December. The error

variation of the remaining days can be seen in Figures S9̲8̶-S1̲4̲1̶3̶. The point source locations simulated based on the inversion framework are mostly in areas with minor relative concentration errors, which can be considered to have a high reliability in simulating point source locations. The emission source location errors for the two experiments are within the ranges of 0.7-1.3 mg m^{-3} and 0.2-0.3 mg m^{-3}. The winter emission source locations exhibit greater stability and accuracy in the inversion results than the summer ones.
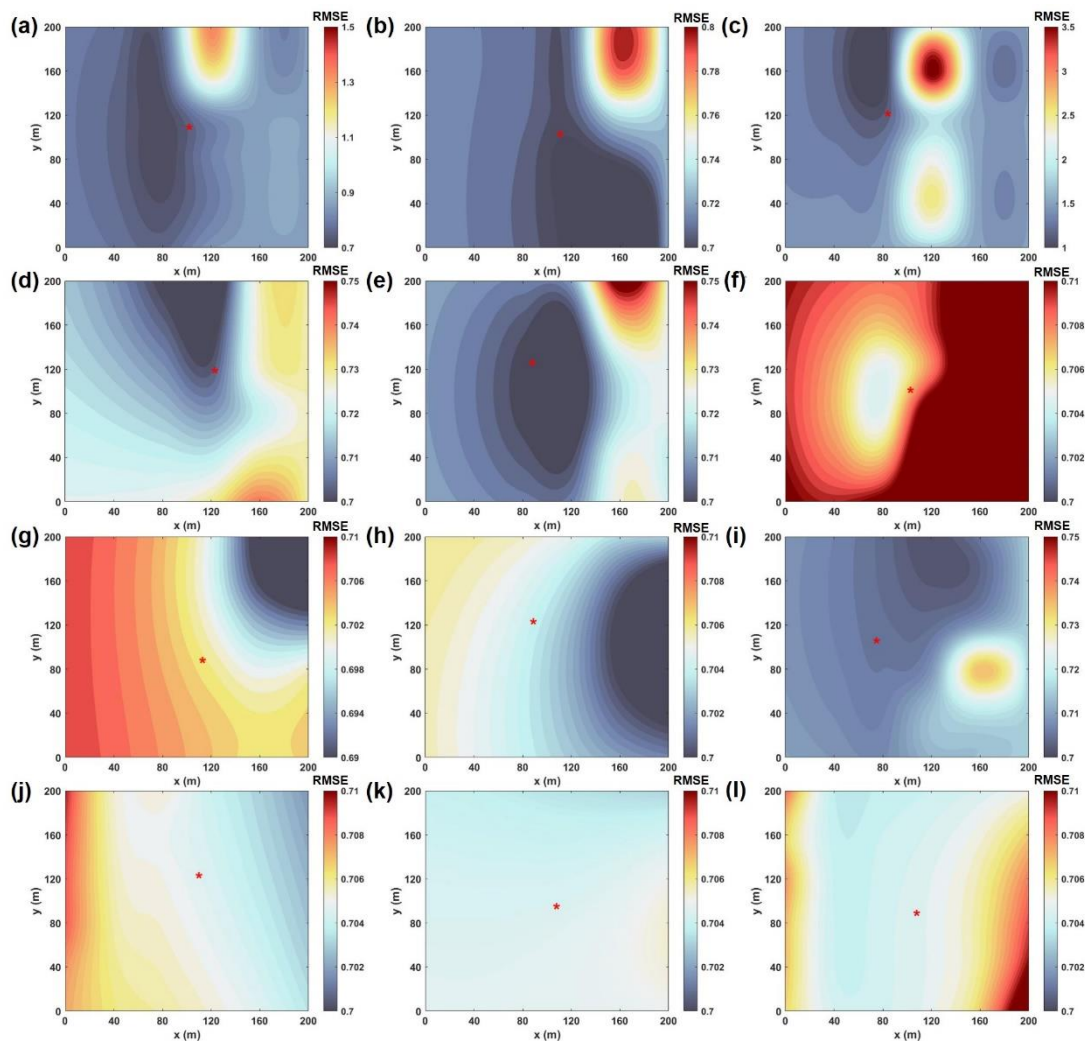
Figure 6. RMSE of monitoring simulated concentration changes with the location of WWTP source on 29th June. The x and y axes denote the horizontal and vertical distances of the simulated point source from the central point of the WWTP. The variation in color signifies the alteration in the root mean square error between the

actual monitored and simulated concentrations, with the red star symbolizing the simulated point source location.
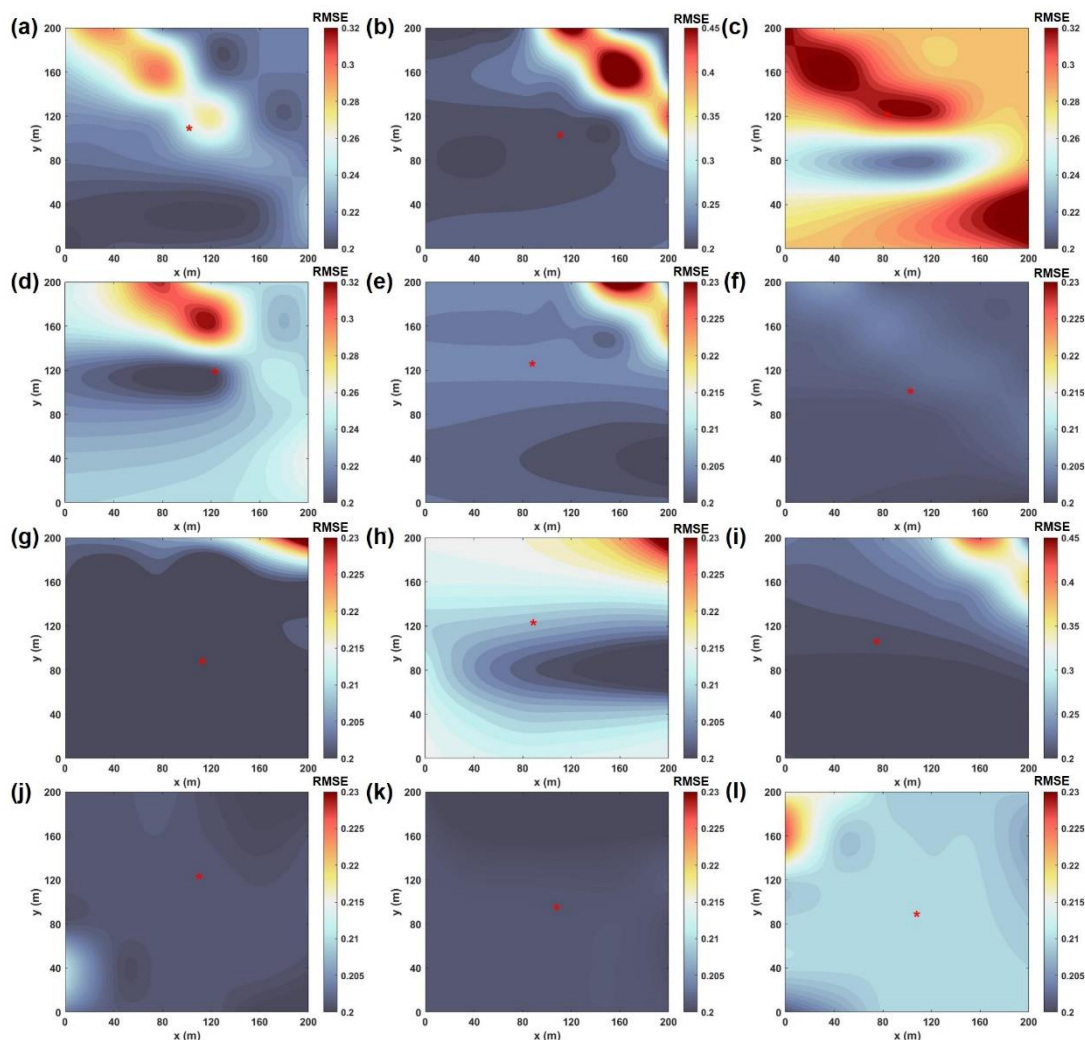
Figure 7. RMSE of monitoring simulated concentration changes with the location of WWTP source on 13th December.

4 Conclusions and outlook

The study carried out ~~CRDS~~ mobile measurements at a WWTP across the summer and winter seasons from Hangzhou 2023. By employing a multi-source Gaussian plume model combined with the genetic algorithm inversion framework, the inversion of CH_4 emission fluxes and their source locations was achieved. ~~A sensitivity analysis of the~~

parameters within the inversion framework was conducted to verify the reliability of the model, offering a strategic approach for the quantification of GHG emissions at the plant scale. The results showed that 12 distinct CH_4 emission sources were pinpointed within the facility through the inversion framework. The average CH_4 emission flux during the summer was calculated to be 68.78 ± 17.40 kg h^{-1} (603.33 ± 152.66 t a^{-1}), and 47.76 ± 21.39 kg h^{-1} (418.95 ± 187.59 t a^{-1}) for the winter. The screen and primary clarifier were the main sources, accounting for 55 % of summer and 67 % of winter emissions. When contrasted with bottom-up emission inventory estimates, tThe summer CH_4 inversion emissions were found to be 2.8 times higher, and the winter inversion emissions were twice as much as the inventory valuesbased estimation.

The inversion framework is capable of validating emission coefficients in the inventory, identifying emission sources within the plant, and monitoring abnormal emissions. It can be applied to various monitoring systems, such as UAV systems and networks of fixed monitoring stations. We believe that it is an excellent point that collaborative monitoring offers significant improvements in the accuracy of emission fluxes and source inversion.collaborative monitoring by different methods can significantly improve the accuracy of emission fluxes and emission sources inversions. Future efforts should aim to refineIt is suggested that future endeavors focus on refining the inversion framework for broader applicability to various pollutant gases, enhancing the inversion efficiency, and extending the validation of the framework through monitoring experiments in a diverse range of industrial facilities.

Data availability. The raw data in this paper can be obtained from the corresponding author upon request.

Author contributions. ZW and YZ administrated the project and determined the main goal of this study. ZX, JY and XP designed the methods and planned the campaign. JY, ZX, YY, SZ and BQ performed the measurements. JY wrote the paper with

contributions from all co-authors.

Competing interests. At least one of the (co-)authors is a member of the editorial board of Atmospheric Chemistry and Physics.

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